Presentation Viewgraphs

for

Quantum Mechanics for Scientists and Engineers

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Introduction

This document contains a complete set of viewgraphs for lecture presentation of all the material in *Quantum Mechanics for Scientists and Engineers* (Cambridge University Press, 2008) (except for the Appendices). It can be used in the form given here, or as a resource for lecturers preparing their own presentation materials.

The material is divided into sections corresponding to those in the book, and also into lectures. All of the sections and lectures can be accessed by bookmarks in this pdf file. The division into lectures is nominal – in presenting this material I have often deviated from the precise divisions here depending on the needs of the students. The lecture units here are paced for approximately 50 minute presentations. A pace of three such lectures per week is suitable for graduate students with a good background in analytical subjects, and is just accessible for well-prepared undergraduates. For a more typical undergraduate class, a slower pace is likely preferable (e.g., 2/3 of this pace), possibly with more worked examples (e.g., from the solved problems available on the book website www.cambridge.org/9780521897839) and extended discussion.

There are 56 lectures altogether. At three lectures per week, in a two quarter sequence with approximately 25 lectures per quarter, the majority of the material in the book can therefore be taught, with some optional sections omitted. With a slightly more relaxed pace, the entire material in the book could be taught in a two semester or three quarter full year course sequence. An undergraduate course omitting some of the more advanced topics and optional material could be taught comfortably in a full year sequence. The possible sequences of material are discussed in the introduction to the book itself, and all optional material is clearly marked throughout the book.

The progression of the viewgraphs exactly follows the text in the book. The only minor exception to this is in Chapter 10 on the hydrogen atom. The solution for the hydrogen atom involves many steps, so a presummary of the radial equation solution is added just before the actual detailed solution, and an overall summary of the entire hydrogen atom solution is added at the end of this chapter's viewgraphs.

All the equations in the book are included in these viewgraphs, with equation numbers. All the figures are also included, here often in color versions. The animations of various of the figures are embedded, and can be accessed by mouse clicks on the indicated areas. To allow embedding of the animations, this pdf file is created using Adobe Acrobat® version 8, so Acrobat® Reader version 8 or later may be required to view them. The embedded animation files are in AVI format, which may require additional plug-ins for viewing, though the Acrobat® software may find these automatically.

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Introduction

Reading – Chapter 1

Quantum mechanics and real life

Quantum mechanics as an intellectual achievement

Using quantum mechanics

Quantum mechanics and real life

Quantum mechanics is part of everyday life!

e.g., quantum mechanics is needed to explain the color of an object

essentially no classical model correctly explains the color of anything

most colors result from specific absorbing transitions in materials

the transition energies

and hence frequencies

and hence colors

are determined quantum mechanically

even the color of the glow of very hot objects is determined by the quantum statistics of radiation.

e.g., quantum mechanics is an essential part of chemistry

Quantum mechanics in engineering

quantum mechanics is essential for handling information

- ***electronics for processing information***
  - **quantum mechanics underpins all of solid state physics**
    - *enables us to make transistors and integrated circuits*
  - **limiting processes in small electronic devices can only be understood through quantum mechanics.**
    - *e.g., tunneling through gate oxide*
  - **new quantum mechanical devices beyond the transistor?**
- ***optics for sending information***
  - **heavily quantum mechanical**
    - *e.g., photons*
  - **optoelectronic devices are quantum mechanical on many different levels**
    - *they are solid state devices*
    - *they send and receive photons*
    - *modern light-emitting diodes, semiconductor lasers, and modulators are quantum mechanically engineered*
- ***storing information***
  - **magnetism of materials is a quantum mechanical phenomenon**
  - **optical storage relies also on quantum-mechanical optoelectronic devices**

Quantum mechanics for understanding how the world works

Quantum mechanics is an astonishing intellectual achievement

- ***arguably the greatest of the twentieth century***
- ***it challenges many of our prior beliefs about how the world actually works***
- ***it is apparently never wrong***

It has bizarre, but true consequences

- ***"tunneling" allows particles to penetrate barriers that are "too high"***
- ***we cannot know simultaneously both the position and the momentum of a particle***
  - **Heisenberg's uncertainty principle**
- ***a particle may exist in a superposition state,***
  - **e.g., it is neither definitely on the left, or on the right**
- ***when we measure it, we always find it to have a definite value***
    - *known as "collapse of the wavefunction"*
  - **e.g., to be definitely on the left or on the right.**

Basic issues raised by quantum mechanics

e.g., what do we mean by a measurement of a quantum system

- ***Schrödinger cat paradox***

quantum mechanics is “non-local”

- ***an event here can apparently instantaneously give a consequence elsewhere***
  - **(though it is not apparently possible to use such a phenomenon to communicate information faster than the velocity of light)**

despite its statistical nature

- ***quantum mechanics may well be a complete theory***
  - **unlike classical statistical mechanics, which presumes well defined positions and momenta exist for all particles**
    - *Bell’s inequalities, and experiments that verify them,*
      - tell us that the world cannot be described by purely local hidden variables
        - (e.g., that we simply have not yet been able to see)
          - all with definite values

Continuing story of quantum mechanics

continuing interest in the theory of elementary particles

- ***and the implications of such theories for the nature of the universe***

some of the strange features of quantum mechanics may be used for handling information

- ***e.g., use quantum mechanics to create "uncrackable" coded transmission of information***
- ***e.g., quantum computing***
  - **quantum mechanics, because it can naturally deal with so-called "entangled states,"**
    - *may enable solution of problems that are practically impossible for any classical computer that could ever be built*

Using quantum mechanics as a practical tool

The recipes for using quantum mechanics in a broad range of practical problems and engineering designs are relatively straightforward

though strange and expressed using a different set of ideas and concepts

If we only ask questions about quantities that can be measured

there are no philosophical problems that prevent us from calculating anything that we could measure

(the philosophical approach of only dealing with questions that can be answered by measurement, and regarding all other questions as meaningless, is known as "logical positivism")

When we use quantum mechanical principles in tangible applications

e.g., electronic or optical devices and systems

the apparently bizarre aspects become routine

Quantum mechanical calculations

The mathematical techniques used in quantum mechanics are familiar

Most calculations require

performing integrals or
manipulating matrices.

Many underlying mathematical concepts are quite familiar to engineers

e.g., Fourier analysis,
or other linear transforms.

Learning quantum mechanics

Arguably the main difficulties in learning quantum mechanics center around

knowing which classical notions have to be discarded, and
what new notions we have to use to replace them.

Learning quantum mechanics

is a qualitative change in one's view of the world
is certainly one of the most fascinating things to do with one's brain!

The Time-Independent Schrödinger Equation - 1

Reading – Sections 2.1 – 2.3

- ***Electrons as waves***
  - **De Broglie hypothesis**
- ***Rationalization of Schrödinger's (time-independent) equation***
- ***Probability amplitudes***
- ***Diffraction by two slits***

Rationalization of Schrödinger's equation

The Schrödinger equation

- ***is a very useful relation***
  - **it solves many problems for quantum mechanical particles that have mass**
    - *e.g., a single electron moving slowly*
      - i.e., much slower than the velocity of light
    - *and neglecting any magnetic effects.*
- ***is a good example of quantum mechanics***
  - **it exposes many general concepts, e.g.,**
    - *working with quantum mechanical amplitudes*
    - *linearity*
    - *eigenstates.*

Why propose such an equation?

- ***consider here the simplest, time-independent case first.***

Electrons as waves

Experimentally, electrons can behave like waves.

- ***e.g., make a beam of electrons by applying a large electric field in a vacuum to pull electrons out of a metal***
  - **arrange that the electrons all have essentially the same kinetic energy**
    - *e.g., by accelerating them through some fixed electric potential*

If we shine this beam of electrons at a crystal,

- ***we will get a diffraction pattern***
  - **e.g., let the scattered electrons land on a phosphor screen**
    - *get a pattern of dots on the screen*
- ***behaves like the diffraction pattern we get when we shine a monochromatic light beam at a periodic structure of periodicity comparable to the wavelength***

The fact that electrons behave both

- ***as particles***
  - **they have a specific mass and a specific charge, for example**

and as waves

- ***is known as "wave-particle duality."***

Electrons as waves

Electrons behave as if they have a wavelength

$$\lambda = \frac{h}{p} \tag{2.1}$$

where p is the electron momentum, and h is Planck's constant

$$h \cong 6.626 \times 10^{-34} \,\text{Joule} \cdot \text{seconds}\,.$$

This is known as de Broglie's hypothesis

E.g., an electron can behave as a plane wave, propagating in the z direction

$$\psi \propto \exp\left(2\pi i z / \lambda\right). \tag{2.2}$$

Hence we need a wave equation for the electron

The simplest choice –

the "Helmholtz" wave equation for a monochromatic wave

in one dimension, the Helmholtz equation is

$$\frac{d^2\psi}{dz^2} = -k^2\psi \tag{2.3}$$

It has solutions such as

$\sin(kz)$, $\cos(kz)$, and $\exp(ikz)$ (and $\sin(-kz)$, $\cos(-kz)$, and $\exp(-ikz)$)

Helmholtz equation in three dimensions

In three dimensions, we can write this as

$$\nabla^2 \psi = -k^2 \psi \tag{2.4}$$

where the symbol ∇^2

known as

the Laplacian operator

“del squared” and

“nabla squared”, and

sometimes written Δ

means

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \tag{2.5}$$

where x, y, *and* z *are the usual Cartesian coordinates, all at right angles to one another*

This has solutions such as

$\sin(\mathbf{k.r})$,

$\cos(\mathbf{k.r})$, and

$\exp(i\mathbf{k.r})$

(and $\sin(-\mathbf{k.r})$, $\cos(-\mathbf{k.r})$, and $\exp(-i\mathbf{k.r})$), where $\mathbf{k}$ and $\mathbf{r}$ are vectors.

Helmholtz equation to Schrödinger equation (1)

In general for our Helmholtz equation

The wavevector magnitude, k, is defined as

$$k = 2\pi / \lambda \tag{2.6}$$

or, equivalently, given the empirical wavelength exhibited by the electrons

$$k = p / \hbar \tag{2.7}$$

where

$$\hbar = h / 2\pi \cong 1.055 \times 10^{-34} \,\text{Joule} \cdot \text{seconds}$$

With our expression for k (Eq. (2.7)), we can rewrite our simple wave equation (Eq. (2.4) $\nabla^2 \psi = -k^2 \psi$) as

$$-\hbar^2 \nabla^2 \psi = p^2 \psi \tag{2.8}$$

Now divide both sides by $2m_o$, where, for the case of an electron, m_o is the free electron rest mass

$$m_o \cong 9.11 \times 10^{-31} \,\text{kg}$$

to obtain

$$-\frac{\hbar^2}{2m_o} \nabla^2 \psi = \frac{p^2}{2m_o} \psi \tag{2.9}$$

Helmholtz equation to Schrödinger equation (2)

But we know from classical mechanics

with $p = m_o v$ ***(with*** v ***as the velocity), that***

$$\frac{p^2}{2m_o} \equiv \text{kinetic energy of electron} \tag{2.10}$$

and, in general,

$$\text{Total energy } (E) = \text{Kinetic energy} + \text{Potential energy } (V(\mathbf{r})) \tag{2.11}$$

Hence, we can postulate that we can rewrite our wave equation (Eq. (2.9) $-\frac{\hbar^2}{2m_o}\nabla^2\psi = \frac{p^2}{2m_o}\psi$**) as**

$$-\frac{\hbar^2}{2m_o}\nabla^2\psi = \left(E - V(\mathbf{r})\right)\psi \tag{2.12}$$

or, in a slightly more standard way of writing this,

$$\left(-\frac{\hbar^2}{2m_o}\nabla^2 + V(\mathbf{r})\right)\psi = E\psi \tag{2.13}$$

which is the time-independent Schrödinger equation for a particle of mass m_o***.***

“Derivation” of Schrödinger’s equation

Note that we have not “derived” Schrödinger’s equation.

- ***We have merely suggested it as an equation that agrees with at least one experiment.***

There is no way to derive Schrödinger’s equation from first principles

- ***there are no “first principles” in the physics that precedes quantum mechanics that predicts anything like such wave behavior for the electron.***

Schrödinger’s equation has to be postulated,

- ***just like Newton’s laws of motion were originally postulated.***

The *only* justification for making such a postulate is that it works!

Probability densities

We find in practice that

- ***the probability $P(\mathbf{r})$ of finding the electron near any specific point $\mathbf{r}$ in space***
  - **is proportional to the modulus squared, $|\psi(\mathbf{r})|^2$, of the wave $\psi(\mathbf{r})$.**

Using the squared modulus

- ***assures that we always have a positive quantity***
  - **we would not know how to interpret a negative probability!**
- ***is consistent with some other uses of squared amplitudes with waves***
  - **e.g., squared amplitude tells us the intensity (power per unit area) or energy density in a wave motion such as a sound wave or an electromagnetic wave**
    - *we would also find electromagnetism that the probability of finding a photon at a specific point was proportional to the squared wave amplitude*
    - *if we choose to use complex notation to describe an electromagnetic wave,*
      - we use the modulus squared of the wave amplitude to describe wave intensity,
        - and hence also the probability of finding a photon at a given point in space

Probability Amplitude or Quantum Mechanical Amplitude

Since the probability is given by the modulus squared of the wavefunction ψ, we call the wavefunction a

"probability amplitude" or

"quantum mechanical amplitude."

Note that this probability amplitude is quite distinct from the probability itself.

The probability amplitude has little or no precedent in classical physics or classical statistics.

For now, we think of that probability amplitude as being the amplitude of a wave

We will find later that the concept of probability amplitudes extends into quite different descriptions,

still retaining the concept of the modulus squared representing a probability.

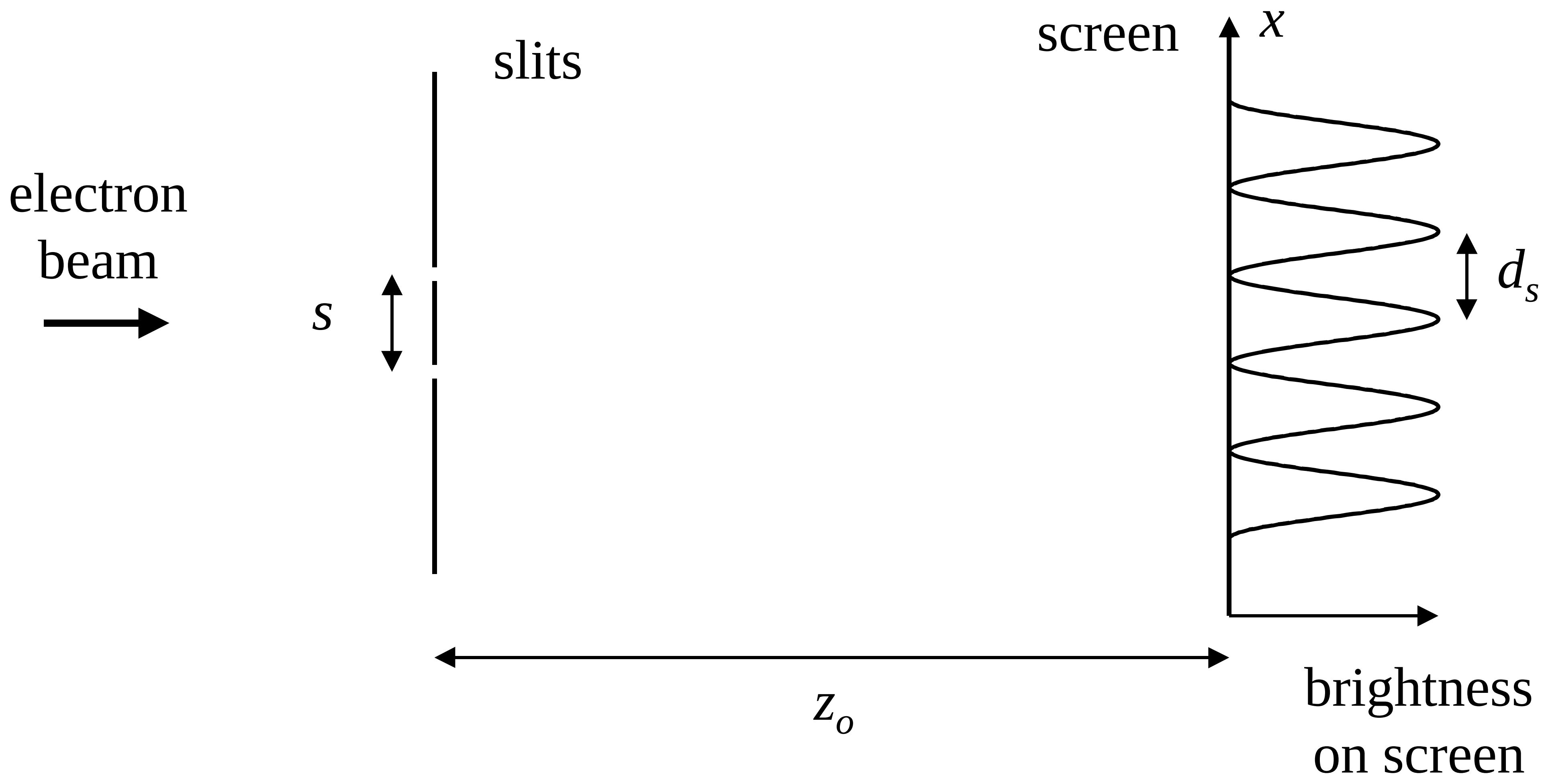
Diffraction by two slits (1)

Now we can calculate a simple electron diffraction problem,

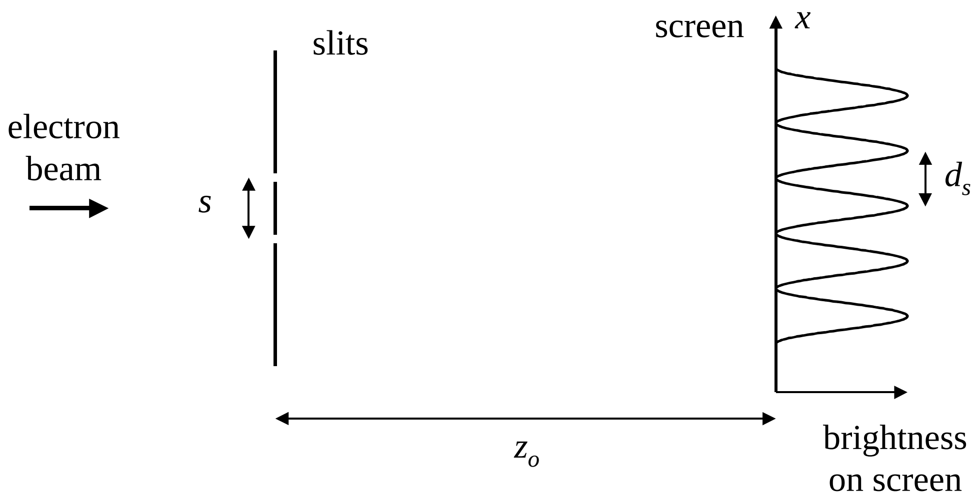
an electron wave being diffracted by a pair of slits

(known as Young's slits in optics)

Consider two very narrow slits, separated by a distance s



Diffraction by two slits (2)



We shine a monochromatic electron beam of wavevector *k* at the screen

We also presume the screen is far away from the slits for simplicity, i.e., $z_o >> s$.

We can use Huygens' principle, taking each source as being a source of circularly expanding waves.

Hence the net wave at the screen is

$$\psi_s(x) \propto \exp\left[ik\sqrt{(x-s/2)^2+z_o^2}\right]+\exp\left[ik\sqrt{(x+s/2)^2+z_o^2}\right] \qquad (2.14)$$

If we presume we are only interested in relatively small angles, i.e., $x << z_o$, then

$$\begin{aligned}\sqrt{(x-s/2)^2+z_o^2} &= z_o\sqrt{1+(x-s/2)^2/z_o^2} \cong z_o+(x-s/2)^2/2z_o \\ &= z_o+x^2/2z_o+s^2/8z_o-sx/2z_o\end{aligned} \qquad (2.15)$$

and similarly for the other exponent (though with opposite sign for the term in s).

Diffraction by two slits (3)

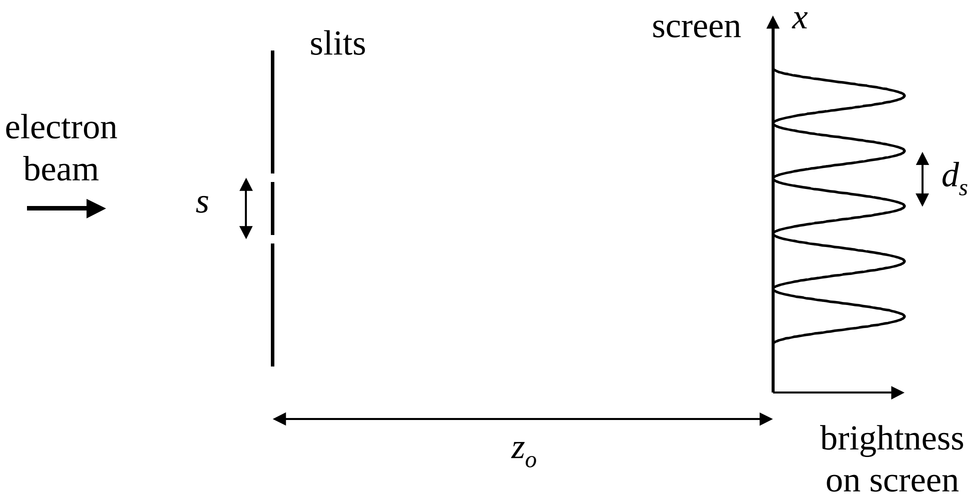
Hence, using $2\cos(\theta) = \exp(i\theta) + \exp(-i\theta)$, we obtain

$$\psi_s(x) \propto \exp(i\phi)\cos(ksx/2z_o) = \exp(i\phi)\cos(\pi sx/\lambda z_o) \qquad (2.16)$$

where ϕ is a real number ($\phi = k\left(z_o + x^2/2z_o + s^2/8z_o\right)$), so $\exp(i\phi)$ is simply a phase factor.

Hence,

$$|\psi_s(x)|^2 \propto \cos^2(\pi sx/\lambda z_o) = \frac{1}{2}\left[1 + \cos(2\pi sx/\lambda z_o)\right] \qquad (2.17)$$



Hence a beam of monoenergetic electrons produces a (co)sinusoidal interference pattern, or "fringes", on the screen,

with the fringes separated by a distance $d_s = \lambda z_o / s$.

Quantum mechanics and electron diffraction by two slits (1)

These interference effects have some bizarre consequences that we simply cannot understand classically

Suppose that we block one of the slits so the electrons can only go through one slit.

Then we would not see the interference fringes

If we now uncover the second slit,

parts of the screen that were formerly bright now become dark

How can we explain that opening a second source of particles actually reduces the number of particles arriving at some point in the screen?

Quantum mechanics and electron diffraction by two slits (2)

We might argue that the particles from the second slit were bouncing off the ones from the first slit,

and hence avoiding some particular part of the screen because of these collisions.

If we repeat the experiment with extremely low electron currents so that there are never two electrons in the apparatus at a given time,

and take a time-exposure picture of the phosphorescent screen,

we will, however, see exactly the same interference pattern emerge.

Hence we must describe the electrons in terms of interference of amplitudes,

and we also find that the wave description postulated above does explain the behavior quantitatively.

Electron interference movie http://www.hqrd.hitachi.co.jp/em/doubleslit.cfm

Use of electron diffraction

Electron diffraction is routinely used as a diagnostic and measurement tool.

- ***The wavelength associated with such accelerated electrons can be very small***
  - **e.g., 1 Å or 0.1 nm**

Diffractive effects are strong when the wavelength is comparable to the size of an object

Electrons diffract strongly off crystal surfaces,

- ***for example, where the spacings between the atoms are on the order of Ångstroms or fractions of a nanometer.***
  - **E.g., reflection high-energy electron diffraction (RHEED), for example, monitors the form of a crystal surface during the growth of crystalline layers**

Electron diffraction is intrinsic to electron microscopes.

- ***The fact the electron wavelength can be so small means that electron microscopes can be used to view very small objects***

The Time-Independent Schrödinger Equation - 2

Reading – Sections 2.4 – 2.6

- ***Linearity of quantum mechanics***
  - **multiplying by a constant**
- ***Normalization of the wavefunction***
  - **getting unit total probability**
- ***Particle in an infinitely deep potential well ("particle in a box")***
  - **classic simple example of quantum mechanics**
    - *shows clear "quantum" behavior of discrete levels*
    - *gives example sizes and energies*

Linearity of quantum mechanics: multiplying by a constant (1)

In Schrödinger's equation

we could multiply both sides by a constant a ***and***

the equation would still hold

If ψ ***is a solution of Schrödinger's equation, so also is*** $a\psi$

possible because Schrödinger's equation is *linear*

wavefunction only appears in first order (i.e., to the power one) in the equation

there are no second order terms,

such as ψ^2,

or any other higher order terms in ψ

Linearity of quantum mechanics: multiplying by a constant (2)

This linearity of equations in quantum mechanics is very general and important

- ***quantum mechanical equations are linear in the quantum mechanical amplitude for which the equation is being solved***

In classical systems

- ***we often use linear equations as a first approximation to nonlinear behavior,***
  - **e.g., a pendulum oscillates at a slightly different frequency for larger amplitudes**
    - *but the equation is not exactly linear in the amplitude*

In quantum mechanics

- ***The linearity of the equations with respect to the quantum mechanical amplitude is not an approximation of any kind***
  - **it is apparently an absolute property of such equations in quantum mechanics**
    - *this linearity allows the full use of linear algebra for the mathematics of quantum mechanics*

Normalization of the wavefunction (1)

We postulated that

the probability $P(\mathbf{r})$ *of finding a particle near a point* $\mathbf{r}$ *is* $\propto |\psi(\mathbf{r})|^2$

Specifically, let us define

$P(\mathbf{r})$ *- the probability per unit volume of finding the particle near point* $\mathbf{r}$

$P(\mathbf{r})$ **is a "probability density"**

For some very small (infinitesimal) volume $d^3\mathbf{r}$ **around** $\mathbf{r}$**,**

the probability of finding the particle in that volume is $P(\mathbf{r})d^3\mathbf{r} \propto |\psi(\mathbf{r})|^2 d^3\mathbf{r}$

The sum of such probabilities should equal unity, i.e.,

$$\int P(\mathbf{r})d^3\mathbf{r} = 1 \qquad (2.18)$$

Normalization of the wavefunction

In general,

unless we have been very lucky,

solving Schrödinger's equation will give some ψ for which $\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} \neq 1$.

This integral will be real, so we will in general have

$$\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} = \frac{1}{|a|^2} \qquad (2.19)$$

where a is some number (possibly complex).

But we know from the discussion above on linearity that,

if ψ is a solution, so also is $\psi_N = a\psi$,

and we now have

$$\int |\psi_N(\mathbf{r})|^2 d^3\mathbf{r} = 1 \qquad (2.20)$$

This wavefunction solution ψ_N is referred to as a "normalized" wavefunction

gives direct correspondence between probability density and the modulus squared of the wavefunction, i.e., $P(\mathbf{r}) = |\psi_N(\mathbf{r})|^2$

Exact solutions of Schrödinger's equation for simple problems

Now we can proceed to solve some simple problems.

The

- **"particle in a box" and the**
- **"harmonic oscillator"**

are both easily solvable and very useful

The particle-in-a-box problem is used to design the "quantum well" optoelectronic structures

The harmonic oscillator problem allows us to understand vibrating systems of many kinds, including

- ***acoustic vibrations in solids***
- ***electromagnetic waves (where it leads to the concept of photons)***

Not many other useful problems can be solved exactly.

Hence it is important to understand the few that can also for the insight they give

Particle in infinitely deep potential well ("particle in a box") (1)

Consider a particle,

***of mass* m,**

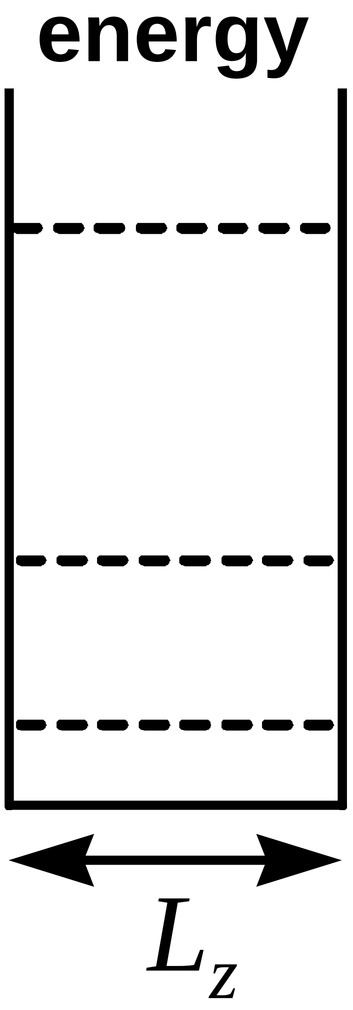
with a spatially-varying potential* V(z) *in the z direction.

The (time-independent) Schrödinger equation for the particle's motion in the z-direction is then the simple differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}+V(z)\psi(z)=E\psi(z) \quad (2.21)$$

where* E *is the energy of the particle and* $\psi(z)$ *is the wavefunction.

Particle in infinitely deep potential well ("particle in a box") (2)



Suppose the potential is a simple "rectangular" (or, equivalently, "square") potential well

> **(i.e., one in what the potential energy is constant inside the well and rises abruptly at the walls)**

of thickness L

Choose the potential $V = 0$ in the well for simplicity

On either side of the well (i.e., for $z < 0$ or $z > L_z$), the potential, V, is presumed infinitely high.

Because these potentials are infinitely high,

but the particle's energy E is presumably finite,

> **we presume there is no possibility of finding the particle in these regions outside the well**

Hence the wavefunction ψ must be zero inside the walls of the well, and

we reasonably ask that the wavefunction must go to zero at the walls

Particle in infinitely deep potential well ("particle in a box") (3)

Formally putting this "infinite well" potential into Eq. (2.21),

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}+V(z)\psi(z)=E\psi(z)$$

we are therefore now solving the equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}=E\psi(z) \tag{2.22}$$

within the well, subject to the boundary conditions

$$\psi=0; \quad z=0,\, L_z \tag{2.23}$$

The general solution to this equation can be written

$$\psi(z)=A\sin(kz)+B\cos(kz) \tag{2.24}$$

where A and B are constants, and

$$k=\sqrt{2mE/\hbar^2}\,.$$

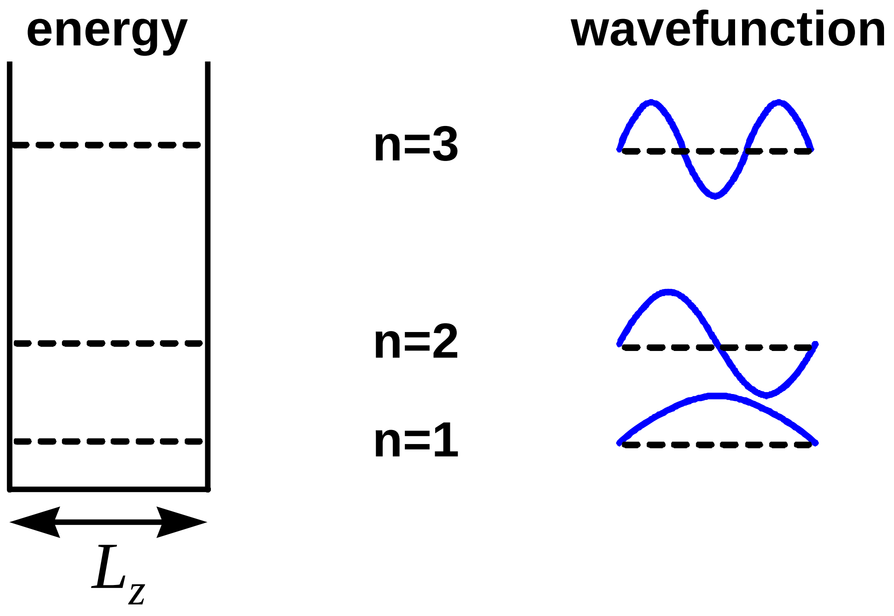
Particle in infinitely deep potential well ("particle in a box") (4)

The requirement that the wavefunction goes to zero at $z=0$ means that $B=0$ in $\psi(z)=A\sin(kz)+B\cos(kz)$ (Eq. (2.24)).

Because we are now left only with the sine part of (2.24),

the requirement that the wavefunction goes to zero also at $z=L_z$ then means

$k=n\pi/L_z$, *where n is an integer.*



Hence, we find that solutions to this equation are, for the wave,

$$\psi_n(z)=A_n\sin\left(\frac{n\pi z}{L_z}\right) \tag{2.25}$$

where A_n is a (real or complex) constant, with associated energies

$$E_n=\frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2 \tag{2.26}$$

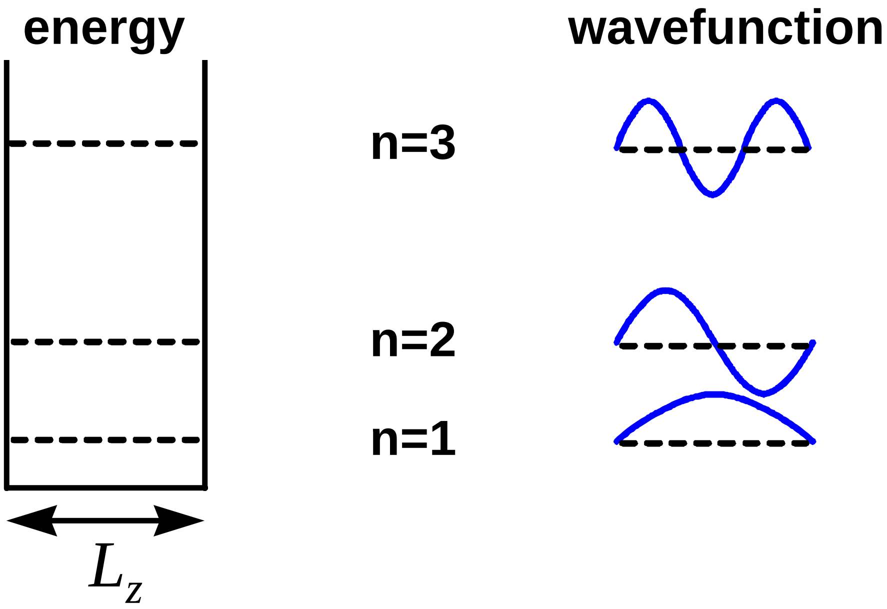
Particle in infinitely deep potential well ("particle in a box") (5)

We can restrict *n* to being a positive integer, i.e.,

$$n = 1,\ 2,\ \ldots \tag{2.27}$$

for the following reasons.

- ***Since*** $\sin(-a) = -\sin(a)$ ***for any real number*** a***,***
  - **the solutions with negative** n **are the same solutions as those with positive** n
- ***The solution with*** $n = 0$ ***is trivial with a zero wavefunction everywhere***
  - **If the wavefunction is zero everywhere, the particle is simply not anywhere, so the** $n = 0$ **can be discarded.**



Eigenvalues and eigenfunctions

Solutions

with a specific set of allowed values of a parameter (here energy)

eigenvalues

and with a particular function solution associated with each such value,

eigenfunctions

are called eigensolutions

It is possible to have more than one eigenfunction with a given eigenvalue,

a phenomenon known as degeneracy.

The number of such states with the same eigenvalue is called the degeneracy.

Here, since the parameter is an energy,

we can call the eigenvalues the

eigenenergies,

and can refer to the eigenfunctions as the

energy eigenfunctions.

Parity – “odd” and “even” functions (1)

Note that the above eigenfunctions have definite symmetry

The lowest ($n = 1$) eigenfunction is the same on the right as on the left.

Such a function is an

“even” function,

or, equivalently, is said to have

“even parity”.

The second ($n = 2$) eigenfunction is an exact inverted image, with

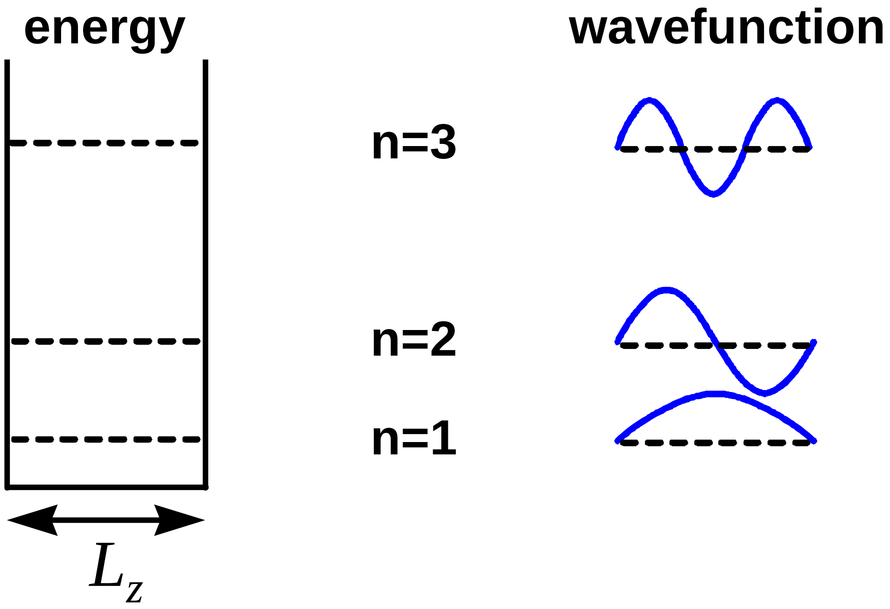
the value at any point to the right of the center being exactly minus the value of the mirror image point on the left of the center.

Such a function is an

“odd” function

or has

“odd parity”.



Parity – "odd" and "even" functions (2)

For this symmetric well problem,

the functions alternate between being even and odd,

and

all of the solutions are either even or odd,

i.e., all the solutions have a definite parity.

Note:

It is quite possible for solutions of quantum mechanical problems not to have either odd or even behavior,

e.g., if the potential was not itself symmetric.

When the potential is symmetric, odd and even behavior is very common

Definite parity is useful since it makes certain integrals vanish exactly.

Normalization of infinite well solutions

Normalizing the eigenfunctions, we have

$$\int_0^{L_z} |A_n|^2 \sin^2\left(\frac{n\pi z}{L_z}\right) dz = |A_n|^2 \frac{L_z}{2} \quad (2.28)$$

To have this integral equal one for a normalized wavefunction,

choose $|A_n| = \sqrt{2/L_z}$ **.**

Note that A_n ***can in general be complex, and it should be noted that the eigenfunctions are arbitrary within a complex factor***

We choose the eigenfunctions to be real for simplicity, so the normalized wavefunctions become

$$\psi_n(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n\pi z}{L_z}\right) \quad (2.29)$$

Emergence of “quantum” behavior

We started out noting that electrons behave like propagating waves

We constructed a simple wave equation that could describe such effects for monochromatic (and hence monoenergetic) electrons.

Now we find that,

if we continue with this equation that assumes the particle has a well-defined energy and

put that particle in a box,

then we find that there are only discrete values of that energy possible,

with specific wave functions associated with each such value of energy.

This is the first truly “quantum” behavior we have seen with “quantum” steps in energy between the different allowed states.

General points about quantum confinement

This "particle-in-a-box" behavior is very different from the classical case

1 - there is only a discrete set of possible values for the energy

2 - there is a minimum possible energy for the particle,

above the energy of the classical "bottom" of the box,

corresponding to $n = 1$,

here $E_1 = \left(\hbar^2 / 2m\right)\left(\pi / L_z\right)^2$

sometimes called a "zero point" energy.

3 - the particle is not uniformly distributed over the box, and

its distribution is different for different energies.

It is almost never found very near to the walls of the box

the probability obeys a standing wave pattern.

In the lowest state ($n=1$),

it is most likely to be found near the center of the box.

In higher states,

there are points inside the box, where the particle will never be found.

Note that each successively higher energy state has one more “zero” in the eigenfunction

this is very common behavior in quantum mechanics.

Orders of magnitude

E.g., confine an electron in a box that is

5 Å (0.5 nm) thick

The first allowed level for the electron is found at

$$E_1 = \left(\hbar^2 / 2m_o\right)\left(\pi / 5\times10^{-10}\right)^2 \cong 2.4\times10^{-19}\,\mathrm{J} \cong 1.5\ \mathrm{eV}$$

(1 eV (electron-volt) $\cong 1.602\times10^{-19}$ ***J is the energy acquired by an electron as it passes through 1 V of electrical potential).***

The separation between the first and second allowed energies is

$(E_2 - E_1 = 3E_1)$ is ~ 4.5 eV,

which is a characteristic size of major energy separations between levels in an atom.

The Time-Independent Schrödinger Equation - 3

Readings – Section 2.7 – 2.8

Properties of sets of eigenfunctions

- **Completeness of sets**
- **Orthogonality**
- **Expansion coefficients**

Particles and barriers of finite heights

- **Boundary conditions**
- **Reflections from barriers of finite heights**

Example of completeness of sets of eigenfunctions – Fourier series

The set of eigenfunctions for this problem is

the set of all the harmonics of a sine wave that has exactly one half period within the well.

This set of functions has a very important mathematical property called “completeness”.

The reader may already understand this from Fourier analysis.

The movement of an audio loudspeaker can be described either

in terms of the actual displacements of the loudspeaker cone at each successive instant in time,

or, equivalently,

in terms of the amplitudes (and phases) of the various frequency components that make up the music being played.

Both are “complete”; any conceivable motion can be described by either

The calculation of the frequency components required is Fourier analysis

The way of representing the motion in terms of these frequency components is called a Fourier series.

Fourier series

When we are interested in the behavior from time zero to time t_o,

an appropriate Fourier series to represent the loudspeaker displacement, $f(t)$ would be

$$f(t)=\sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi t}{t_o}\right) \tag{2.30}$$

where a_n are the relevant amplitudes.

We could similarly represent any function $f(z)$ between the positions $z=0$ and $z=L_z$ as what we will now call,

an "expansion in the set of eigenfunctions", $\psi_n(z)$

$$f(z)=\sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi z}{L_z}\right)=\sum_{n=1}^{\infty} b_n \psi_n(z) \tag{2.31}$$

where $b_n=\sqrt{L_z/2}\,a_n$ to account for our formal normalization of the ψ_n.

We have found that

we can express any function between positions $z=0$ and $z=L_z$ as

an expansion in the eigenfunctions of this quantum mechanical problem.

Note that there are many other sets of functions that are also complete.

Basis sets

A set of functions such as the ψ_n that can be used to represent a function such as the $f(z)$ is referred to as

a “basis set of functions”

or, more simply,

a “basis”.

The set of coefficients (amplitudes) b_n is then

the “representation” of $f(z)$ in the basis ψ_n.

Because of the completeness of the set of basis functions ψ_n,

this representation is just as good a one as the set of the amplitudes at every point z between zero and L_z required to specify or “represent” the function $f(z)$ in ordinary space.

The eigenfunctions of differential equations are very often complete sets of functions.

The sets of eigenfunctions we encounter in solving quantum mechanical problems are complete sets,

which is mathematically very useful.

Example of orthogonality of eigenfunctions

In addition to being "complete",

the set of functions $\psi_n(z)$ ***are "orthogonal".***

In this context, two functions $g(z)$ **and** $h(z)$ **are orthogonal if**

$$\int_0^{L_z} g^*(z)h(z)dz = 0 \tag{2.32}$$

It is easy to show for the specific ψ_n *sine functions* $\psi_n(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$ *(Eq. (2.29)) that*

$$\int_0^{L_z} \psi_n^*(z)\psi_m(z)dz = 0 \text{ for } n \neq m \tag{2.33}$$

and hence that the different eigenfunctions are orthogonal to one another.

Orthonormality

Introducing the notation known as the Kronecker delta

$$\begin{aligned}\delta_{nm} &= 0,\ n \neq m \\ \delta_{nn} &= 1\end{aligned} \qquad (2.34)$$

we can therefore write

$$\int_0^{L_z} \psi_n^*(z)\psi_m(z)\,dz = \delta_{nm} \qquad (2.35)$$

because the functions are normalized.

A set of functions that is both normalized and mutually orthogonal, i.e., obeying a relation like Eq. (2.35), is said to be “orthonormal”

Eq. (2.35) is sometimes described as the orthonormality condition.

Orthonormal sets are very convenient mathematically, so most basis sets are chosen to be orthonormal.

Note that orthogonality of different eigenfunctions is very common in quantum mechanics,

and is not restricted to this specific example where the eigenfunctions are sine waves.

Expansion coefficients

The orthogonality (and orthonormality) of a set of functions makes it very easy to evaluate the expansion coefficients.

Suppose we want to write the function $f(x)$ in terms of a complete set of orthonormal functions $\psi_n(x)$, i.e.,

$$f(x) = \sum_n c_n \psi_n(x) \tag{2.36}$$

It is simple to evaluate the expansion coefficients c_n in Eq. (2.36).

Explicitly, multiplying Eq. (2.36) on the left by $\psi_m^*(x)$ and integrating, we have

$$\begin{aligned}\int \psi_m^*(x) f(x)\,dx &= \int \psi_m^*(x)\left[\sum_n c_n \psi_n(x)\right]dx \\ &= \sum_n c_n \int \psi_m^*(x)\psi_n(x)\,dx \\ &= \sum_n c_n \delta_{mn} \\ &= c_m\end{aligned} \tag{2.37}$$

Boundary conditions (1)

Now we consider problems with finite potentials, such as a finite potential step.

What should be the boundary conditions on

the wavefunction, ψ**,**

and its derivative, $d\psi/dz$**,**

at such a step?

The basic theory of second order differential equations says,

if we know both of these quantities on the boundaries,

we can solve the equation.

We want solutions for situations where

V ***is finite everywhere, and***

where the eigenenergy E ***is also a finite number.***

Boundary conditions (2)

If E and V are to be finite, then,

$d^2\psi/dz^2$ ***must also be finite everywhere.***

For $d^2\psi/dz^2$ to be finite,

$$d\psi/dz \text{ must be continuous} \tag{2.38}$$

(if there were a jump in $d\psi/dz$, $d^2\psi/dz^2$ would be infinite at the position of the jump)

and

$d\psi/dz$ ***must be finite***

(otherwise $d^2\psi/dz^2$ could also be infinite, being a limit of a difference involving an infinite quantity).

For $d\psi/dz$ to be finite,

$$\psi \text{ must be continuous} \tag{2.39}$$

These two conditions will be the boundary conditions we will use to solve problems with finite steps in the potential.

Particle incident on a potential step

A classical particle, such as a ball, when it encounters a finite potential barrier

- *will reflect off a wall,*
  - even if the kinetic energy of the ball is more than the potential energy it would have at the top of the wall

If the barrier is a slope, the ball

- *will continue over the barrier if its kinetic energy exceeds the (potential energy) height of the barrier.*

The ball could not get to the other side of the barrier if its kinetic energy was less than the barrier height.

The ball could never be found inside the barrier.

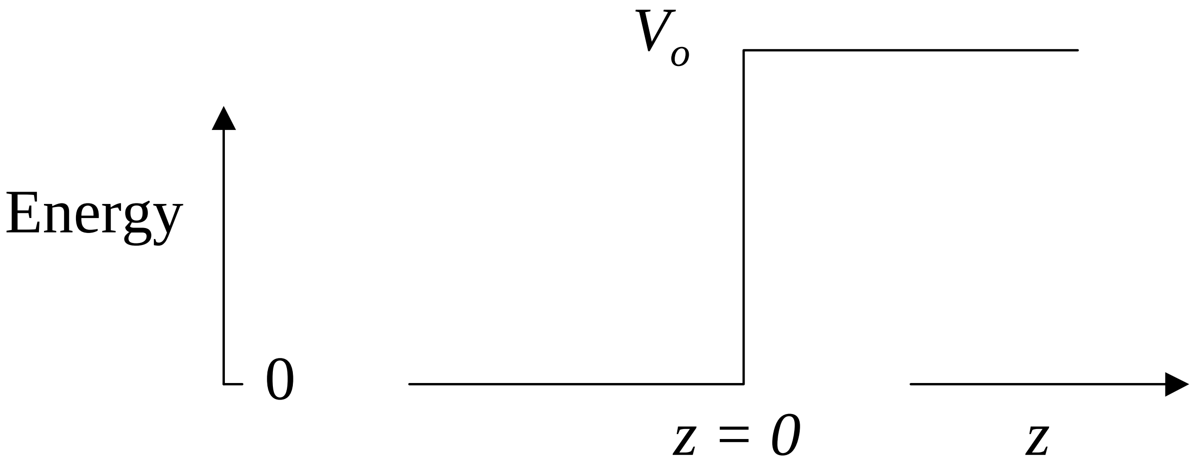
A quantum mechanical particle

- *can be found within the barrier and*
- *can get to the other side of the barrier,*
  - even if its energy is less than the height of the potential barrier.

Infinitely thick barrier (1)

Consider a barrier of finite height, V_o, and infinite thickness.

Choose the potential to be zero in the region to the left of the barrier.



A quantum mechanical wave is incident from the left on the barrier

Presume the energy, E, associated with this wave, is positive (i.e., $E > 0$).

Infinitely thick barrier (2)

We allow for reflection of the wave from the barrier into the region on the left.

We use the general solution of the wave equation in this region.

We choose complex exponential waves

$$\psi_{left}(z) = C\exp(ikz) + D\exp(-ikz) \tag{2.40}$$

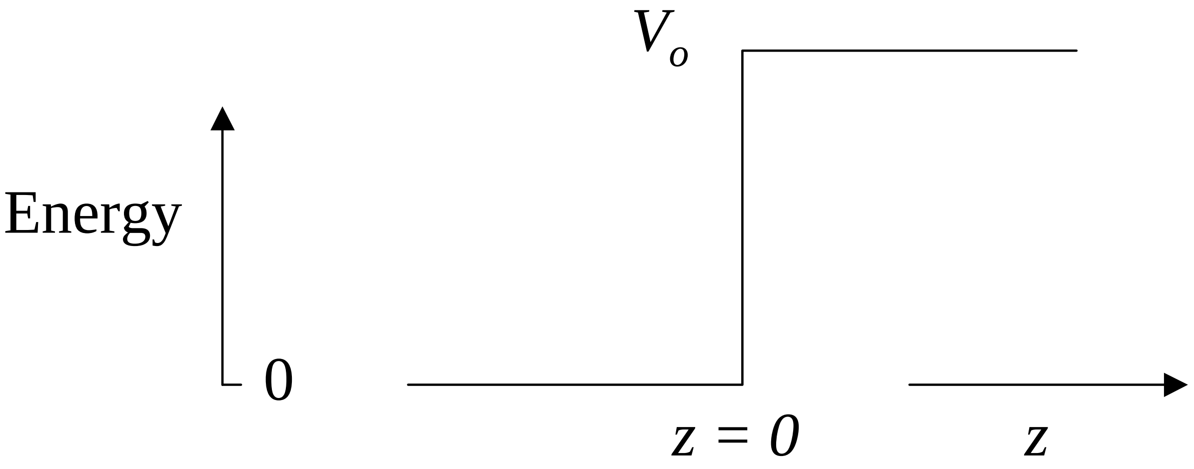
where we have, as before, $k = \sqrt{2mE/\hbar^2}$ **.**

$\exp(ikz)$ *represents a wave traveling to the right (i.e., in the positive* z *direction).*

$\exp(-ikz)$ *represents a wave traveling to the left (i.e., in the negative* z *direction).*

The right traveling wave, $C\exp(ikz)$***, is the incident wave.***

The left-traveling wave, $D\exp(-ikz)$***, is the reflected wave from the barrier.***



Infinitely thick barrier (3)

Presume that $E < V_o$,

i.e., the particle does not have enough energy to get over this barrier.

Inside the barrier, the wave equation therefore becomes

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dz^2} = -\left(V_o - E\right)\psi \tag{2.41}$$

The solution is straightforward, for the wave, ψ_{right}, on the right (i.e., for $z > 0$),

$$\psi_{right}\left(z\right) = F\exp\left(\kappa z\right) + G\exp\left(-\kappa z\right) \tag{2.42}$$

where $\kappa = \sqrt{2m\left(V_o - E\right)/\hbar^2}$

We presume that $F = 0$.

Otherwise the wave increases exponentially to the right for ever,

which does not correspond to any classical or quantum mechanical behavior we see for particles incident from the left. Hence

$$\psi_{right}\left(z\right) = G\exp\left(-\kappa z\right) \tag{2.43}$$

This solution proposes that the wave inside the barrier is not zero;

it falls off exponentially!

Infinitely thick barrier (4)

We formally complete the mathematical solution here.

Continuity of the wavefunction (2.39) gives us

$$C + D = G \tag{2.44}$$

and continuity of the derivative, (2.38), gives us

$$C - D = \frac{i\kappa}{k} G \tag{2.45}$$

Addition of Eqs. (2.44) and (2.45) gives us

$$G = \frac{2k}{k + i\kappa} C = \frac{2k\left(k - i\kappa\right)}{k^2 + \kappa^2} = 2\frac{E - i\sqrt{(V_o - E)E}}{V_o} C \tag{2.46}$$

Subtraction of Eqs. (2.44) and (2.45) gives us

$$D = \frac{k - i\kappa}{k + i\kappa} C = \frac{2E - V_o - 2i\sqrt{\left(V_o - E\right)E}}{V_o} \tag{2.47}$$

Just as a check here, we find from Eq. (2.47) that $|D/C|^2 = 1$**,**

so any incident particle is completely reflected.

D/C **is, however, complex,**

which means that there is a phase shift on reflection from the barrier,

an effect with no classical precedent.

Tunneling (1)

Note the exponential decay of the wavefunction into the barrier.

So there must be a probability of finding the particle inside the barrier.

This kind of behavior is sometimes called

"tunneling" or "tunneling penetration",

by analogy with the classical idea of digging a tunnel.

There is, however, no mathematical connection between the classical idea of a tunnel and this quantum mechanical process.

The wavefunction has fallen off to 1/*e* of its initial amplitude in a distance $1/\kappa$.

That distance is short when $E << V_o$***,***

becoming longer as E **approaches** V_o**;**

the smaller the energy deficit, $V_o - E$*, the longer the tunneling penetration into the barrier.*

Tunneling (2)

Suppose that the barrier is $V_o = 2$ eV high and that we are considering incident electrons with 1 eV energy. Then

$$\kappa = \sqrt{2\times 9.1095\times 10^{-31}\times\left(2-1\right)\times 1.602\times 10^{-19} / \left(1.055\times 10^{-34}\right)^{2}} \cong 5\times 10^{9}\,\mathrm{m}^{-1}$$

I.e., the attenuation length of the wave amplitude into the barrier (i.e., the length to fall to 1/e of its initial value) is

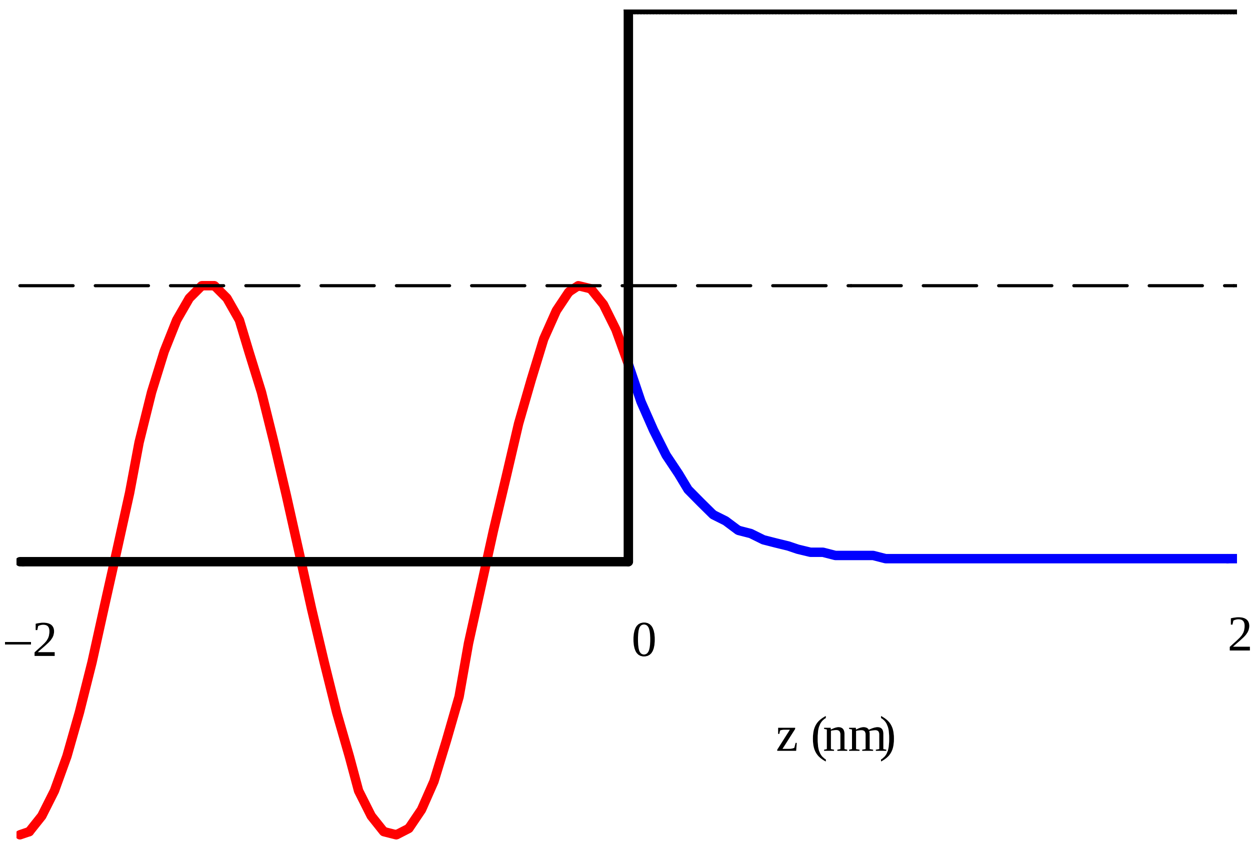
$$1/\kappa \cong 0.2\ \mathrm{nm} \equiv 2\text{Å}.$$

Note that the probability amplitude falls off twice as fast, i.e.,

$$\left|\psi\left(z\right)\right|^{2} \propto \exp\left(-2\kappa z\right),$$

so the penetration depth of the electron into the barrier is $\sim 1/2\kappa \cong 1\text{Å}$.

Wavefunction at an infinitely thick barrier



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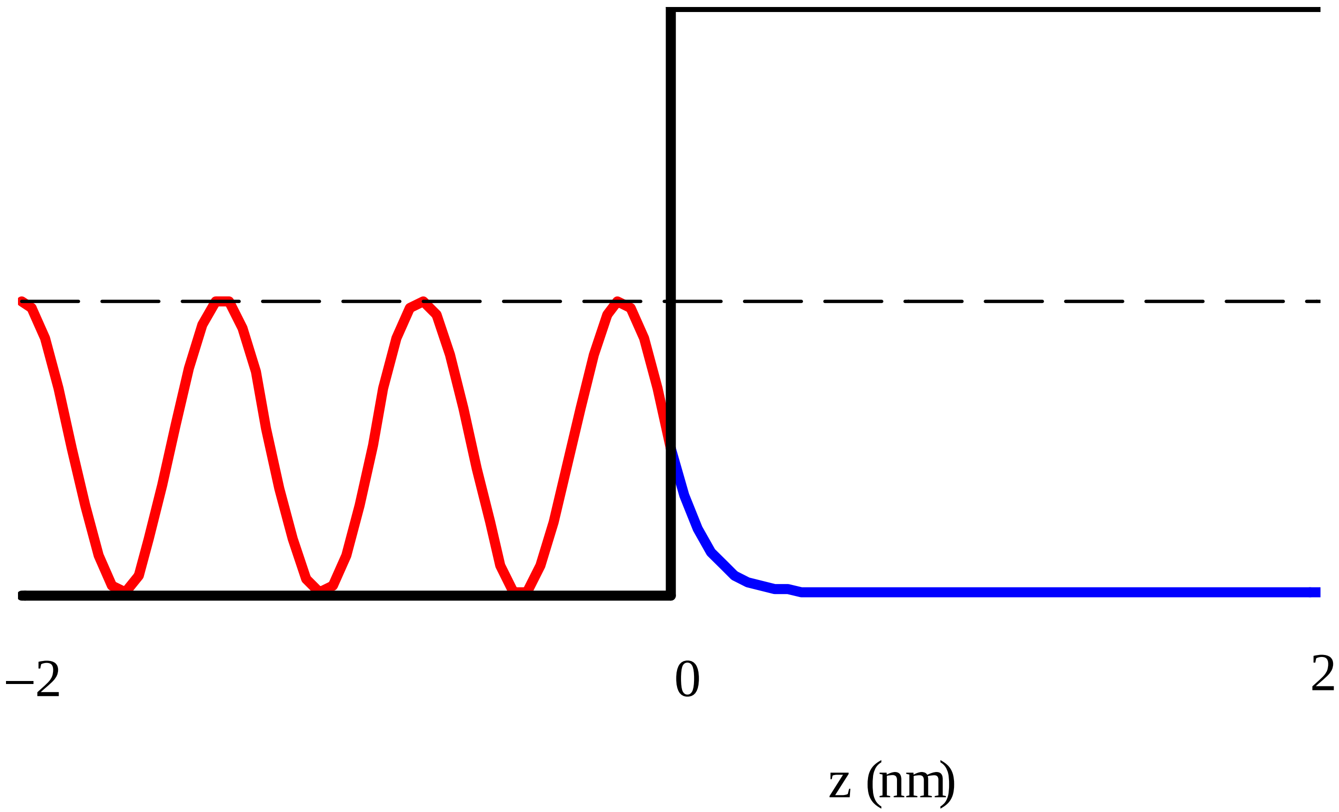
Probability Density at an Infinitely Thick Barrier



Click on the image for animation

Reflection from an infinitely thick barrier

Note that the reflection from the barrier leads to a standing wave pattern in the electron wavefunction and probability density.

The position of the standing wave pattern depends on the phase change on reflection from the barrier,

and this changes as the electron energy changes.

For a very high barrier,

the phase change on reflection is π

(i.e., 180°, or, equivalently, phase reversal), and

when the electron energy approaches the barrier energy,

the phase change becomes ~ 0.

Examples of Solving Schrödinger’s Equation - 1

Readings – Sections 2.9 – 2.10

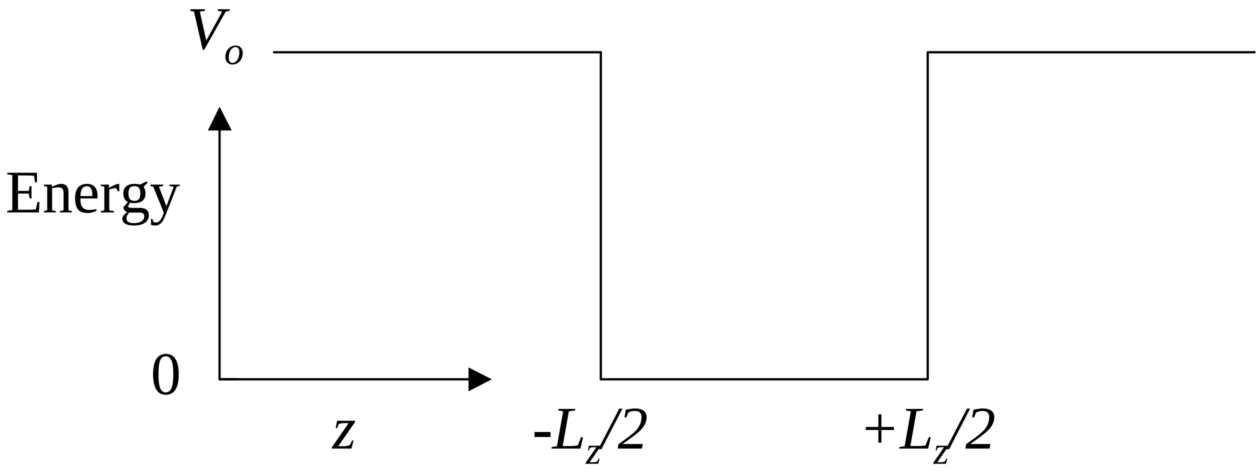
Particle in a finite potential well

Harmonic oscillator

Particle in a finite potential well - 1

Now we consider a particle in a "square" potential well of finite depth.

Here we choose the origin for z in the middle of the potential well.



We consider the case where $E < V_o$.

Such solutions are known as bound states.

We know the nature of the solutions in the barriers

exponential decays away from the potential well

and in the well

sinusoidal

and the boundary conditions that link these solutions.

Particle in a finite potential well - 2

We first need to find

> *the values of the energy for which there are solutions to the Schrödinger equation, then*
>
> **deduce the corresponding wavefunctions.**

In the potential well,

> *the form of Schrödinger's equation*
>
> *and the form of the solutions,*

are the same as we had for the infinite well, though

> *the valid energies* E
>
> *and the corresponding values of* k *(*$=\sqrt{2mE/\hbar^2}$ *)*

will be different from the infinite well case.

In the barriers,

> *the solution in the barrier is exponential*
>
> *but the solution in the left barrier will be exponentially decaying to the left.*

Particle in a finite potential well - 3

Hence, formally, the solutions are of the form

$$\psi(z) = G\exp(\kappa z),\ z < -L_z/2$$

$$\psi(z) = A\sin kz + B\cos kz,\ -L_z/2 < z < +L_z/2 \tag{2.48}$$

$$\psi(z) = F\exp(-\kappa z),\ z > L_z/2$$

where amplitudes A***,*** B***,*** F***,*** G***, and energy*** E

(and consequently k, and $\kappa = \sqrt{2m(V_o - E)/\hbar^2}$ *)*

are constants to be determined.

For simplicity of notation, we choose to write

$$X_L = \exp(-\kappa L_z/2),\ S_L = \sin(kL_z/2),\ C_L = \cos(kL_z/2)$$

so the boundary conditions give

from continuity of the wavefunction

$$GX_L = -AS_L + BC_L \tag{2.49}$$

$$FX_L = AS_L + BC_L \tag{2.50}$$

from continuity of the derivative of the wavefunction

$$\frac{\kappa}{k}GX_L = AC_L + BS_L \tag{2.51}$$

$$-\frac{\kappa}{k}FX_L = AC_L - BS_L \tag{2.52}$$

Particle in a finite potential well - 4

Adding Eqs. (2.49) $GX_L = -AS_L + BC_L$ **and (2.50)** $FX_L = AS_L + BC_L$ **gives**

$$2BC_L = \left(F+G\right)X_L \tag{2.53}$$

Subtracting Eq. (2.52) $-\frac{\kappa}{k}FX_L = AC_L - BS_L$ **from Eq. (2.51)** $-\frac{\kappa}{k}FX_L = AC_L - BS_L$ **gives**

$$2BS_L = \frac{\kappa}{k}\left(F+G\right)X_L \tag{2.54}$$

As long as $F \neq -G$**, we can divide Eq. (2.54) by Eq. (2.53) to obtain**

$$\tan\left(kL_z/2\right) = \kappa/k \tag{2.55}$$

Alternatively, subtracting Eq. (2.49) $GX_L = -AS_L + BC_L$ **from Eq. (2.50)** $FX_L = AS_L + BC_L$ **gives**

$$2AS_L = \left(F-G\right)X_L \tag{2.56}$$

and adding Eqs. (2.51) $\frac{\kappa}{k}GX_L = AC_L + BS_L$ **and (2.52)** $-\frac{\kappa}{k}FX_L = AC_L - BS_L$ **gives**

$$2AC_L = -\frac{\kappa}{k}\left(F-G\right)X_L \tag{2.57}$$

Hence, as long as $F \neq G$**, we can divide Eq. (2.57) by Eq. (2.56) to obtain**

$$-\cot\left(kL_z/2\right) = \kappa/k \tag{2.58}$$

Particle in a finite potential well - 5

For any situation other than $F = G$

(which leaves Eq. (2.55) $\tan(kL_z/2) = \kappa/k$ applicable but Eq. (2.58) $-\cot(kL_z/2) = \kappa/k$ not)

or $F = -G$

(which leaves Eq. (2.58) applicable but Eq. (2.55) not),

the two relations (2.55) and (2.58) would contradict each other,

so the only possibilities are

(i) $F = G$ with relation (2.55), and

(ii) $F = -G$ with relation (2.58).

For $F = G$, we see from Eqs. (2.56) $2AS_L = (F - G)X_L$ and (2.57) $2AC_L = -\frac{\kappa}{k}(F - G)X_L$ that $A = 0$,

so we are left with only the cosine wavefunction in the well,

and the overall wavefunction is symmetrical from left to right

(i.e., has even parity).

Similarly, for $F = -G$, $B = 0$,

we are left only with the sine wavefunction in the well,

and the overall wavefunction is antisymmetric from left to right

(i.e., has odd parity).

Particle in a finite potential well - 6

Hence, we are left with two sets of solutions.

To write these solutions more conveniently, we change notation.

We define a useful energy unit,

the energy of the first level in the infinite potential well of the same width *L_z*,

$$E_1^\infty = \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 \qquad (2.59)$$

and define a dimensionless energy

$$\varepsilon \equiv \frac{E}{E_1^\infty} \qquad (2.60)$$

and a dimensionless barrier height

$$v_o \equiv \frac{V_o}{E_1^\infty} \qquad (2.61)$$

Particle in a finite potential well - 7

Consequently,

$$\frac{\kappa}{k} = \sqrt{\frac{V_o - E}{E}} = \sqrt{\frac{v_o - \varepsilon}{\varepsilon}} \tag{2.62}$$

$$\frac{kL_z}{2} = \frac{\pi}{2}\sqrt{\frac{E}{E_1^\infty}} = \frac{\pi}{2}\sqrt{\varepsilon} \tag{2.63}$$

$$\frac{\kappa L_z}{2} = \frac{\pi}{2}\sqrt{\frac{V_o - E}{E_1^\infty}} = \frac{\pi}{2}\sqrt{v_o - \varepsilon} \tag{2.64}$$

We can also conveniently define two quantities that will appear in the wavefunctions

$$c_L = \frac{C_L}{X_L} = \frac{\cos(kL_z/2)}{\exp(-\kappa L_z/2)} = \frac{\cos\left(\pi\sqrt{\varepsilon}/2\right)}{\exp\left(-\pi\sqrt{v_o - \varepsilon}/2\right)} \tag{2.65}$$

$$s_L = \frac{S_L}{X_L} = \frac{\sin(kL_z/2)}{\exp(-\kappa L_z/2)} = \frac{\sin\left(\pi\sqrt{\varepsilon}/2\right)}{\exp\left(-\pi\sqrt{v_o - \varepsilon}/2\right)} \tag{2.66}$$

and it will be convenient to define a dimensionless distance

$$\zeta = z/L_z \tag{2.67}$$

Particle in a finite potential well - 8

We can therefore write the two sets of solutions as follows.

Symmetric solution

The allowed energies satisfy

$$\sqrt{\varepsilon}\tan\left(\frac{\pi}{2}\sqrt{\varepsilon}\right)=\sqrt{v_o-\varepsilon} \tag{2.68}$$

The wavefunctions are

$$\begin{aligned}\psi(\zeta)&=Bc_L\exp\left(\pi\sqrt{v_o-\varepsilon}\zeta\right),\ \zeta<-1/2\\ \psi(\zeta)&=B\cos\left(\pi\sqrt{\varepsilon}\zeta\right),\ -1/2<\zeta<1/2\\ \psi(\zeta)&=Bc_L\exp\left(-\pi\sqrt{v_o-\varepsilon}\zeta\right),\ \zeta>1/2\end{aligned} \tag{2.69}$$

Antisymmetric solution

The allowed energies satisfy

$$-\sqrt{\varepsilon}\cot\left(\frac{\pi}{2}\sqrt{\varepsilon}\right)=\sqrt{v_o-\varepsilon} \tag{2.70}$$

The wavefunctions are

$$\begin{aligned}\psi(\zeta)&=-As_L\exp\left(\pi\sqrt{v_o-\varepsilon}\zeta\right),\zeta<-1/2\\ \psi(\zeta)&=A\sin\left(\pi\sqrt{\varepsilon}\zeta\right),\ -1/2<\zeta<1/2\\ \psi(\zeta)&=As_L\exp\left(-\pi\sqrt{v_o-\varepsilon}\zeta\right),\ \zeta>1/2\end{aligned} \tag{2.71}$$

Particle in a finite potential well - 8

In these solutions A and B are normalization coefficients that will in general be different for each different solution.

The relations (2.68)

$$\sqrt{\varepsilon}\tan\left(\frac{\pi}{2}\sqrt{\varepsilon}\right)=\sqrt{v_o-\varepsilon}$$

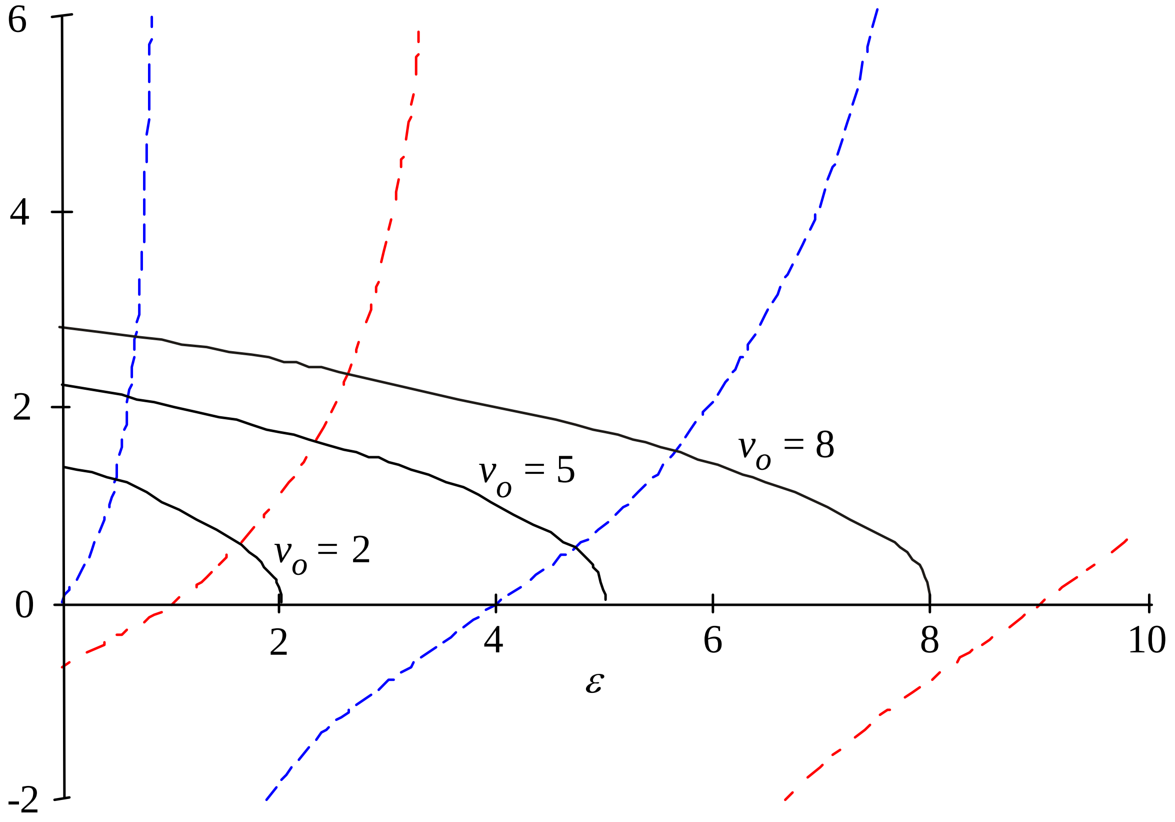
and (2.70)

$$-\sqrt{\varepsilon}\cot\left(\frac{\pi}{2}\sqrt{\varepsilon}\right)=\sqrt{v_o-\varepsilon}$$

do not give simple formulae for the allowed energies;

these relations have to be solved to deduce the allowed energies.

Graphical solution for energies



Allowed energies ε correspond to points where the appropriate solid curve

(corresponding to the right hand side of these relations)

intersects with one of the broken curves

(corresponding to the left hand sides of these relations)

dashed curve intersections correspond to a symmetric solution, and

dot-dashed curve intersections correspond to an antisymmetric solution.

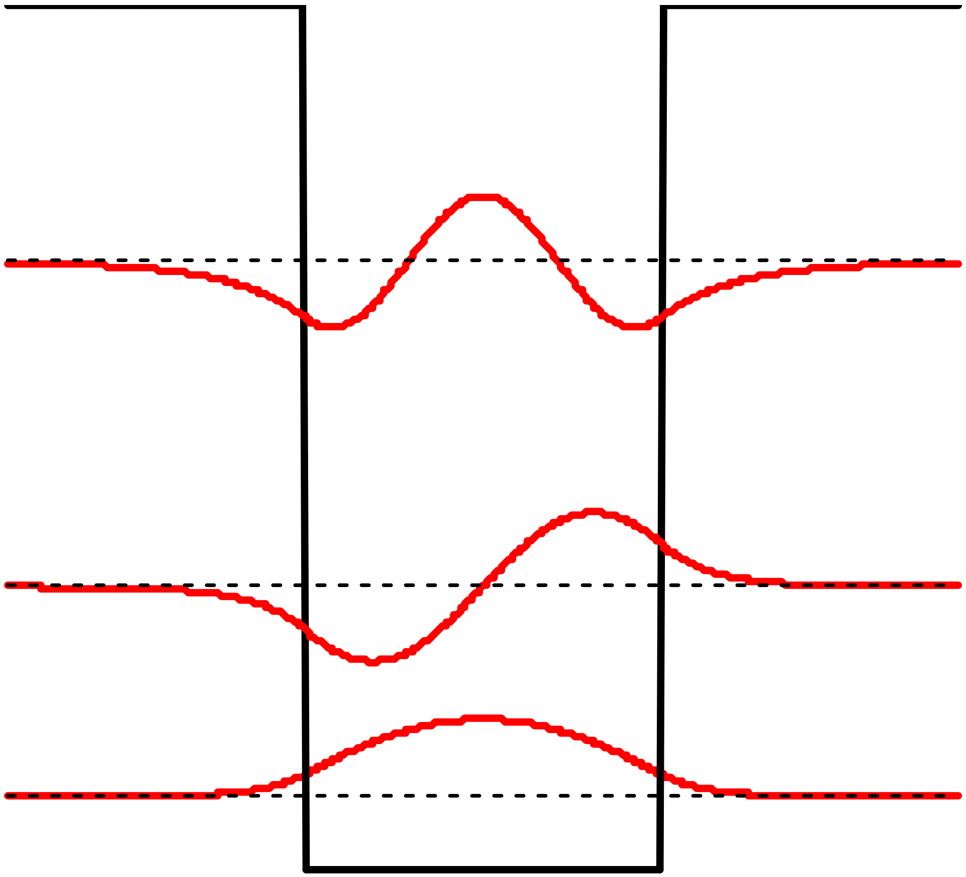
Example solution for finite well

For $v_o = 8$, there are three possible solutions:

(i) a symmetric solution at $\varepsilon = 0.663$;

(ii) an antisymmetric solution at $\varepsilon = 2.603$; and

(iii) a symmetric solution at $\varepsilon = 5.609$.



Solutions for the finite well

Note that these solutions for $E < V_o$ have two important characteristics.

- ***(1) there are solutions of the time-independent Schrödinger equation only for specific discrete energies.***

- ***(2) the particle is still largely found in the vicinity of the potential well,***
  - **though there is some probability of finding the particle in the barriers near the well.**

This problem can also be solved for energies above the top of the barrier.

- ***In that case, there are solutions possible for all energies,***
  - **a so-called continuum of energy eigenstates,**
- ***just as there are solutions possible for all energies in the simple problem where V is a constant everywhere***
  - **(the well-known plane waves we have been using to discuss diffraction and waves reflecting from single barriers).**

Harmonic oscillator

Consider the harmonic oscillator,

another quantum mechanical problem that can be solved exactly.

This system is one of the most useful in quantum mechanics,

being the first approximation to nearly all oscillating systems

e.g., describing photons.

We consider here a simple mechanical oscillator.

Classical harmonic oscillator

Classical harmonic oscillators give a simple, sinusoidal oscillation in time.

E.g., with linear springs whose (restoring) force,

***F*, is proportional to distance, z,**

with some spring constant, s,

i.e., $F = -sz$.

With a mass *m*, we obtain from Newton's second law

(*$F = ma$ *where a is acceleration,* d^2z/dt^2*)

$$m\frac{d^2z}{dt^2} = -sz \qquad (2.72)$$

The solutions to such a classical motion are sinusoidal with angular frequency

$$\omega = \sqrt{s/m} \qquad (2.73)$$

e.g., of the form $\sin(\omega t)$

Quantum mechanical harmonic oscillator - 1

To analyze this using Schrödinger's equation,

we need to cast the problem in terms of potential energy.

The potential energy, $V(z)$, is the integral of

force exerted on the spring (i.e., $-F$) times distance, i.e.,

$$V(z) = \int_0^z -F\,dz = \frac{1}{2}sz^2 = \frac{1}{2}m\omega^2 z^2 \tag{2.74}$$

Hence, for a quantum mechanical oscillator, we have a Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + \frac{1}{2}m\omega^2 z^2\psi = E\psi \tag{2.75}$$

To make this more manageable mathematically, we define a dimensionless unit of distance

$$\xi = \sqrt{\frac{m\omega}{\hbar}}\,z \tag{2.76}$$

Changing to this variable, and dividing by $-\hbar\omega$, we obtain

$$\frac{d^2\psi}{d\xi^2} - \xi^2\psi = -\frac{2E}{\hbar\omega}\psi \tag{2.77}$$

Quantum mechanical harmonic oscillator - 2

One specific solution to this equation $\frac{d^2\psi}{d\xi^2} - \xi^2\psi = -\frac{2E}{\hbar\omega}\psi$ is of the form

$$\psi \propto \exp(-\xi^2/2)$$

(with a corresponding energy $E = \hbar\omega/2$).

This suggests that we make a choice of form of function

$$\psi_n(\xi) = A_n \exp\left(-\xi^2/2\right) H_n(\xi) \tag{2.78}$$

where $H_n(\xi)$ is some set of functions still to be determined.

Substituting this form in the Schrödinger equation (2.77), we obtain

$$\frac{d^2 H_n(\xi)}{d\xi^2} - 2\xi \frac{dH_n(\xi)}{d\xi} + \left(\frac{2E}{\hbar\omega} - 1\right) H_n(\xi) = 0 \tag{2.79}$$

This equation is the defining differential equation for the Hermite polynomials.

Solutions exist provided

$$\frac{2E}{\hbar\omega} - 1 = 2n, \; n = 0, 1, 2, \ldots \tag{2.80}$$

i.e.,

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \tag{2.81}$$

(Note that here n starts from zero, not 1.)

Quantum mechanical harmonic oscillator - 3

Here we see the first remarkable property of the harmonic oscillator

> ***the allowed energy levels are equally spaced,***
>
> > **separated by an amount $\hbar\omega$,**
> >
> > > *where* ω *is the classical oscillation frequency.*

Like the potential well, there is also a "zero point energy"

> ***the first allowed state is not at zero energy,***
>
> > **but instead here at $\hbar\omega/2$ compared to the classical minimum energy.**

Hermite polynomials

The first few Hermite polynomials are as follows.

$$H_0 = 1 \tag{2.82}$$

$$H_1(\xi) = 2\xi \tag{2.83}$$

$$H_2(\xi) = 4\xi^2 - 2 \tag{2.84}$$

$$H_3(\xi) = 8\xi^3 - 12\xi \tag{2.85}$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \tag{2.86}$$

Note that

the functions are either entirely odd or entirely even,

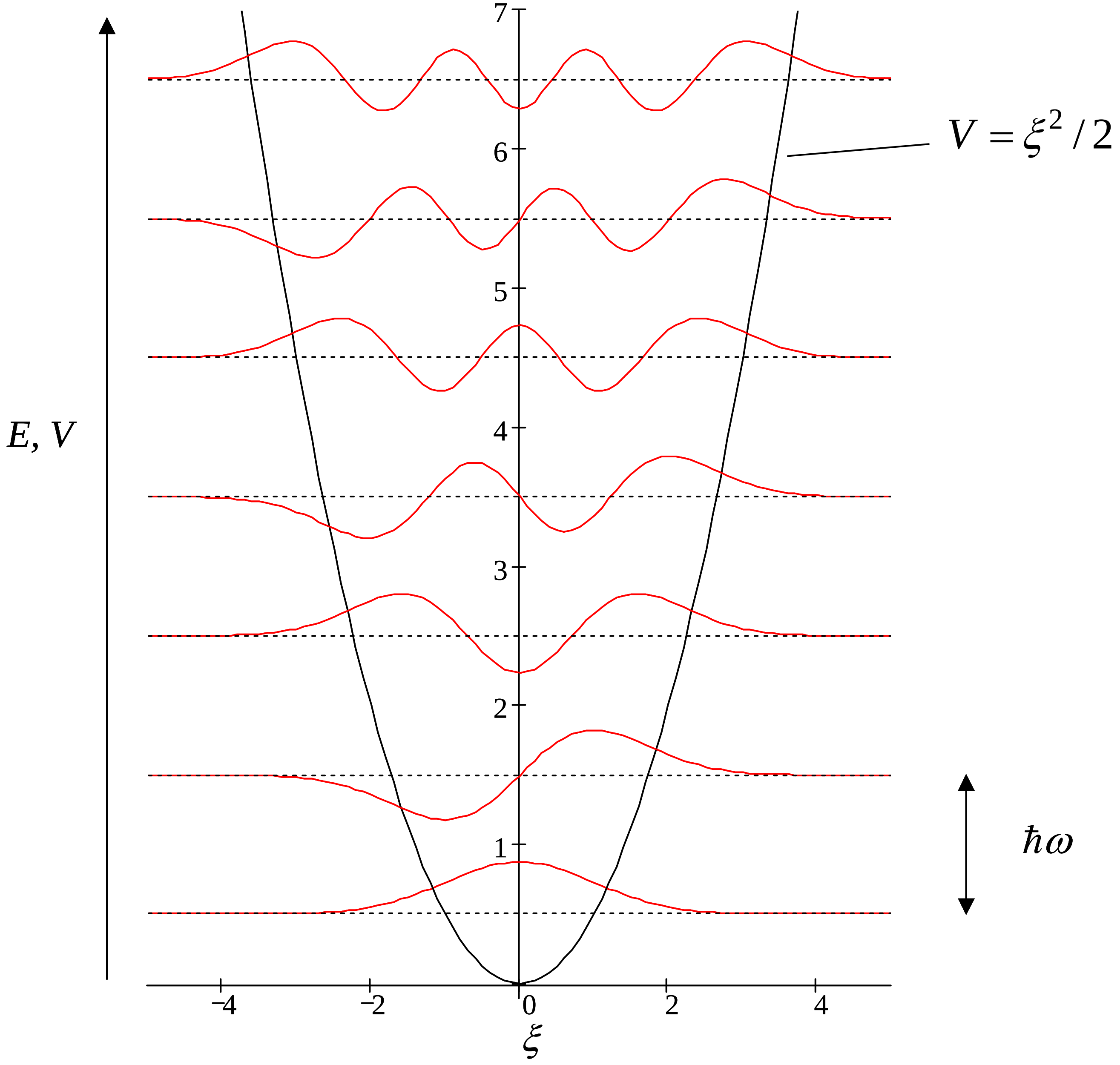
i.e., they have a definite parity.

The polynomials satisfy a "recurrence relation"

$$H_n(\xi) = 2\xi H_{n-1}(\xi) - 2(n-1)H_{n-2}(\xi) \tag{2.87}$$

the successive Hermite polynomials can be calculated from the previous two.

Harmonic oscillator solutions - 1



Harmonic oscillator solutions - 2

The normalization coefficient, A_n, in the wavefunction (2.78)

$$`\psi_n(\xi) = A_n \exp\left(-\xi^2/2\right) H_n(\xi)$$

is

$$A_n = \sqrt{\frac{1}{\sqrt{\pi}\, 2^n n!}} \tag{2.88}$$

and the wavefunction can be written explicitly in the original coordinate system as

$$\psi_n(z) = \sqrt{\frac{1}{2^n n!}\sqrt{\frac{m\omega}{\pi\hbar}}} \exp\left(-\frac{m\omega}{2\hbar}z^2\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}}z\right) \tag{2.89}$$

Harmonic oscillator and oscillations

Note we have found the solution to Schrödinger's time-independent wave equation for the case of the harmonic oscillator,

just as we did for the infinite and finite potential wells.

But why is it not oscillating?

We have calculated stationary states for this oscillator,

including stationary states in which the oscillator has energy much greater than zero.

This would be meaningless classically;

an oscillator that has energy ought to oscillate!?

To understand how we recover oscillating behavior,

we need to understand the time-dependent Schrödinger equation.

Examples of Solving Schrödinger's Equation - 2

Reading – Section 2.11

Particle in a linearly varying potential

Particle in a linearly varying potential - 1

Another common situation is a

uniform electric field, E***, e.g., in the*** z ***direction***

leading to a potential that varies linearly in distance.

An electron will see a potential energy of

$$V = e\mathsf{E}z \tag{2.90}$$

E.g., in semiconductor devices

in the formal solution for tunneling into the gate oxide in Metal-Oxide-Semiconductor (MOS) transistors

as used in semiconductor optical modulators with field-dependent optical absorption

This is of basic interest also to

understand how an electron is accelerated by a field

Approach - put this potential into the Schrödinger equation and solve

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2} + e\mathsf{E}z\psi(z) = E\psi(z) \tag{2.91}$$

This kind of equation has solutions that are "Airy" functions.

Particle in a linearly varying potential - 2

The standard form of differential equation that defines Airy functions is

$$\frac{d^2 f(\zeta)}{d\zeta^2} - \zeta f(\zeta) = 0 \qquad (2.92)$$

The solutions are formally the Airy functions $Ai(\zeta)$ ***and*** $Bi(\zeta)$***,***

i.e., the general solution to this equation is

$$f(\zeta) = a\,Ai(\zeta) + b\,Bi(\zeta) \qquad (2.93)$$

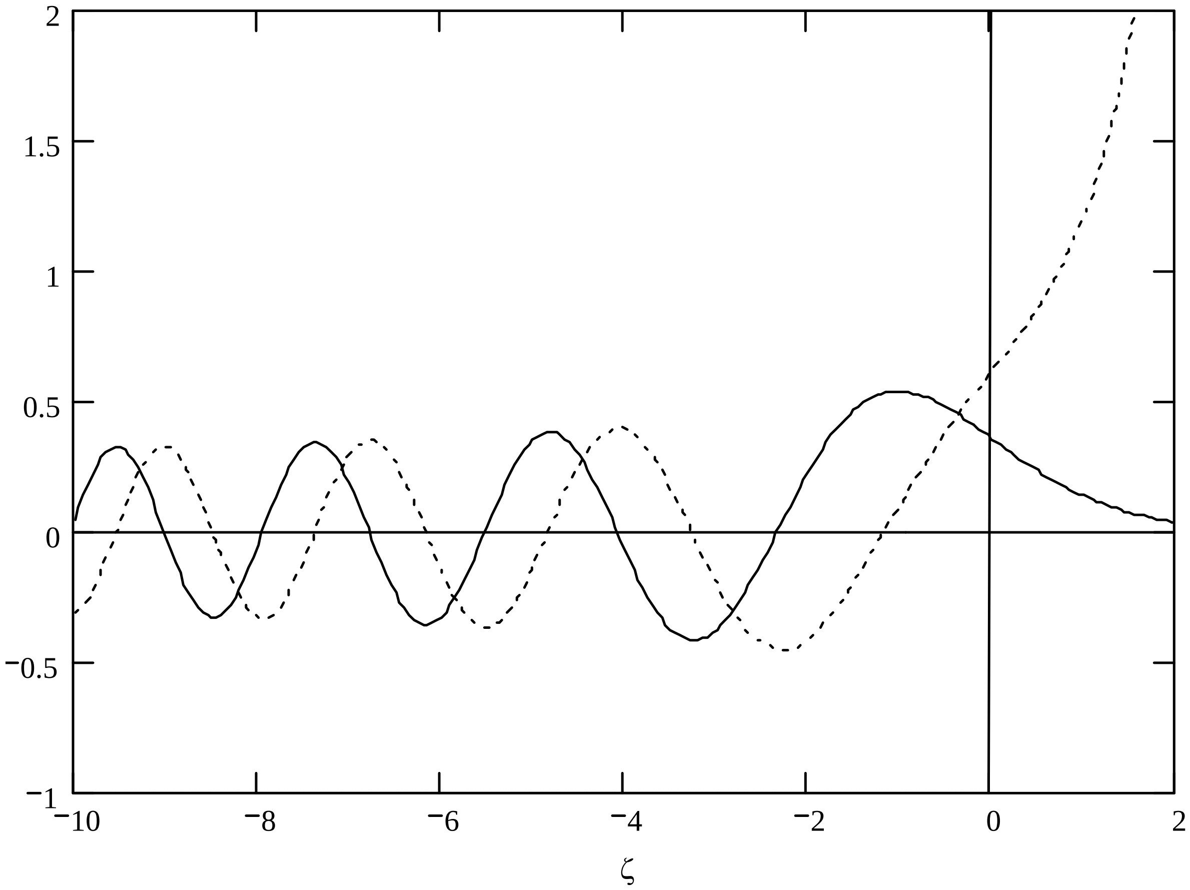
To get Eq. (2.91)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2} + e\mathrm{E}z\psi(z) = E\psi(z)$$

into the form of Eq. (2.92), we make a change of variable to

$$\zeta = \left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(z - \frac{E}{e\mathrm{E}}\right) \qquad (2.94)$$

Airy functions



Airy functions $Ai(\zeta)$ (solid line) and $Bi(\zeta)$ (broken line)
Note that

(i) both functions are oscillatory for negative arguments, with a shorter and shorter period as the argument becomes more negative.

(ii) The Ai function decays in an exponential-like fashion for positive arguments.

(iii) The Bi function diverges for positive arguments.

Linear potential without boundaries - 1

Consider a potential that varies linearly without any boundaries or walls.

There are two possible solutions,

one based on the Ai function,

and the other based on the Bi function.

Physically, we discard the Bi solution here because it diverges for positive arguments, becoming larger and larger.

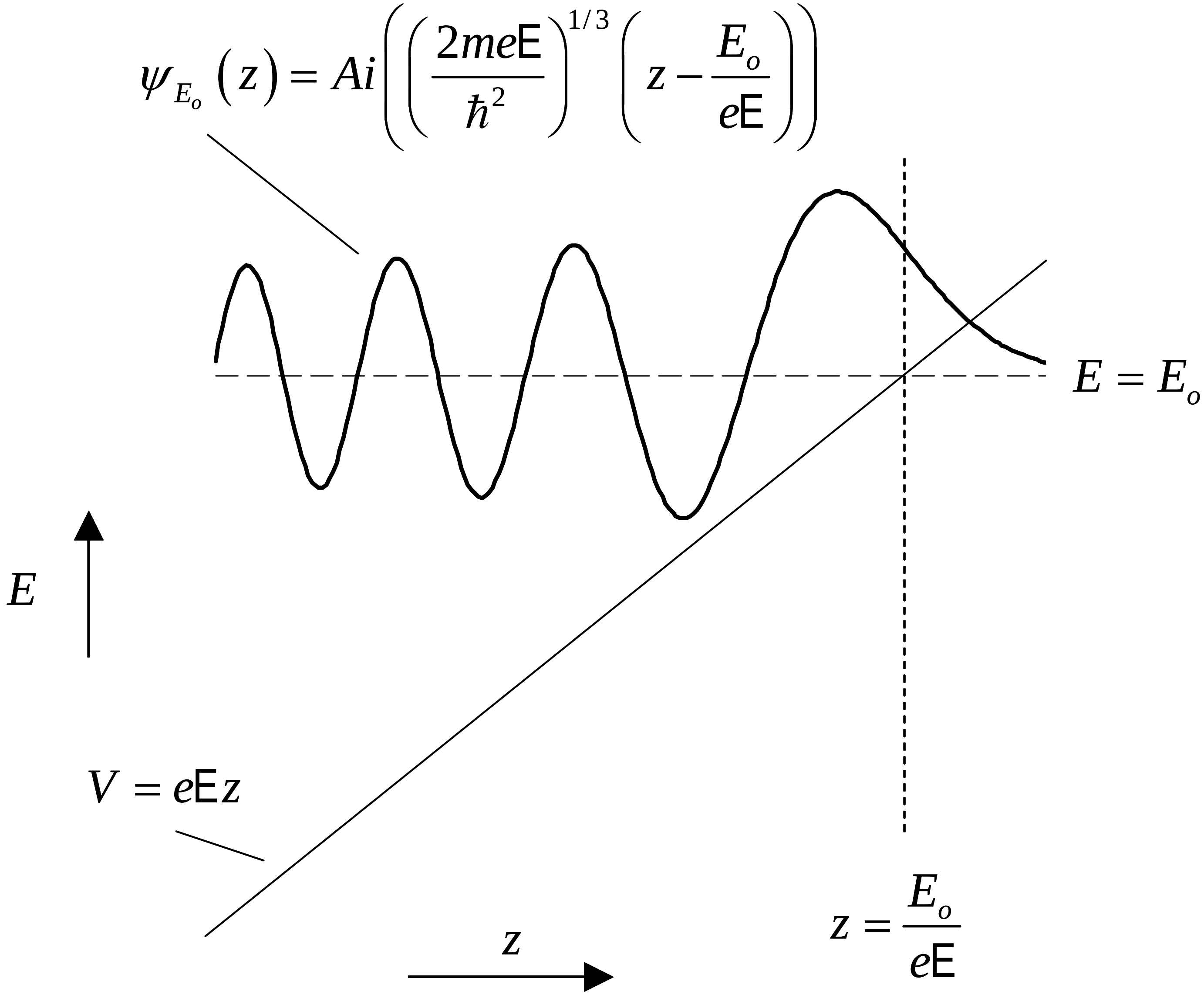
We are left only with the Ai function in this case.

Substituting back from the change of variable, Eq. (2.94), the $Ai(\zeta)$ solution becomes explicitly

$$\psi_E(z) = Ai\left(\left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(z - \frac{E}{e\mathrm{E}}\right)\right) \qquad (2.95)$$

Linear potential without boundaries - 2

This solution is sketched, for a specific eigenenergy *E_o*, together with the potential energy.



$$\psi_{E_o}(z) = Ai\left(\left(\frac{2me\mathsf{E}}{\hbar^2}\right)^{1/3}\left(z - \frac{E_o}{e\mathsf{E}}\right)\right)$$

$E = E_o$

E

$V = e\mathsf{E}z$

z

$z = \frac{E_o}{e\mathsf{E}}$

Linear potential without boundaries - 3

There are several interesting aspects about this solution.

- ***(i) There are mathematical solutions for any possible value of the eigenenergy E.***
  - **This behavior reminds us of the uniform zero potential (i.e., $V = 0$ everywhere),**
    - *which leads to plane wave solutions for any positive energy.*
  - **In the present case also, the allowed values of the eigenenergies are continuous, not discrete.**
    - *Also like the uniform potential problem, it is a problem in which the eigenstates are not bound to some finite region (at least for negative z).*
- ***(ii) The solution is oscillatory when the eigenenergy is greater than the potential energy,***
    - *which occurs on the left of the point $z = E_o / e\mathcal{E}$,*
  - **and decaying to the right of this point.**
    - *This point is known as the classical turning point, because it is the furthest to the right that a classical particle of energy E_o could go.*
- ***(iii) The eigenfunction solutions for different energies are the same except they are shifted sideways (i.e., shifted in z).***
- ***(iv) Unlike the uniform potential, the solutions are not running waves;***
  - **rather, they are standing waves, more like the case of the particle in a box.**

Linear potential without boundaries - 4

Just like the harmonic oscillator

we have eigenstates, i.e., states that are stable in time.

Just as in the harmonic oscillator case, where we expected to get an oscillation

here we would have expected to get states that correspond to the electron being accelerated.

We have put an electron in an electric field, and the electron is not moving!

Again, to resolve this

we need to consider the time-dependent Schrödinger equation

Linear potential without boundaries - 5

How could we even have a standing wave in this case?

For particle in a box, we can rationalize that the particle is reflecting off of the walls

In the present case, we could accept that the particle should bounce off the increasing potential,

so we see why there is a reflection at the right.

The reason why there is any reflection on the left is that

any change in potential (or change of impedance in the case of acoustic or electromagnetic waves),

even if it is smooth rather than abrupt,

leads to reflections.

Effectively, there is a distributed reflection on the left from the continuously changing potential there.

The fact that there is such a distributed reflection explains why the wave amplitude decreases progressively as we go to the left.

The fact that we have a standing wave is apparently because, integrated up, that reflection does eventually add up to 100%.

Linear potential without boundaries - 6

Why does the period of the oscillations in the wave decrease (i.e., the oscillations become faster) as we move to the left?

Suppose in Schrödinger's equation we divide both sides by ψ, so

$$\frac{-\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dz^2}+V(z)=E \tag{2.96}$$

For any eigenstate of the Schrödinger equation, E is a constant (the eigenenergy).

In such a state, if V decreases, then -$(1/\psi)(d^2\psi/dz^2)$ must increase.

If we imagine that we have an oscillating wave,

which we presume is locally approximately sinusoidal, of the form $\sim\sin(kz+\theta)$ for some phase angle θ,

$$\frac{-1}{\psi}\frac{d^2\psi}{dz^2}\simeq k^2 \tag{2.97}$$

Hence, if V decreases, the wavevector k must increase (the period decreases).

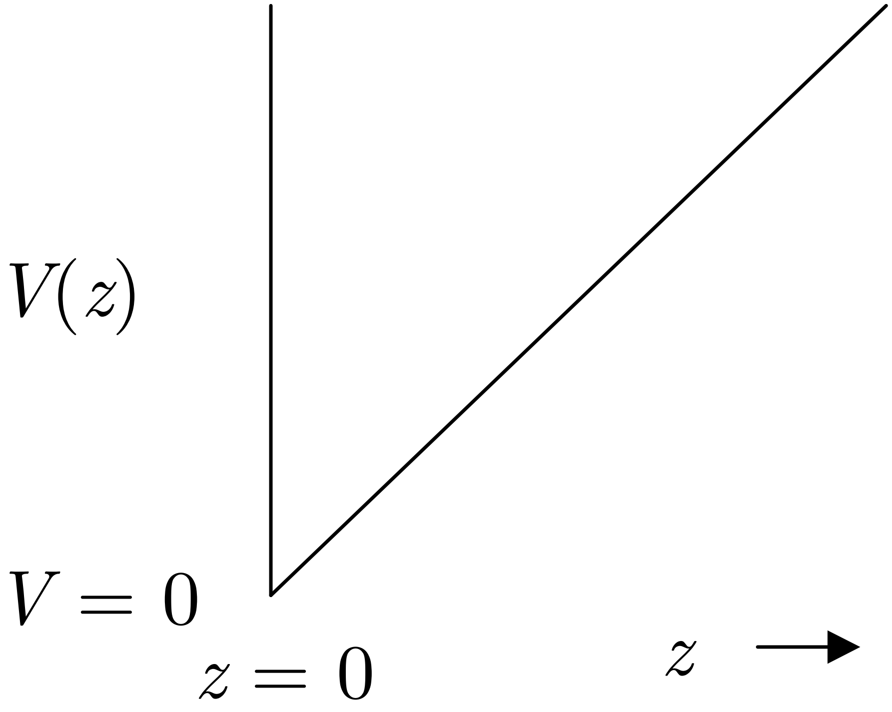
We could imagine that the particle is going increasingly fast as it goes towards the left, consistent with smaller periods as we go to the left.

This particle view is weak reasoning, though there is a kernel of truth to it, but for a full understanding in terms of particle motion, we need the time-dependent Schrödinger equation.

Triangular potential well - 1

If we put a hard barrier on the left, we again get a discrete set of eigenenergies.

Formally, put an infinitely high potential barrier at $z=0$, with the potential taken to be zero at $z=0$ (or at least just to the right of $z=0$).



For all $z>0$, we have the same potential as we considered above.

Triangular potential well - 2

Again we can discard the Bi solution because it diverges, so we are left with the Ai solution.

Now we have the additional boundary condition imposed by the infinitely high potential at $z = 0$,

which means the wavefunction must go to zero there.

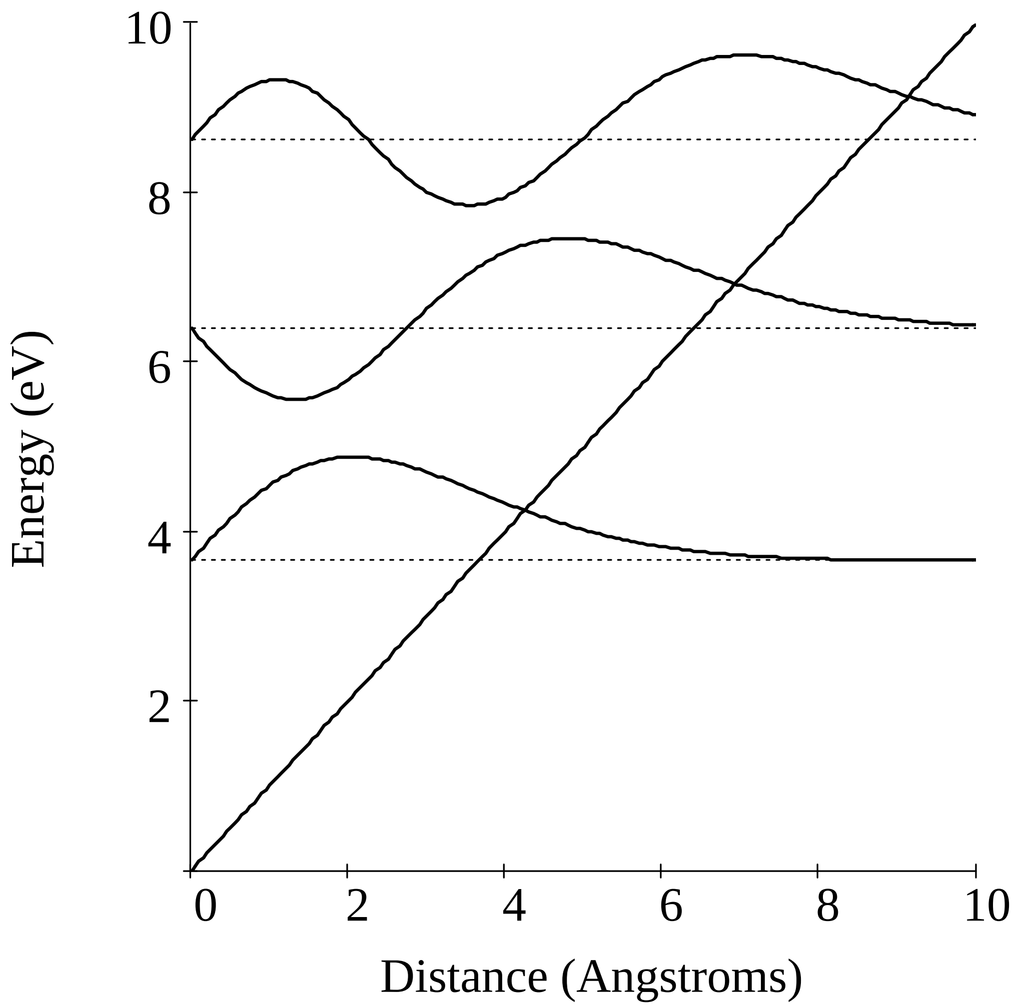
This is easily achieved with the Ai function if we position it laterally so that one of its zeros is found at $z = 0$.

The $Ai(\zeta)$ function will have zeros for a set of values ζ_i.

The first few of these are

$$\begin{aligned} \zeta_1 &\simeq -2.338 \\ \zeta_2 &\simeq -4.088 \\ \zeta_3 &\simeq -5.521 \\ \zeta_4 &\simeq -6.787 \\ \zeta_5 &\simeq -7.944 \end{aligned} \tag{2.98}$$

Triangular potential well - 3



Graphs of wavefunctions and energy levels for the first three levels in a triangular potential well, for a field of 1V/Å.

Triangular potential well - 4

To get the solution Eq. (2.95)

$$\psi_E(z) = Ai\left(\left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(z - \frac{E}{e\mathrm{E}}\right)\right)$$

to be zero at $z = 0$ means therefore that

$$Ai\left(\left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(0 - \frac{E}{e\mathrm{E}}\right)\right) = 0 \qquad (2.99)$$

i.e., the argument must be one of the zeros of the Ai function,

$$\left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(-\frac{E}{e\mathrm{E}}\right) = \zeta_i \qquad (2.100)$$

or, equivalently, the possible energy eigenvalues are

$$E_i = -\left(\frac{\hbar^2}{2m}\right)^{1/3}(e\mathrm{E})^{2/3}\zeta_i \qquad (2.101)$$

Infinite potential well with field - 1

Now include also an infinitely high barrier on the right.

Now have the additional boundary condition that the potential is infinite, and hence the wavefunction is zero, at $z = L_z$.

Now we cannot discard the Bi solution

the potential forces the wavefunction to zero at the right wall

so there will be no wavefunction amplitude to the right

and so the divergence of the Bi function no longer matters for normalization

(we would only be normalizing inside the box)

Hence we have to work with the general solution, Eq. (2.93), with both Ai and Bi functions.

The two boundary conditions are that the wavefunction must be zero at $z = 0$ and at $z = L_z$, or equivalently at $\zeta = \zeta_0$ and $\zeta = \zeta_L$, where

$$\zeta_0 \equiv -\left(\frac{2m}{\hbar^2 e^2 \mathrm{E}^2}\right)^{1/3} E \tag{2.102}$$

$$\zeta_L \equiv \left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3} \left(L_z - \frac{E}{e\mathrm{E}}\right) \tag{2.103}$$

These boundary conditions will establish what the possible values of E are, i.e., the energy eigenvalues.

Infinite potential well with field - 2

These boundary conditions result in two equations

$$a\,Ai\left(\zeta_0\right)+b\,Bi\left(\zeta_0\right)=0 \tag{2.104}$$

$$a\,Ai\left(\zeta_L\right)+b\,Bi\left(\zeta_L\right)=0 \tag{2.105}$$

or, in matrix form

$$\begin{bmatrix} Ai\left(\zeta_0\right) & Bi\zeta_0 \\ Ai\left(\zeta_L\right) & Bi\left(\zeta_L\right) \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix}=0 \tag{2.106}$$

The usual condition for a solution of such equations is

$$\begin{vmatrix} Ai\left(\zeta_0\right) & Bi\left(\zeta_0\right) \\ Ai\left(\zeta_L\right) & Bi\left(\zeta_L\right) \end{vmatrix}=0 \tag{2.107}$$

or, equivalently,

$$Ai\left(\zeta_0\right)Bi\left(\zeta_L\right)-Ai\left(\zeta_L\right)Bi\left(\zeta_0\right)=0 \tag{2.108}$$

Infinite potential well with field - 3

The next mathematical step is to find for what values of ζ_L Eq. (2.108)

$$Ai(\zeta_0)Bi(\zeta_L) - Ai(\zeta_L)Bi(\zeta_0) = 0$$

can be satisfied. This can be done numerically.

First, we change to dimensionless units.

In this problem, there are two relevant energies.

One is the natural unit for discussing potential well energies – the energy of the lowest state in an infinitely deep potential well,

$$(\hbar^2 / 2m)(\pi / L_z)^2$$

which here we will call E_1^∞ to avoid confusion with the final energy eigenstates for this problem

Hence we will use the dimensionless "energy"

$$\varepsilon \equiv E / E_1^\infty$$

The second energy in the problem is the potential drop from one side of the well to the other resulting from the electric field, which is

$$V_L = e\mathrm{E} L_z \qquad (2.109)$$

or, in dimensionless form

$$\nu_L = V_L / E_1^\infty \qquad (2.110)$$

Infinite potential well with field - 4

With these definitions $\varepsilon \equiv E / E_1^\infty$ and $\nu_L = V_L / E_1^\infty$, we can rewrite Eqs. (2.102) ($\zeta_0 \equiv -\left(\frac{2m}{\hbar^2 e^2 \mathrm{E}^2}\right)^{1/3} E$) and (2.103) ($\zeta_L \equiv \left(\frac{2me\mathrm{E}}{\hbar^2}\right)^{1/3}\left(L_z - \frac{E}{e\mathrm{E}}\right)$) as, respectively,

$$\zeta_0 \equiv -\left(\frac{\pi}{\nu_L}\right)^{2/3} \varepsilon \tag{2.111}$$

$$\zeta_L = \left(\frac{\pi}{\nu_L}\right)^{2/3} \left(\nu_L - \varepsilon\right) \tag{2.112}$$

Now we choose a specific ν_L, which corresponds to choosing the electric field for a given well width.

Suppose, for example, that we consider a 6 Å wide well with a field of 1 V/Å. Then $E_1^\infty \simeq 1.0455$eV, and $\nu_L \simeq 5.739$ (i.e., the potential change from one side of the well to the other is $\simeq 5.739\,E_1^\infty$).

Next we numerically find the values of ε that make the determinant function from Eq. (2.108),

$$D(\varepsilon) = Ai\left(\zeta_0(\varepsilon)\right)Bi\left(\zeta_L(\varepsilon)\right) - Ai\left(\zeta_L(\varepsilon)\right)Bi\left(\zeta_0(\varepsilon)\right) \tag{2.113}$$

equal to zero

e.g., graph this function from $\varepsilon = 0$ upwards to find the approximate position of the zero crossings, then use a numerical root finder

Infinite potential well with field - 5

With these eigenvalues of ε we can evaluate the wavefunctions.

From Eq. (2.104) ($a\,Ai(\zeta_0)+b\,Bi(\zeta_0)=0$), we have for the coefficients a and b of the general solution, Eq. (2.93) ($f(\zeta)=a\,Ai(\zeta)+b\,Bi(\zeta)$) , for each eigenenergy ε_i,

$$\frac{b_i}{a_i}=-\frac{Ai(\zeta_0(\varepsilon_i))}{Bi(\zeta_0(\varepsilon_i))} \tag{2.114}$$

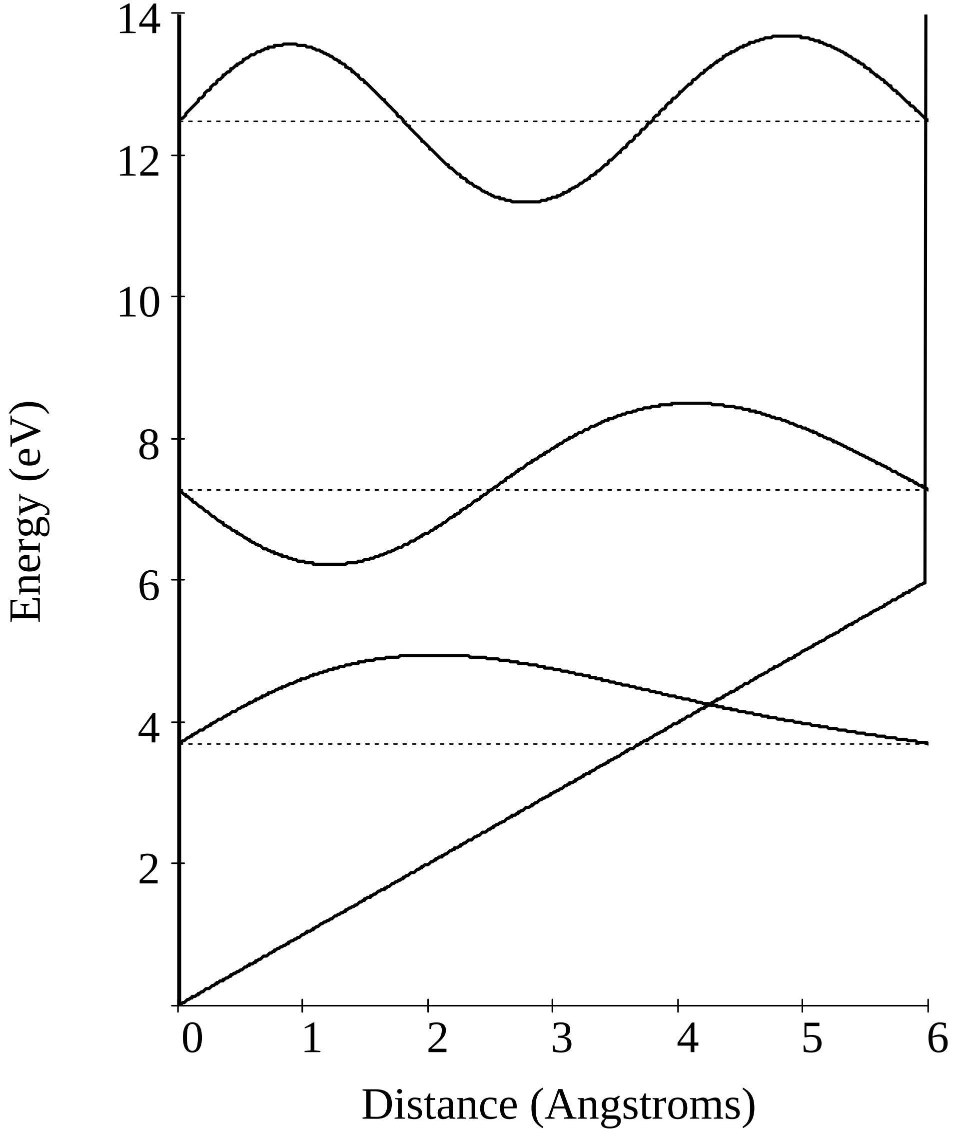
The resulting wavefunction is therefore, for a given energy eigenstate, using the same notation as for Eqs. (2.111) and (2.112) with the dimensionless energies

$$\psi_i(z)=a_i Ai\left(\left(\frac{\pi}{\nu_L}\right)^{2/3}\left(\nu_L\frac{z}{L_z}-\varepsilon\right)\right)+b_i Bi\left(\left(\frac{\pi}{\nu_L}\right)^{2/3}\left(\nu_L\frac{z}{L_z}-\varepsilon\right)\right) \tag{2.115}$$

For the example numbers here, we have

	ε_i	E_i (eV)	b/a
First level (i = 1)	3.53	3.69	-0.04
Second level (i = 2)	6.95	7.27	-2.48
Third level (i = 3)	11.93	12.47	-0.12

Infinite potential well with field – 6



First three eigenstates in a 6 Å potential well with infinitely high barriers at each side, for an electron in a field of 1 V/Å. The potential is also sketched.

Infinite potential well with field - 7

Note that

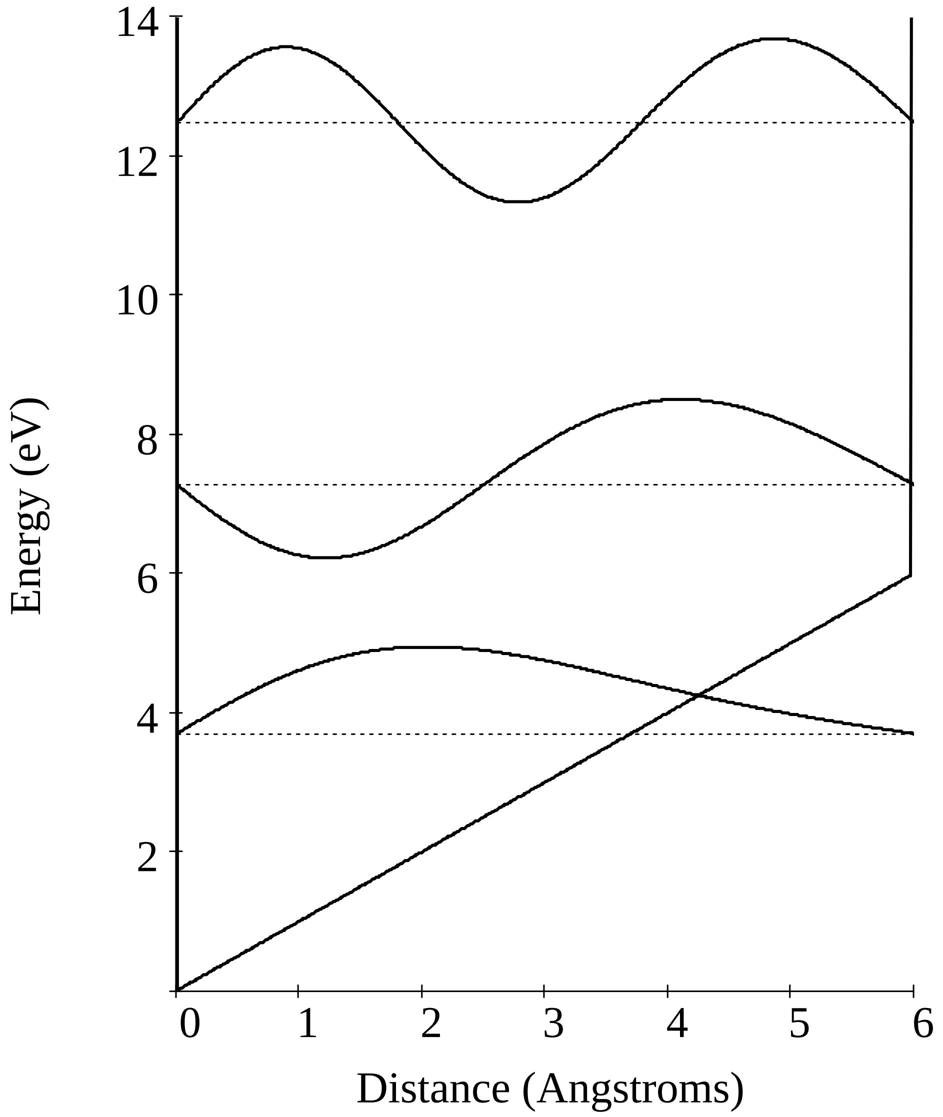
(i) All the wavefunctions go to zero at both sides of the well,

as required by the infinitely high potential energies there.

(ii) The lowest solution is almost identical in energy and wavefunction to that of the lowest state in the triangular well.

The fraction of the *Bi* Airy function is very small, -0.04.

The energy is actually slightly higher because the wavefunction is slightly more confined.



Infinite potential well with field - 8

(iii) The second solution is now quite strongly influenced by the potential barrier at the right,

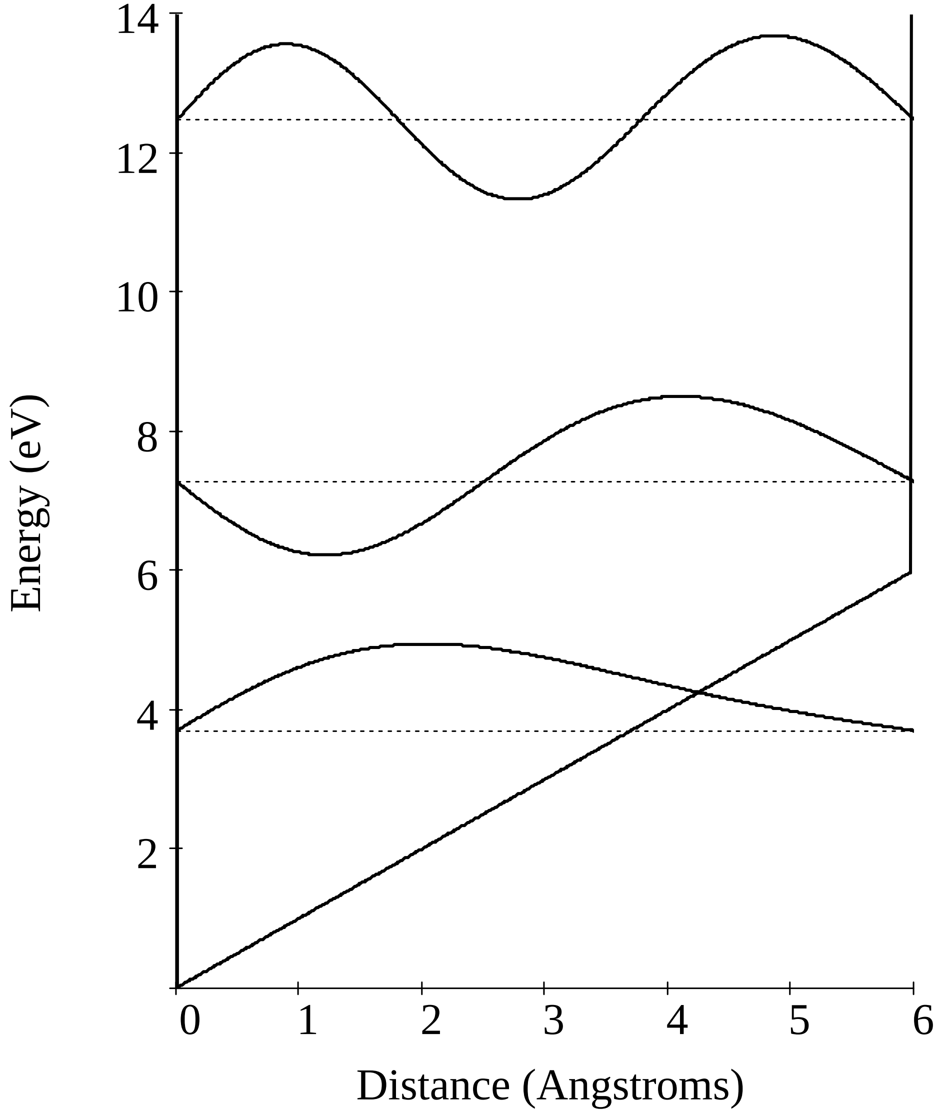
with a significantly higher energy than in the triangular well.

(iv) The third solution is very close in form to that of the third level of a simple rectangular well.

To the eye, it looks to be approximately sinusoidal,

though the period is slightly shorter on the left hand side,

consistent with our previous discussion of the effect on the wavefunction oscillation period from changes in potential.



Infinite potential well with field - 9

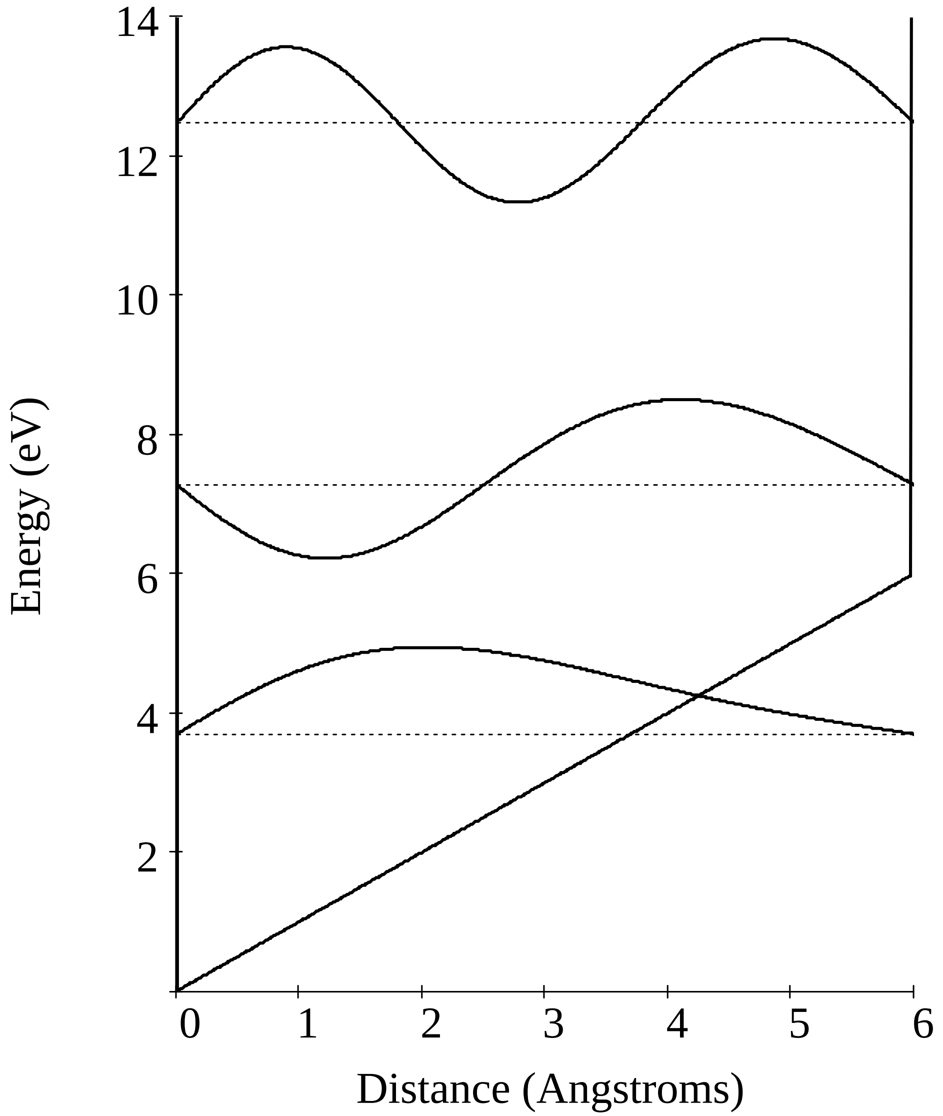
In the lowest state, the electron is pulled closer to the left hand side,

as we would expect classically from such an electric field.

Note, though, that our classical intuition does not work for the higher levels.

In fact, in the second level,

the electron is more likely to be in the right half (~ 64%) of the well than in the left half (~ 36%)!



Time-Dependent Schrödinger Equation - 1

Reading – Sections 3.1 – 3.5

Rationalization of the time-dependent Schrödinger equation

Relation to the time-independent Schrödinger equation

Solutions of the time-dependent Schrödinger equation

Linearity of quantum mechanics: linear superposition

Time dependence and expansion in the energy eigenstates

Time-dependent Schrödinger equation

So far, we presumed the spatial probability distribution was steady in time

but quantum mechanics must model situations that are not stationary.

To understand such changes

we need a time-dependent extension of Schrödinger's equation.

Here we rationalize a time-dependent version of Schrödinger's equation.

It differs from the kind of time-dependent wave equation typical for classical waves.

Then we introduce a very important concept in quantum mechanics,

superposition states.

These let us handle time evolution of quantum mechanical systems easily.

Rationalization of the relation between frequency and energy

The key to understanding time-dependence and Schrödinger's equation is

the relation between frequency and energy in quantum mechanics.

One well known example is the case of electromagnetic waves and photons.

Imagine two experiments with a monochromatic electromagnetic wave.

In one experiment, we measure the frequency of the oscillation in the wave.

In a second experiment, we count the number of photons per second.

Hence we can count how many photons per second correspond to a particular power at this frequency.

We would find in such an experiment that the energy per photon was

$$E = h\nu = \hbar\omega \tag{3.1}$$

i.e., energy proportional to frequency

This discussion is for photons,

not the electrons or other particles with mass

for which the Schrödinger equation supposedly applies.

But hydrogen atoms emit photons as they transition between energy levels

We expect some oscillation in the electrons at the corresponding frequency during the emission of the photon,

so we expect a similar relation between energy and frequency associated with the electron levels.

Rationalization of the time-dependent Schrödinger equation

We want a wave equation

with this relation $E = h\nu = \hbar\omega$ *between energy and frequency,*

and with a solution of the form $\exp\left[i\left(kz - \omega t\right)\right]$ *in a uniform potential*

Schrödinger postulated the time-dependent equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi\left(\mathbf{r},t\right) + V\left(\mathbf{r},t\right)\Psi\left(\mathbf{r},t\right) = i\hbar\frac{\partial\Psi\left(\mathbf{r},t\right)}{\partial t} \tag{3.2}$$

Waves of the form

$$\exp\left[-i\left(\frac{Et}{\hbar} \pm kz\right)\right] \equiv \exp\left(-i\frac{Et}{\hbar}\right)\exp\left(\mp ikz\right)$$

with $E = \hbar\omega$ and $k = \sqrt{2mE/\hbar^2}$,

are indeed solutions when $V = 0$ *everywhere.*

Schrödinger chose a specific sign on the right hand side,

so a wave with a spatial part $\propto \exp\left(ikz\right)$ *is definitely a wave propagating in the positive* z *direction for all positive energies* E

(i.e., the wave, including its time-dependence, would be of the form $\exp\left[i\left(kz - Et/\hbar\right)\right]$).

Contrast to common wave equations

The more common classical wave equation has the different form

$$\nabla^2 f = \frac{k^2}{\omega^2}\frac{\partial^2 f}{\partial t^2} \tag{3.3}$$

for which $f \propto \exp\left[i\left(kz - \omega t\right)\right]$ ***would also be solution.***

This equation (3.3) has a second derivative with respect to time,

as opposed to the *first* derivative in the time-dependent Schrödinger equation (3.2).

Note, incidentally, that Schrödinger's use of complex notation means that

the wavefunction is required to be a complex entity.

Unlike the use of complex notation with classical waves,

it is not the case that the "actual" wave is taken at the end of the calculation to be the real part of the calculated wave.

Relation to the time-independent Schrödinger equation - 1

Suppose that we had a solution where the spatial behavior of the wavefunction did not change its form with time.

We could allow for a time-varying multiplying factor, $A(t)$***, in front of the spatial part of the wavefunction, i.e., we could write***

$$\Psi(\mathbf{r},t) = A(t)\psi(\mathbf{r}) \qquad (3.4)$$

where, explicitly, we are presuming that $\psi(\mathbf{r})$ *is not changing in time.*

Solutions whose spatial behavior is steady in time should satisfy the time-independent equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (3.5)$$

Adding the factor $A(t)$ **in front of** $\psi(\mathbf{r})$ **makes no difference in Eq. (3.5)**

$\Psi(\mathbf{r},t)$ ***would also be a solution of Eq. (3.5), regardless of the form of*** $A(t)$***,***

i.e., we would have

$$A(t)\left[-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right] = EA(t)\psi(\mathbf{r}) \qquad (3.6)$$

Relation to the time-independent Schrödinger equation - 2

Substituting the form (3.4) $\Psi(\mathbf{r},t) = A(t)\psi(\mathbf{r})$ into the time-dependent Schrödinger equation (3.2) (presuming the potential *V* is constant in time) then gives

$$A(t)\left[-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right] = EA(t)\psi(\mathbf{r}) = i\hbar\psi(\mathbf{r})\frac{\partial A(t)}{\partial t} \quad (3.7)$$

so

$$EA(t) = i\hbar\frac{\partial A(t)}{\partial t} \quad (3.8)$$

i.e., for some constant A_o

$$A(t) = A_o \exp(-iEt/\hbar) \quad (3.9)$$

Hence, if the spatial part of the wavefunction is steady in time

the full time-dependent wavefunction can be written in the form

$$\Psi(\mathbf{r},t) = A_o \exp(-iEt/\hbar)\psi(\mathbf{r}) \quad (3.10)$$

We do now have a time-dependent part to the wavefunction for a situation that is stable in time.

But the probability density is stable in time. Explicitly,

$$|\Psi(\mathbf{r},t)|^2 = \left[\exp(+iEt/\hbar)\psi^*(\mathbf{r})\right]\times\left[\exp(-iEt/\hbar)\psi(\mathbf{r})\right] = |\psi(\mathbf{r})|^2 \quad (3.11)$$

Hence, with the choice Eq. (3.9), the time-independent and time-dependent Schrödinger equations are consistent.

Solutions of the time-dependent Schrödinger equation - 1

The time-dependent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)+V(\mathbf{r},t)\Psi(\mathbf{r},t)=i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

unlike the time-independent one,

is not an eigenvalue equation.

It is not an equation that only has solutions for a particular set of values of some parameter.

Instead, it allows us to calculate what happens in time

If we knew the wavefunction at every point in space at some time t_o**,**

i.e., if we knew $\Psi(\mathbf{r},t_o)$ **for all** r**,**

we could evaluate the left hand side of the equation at that time for all *r.*

So we would know how the wavefunction changes in time at every position

i.e., we would know $\partial\Psi(\mathbf{r},t)/\partial t$ ***for all*** *r,*

so we could integrate the equation to deduce $\Psi(\mathbf{r},t)$ **at all times.**

Solutions of the time-dependent Schrödinger equation - 2

Explicitly, we would have

$$\Psi\left(\mathbf{r},t_o+\delta t\right)\cong\Psi\left(\mathbf{r},t_o\right)+\left.\frac{\partial\Psi}{\partial t}\right|_{\mathbf{r},t_o}\delta t \qquad (3.12)$$

Because Schrödinger's equation tells us $\partial\Psi/\partial t$ **at time t_o if we know** $\Psi\left(\mathbf{r},t_o\right)$**,**

we have everything we need to know to calculate $\Psi\left(\mathbf{r},t_o+\delta t\right)$**.**

In other words,

the whole subsequent evolution of the wavefunction could be deduced from its spatial form at some given time.

Solutions of the time-dependent Schrödinger equation - 3

We could view this ability to deduce the wave function at all future times as the reason why this equation has a first derivative in time

- ***as opposed to the second derivative in common classical wave equations***
  - **Knowing only the second time derivative would not be sufficient to deduce the evolution in time.**

Any spatial function could be a solution of the time-dependent Schrödinger equation at a given time

- ***as long as it has a finite, well-behaved second derivative***

That spatial function sets the subsequent time-evolution of the wavefunction

- ***Note that***
  - **if the spatial wavefunction is in an eigenstate,**
    - *there is no subsequent variation in time of the wavefunction,*
      - other than the oscillation $\exp(-iEt/\hbar)$.

Linearity of quantum mechanics: linear superposition

The time-dependent Schrödinger equation is linear in the wavefunction Ψ

No higher powers of Ψ appear anywhere in the equation.

Hence, if Ψ is a solution, then so also is $A\Psi$, where A is any constant.

Another consequence of linearity is linear superposition of solutions

If $\Psi_a(\mathbf{r},t)$ and $\Psi_b(\mathbf{r},t)$ are solutions,

then so also is $\Psi_{a+b}(\mathbf{r},t) = \Psi_a(\mathbf{r},t) + \Psi_b(\mathbf{r},t)$. (3.13)

This is easily verified by substitution into the time-dependent Schrödinger equation.

We can also multiply the individual solutions by arbitrary constants and still have a solution to the equation, i.e.,

$$\Psi_c(\mathbf{r},t) = c_a\Psi_a(\mathbf{r},t) + c_b\Psi_b(\mathbf{r},t) \quad (3.14)$$

where c_a and c_b are (complex) constants

is also a solution.

Concept of linear superposition

The concept of linear superposition solutions is strange classically

In classical mechanics,

a particle simply has a "state" that is defined by its position and momentum,

Now we say a particle may exist in a superposition of states

each of which may have different energies (or possibly positions or momenta).

Such superpositions are actually necessary in quantum mechanics

so we can recover the behavior we expect classically from particles

Time dependence and expansion in the energy eigenstates - 1

We expand the wavefunction in the energy eigenfunction basis.

If V is constant in time,

each of the energy eigenstates is separately a solution of the time-dependent Schrödinger equation.

Explicitly, the n-th energy eigenfunction can be written, following Eq. (3.10) above

$$\Psi_n(\mathbf{r},t) = \exp(-iE_n t/\hbar)\psi_n(\mathbf{r}) \tag{3.15}$$

where E_n is the *n*th energy eigenvalue,

and now we presume that the ψ_n (and consequently the Ψ_n) are normalized.

This function is a solution of the time-dependent Schrödinger equation.

Because of the linear superposition defined above,

any sum of such solutions is also a solution.

Hence the usefulness of linear superpositions for the time-dependent Schrödinger equation

Time dependence and expansion in the energy eigenstates - 2

Suppose we expand the original spatial solution at time $t=0$ in energy eigenfunctions, i.e.,

$$\psi(\mathbf{r})=\sum_n a_n \psi_n(\mathbf{r}) \tag{3.16}$$

where the a_n are the expansion coefficients

(the a_n are fixed complex numbers).

Any spatial function $\psi(\mathbf{r})$ can be expanded this way because of the completeness of the eigenfunctions $\psi_n(\mathbf{r})$

We can now write a corresponding time-dependent function

$$\Psi(\mathbf{r},t)=\sum_n a_n \Psi_n(\mathbf{r},t)=\sum_n a_n \exp(-iE_n t/\hbar)\psi_n(\mathbf{r}) \tag{3.17}$$

We know this is a solution to the time-dependent Schrödinger equation

because it is made up from a linear combination of solutions to the equation.

As a check, at $t=0$ this correctly gives the known spatial form of the solution.

Time dependence and expansion in the energy eigenstates - 3

Hence Eq. (3.17)

$$\Psi(\mathbf{r},t)=\sum_n a_n \Psi_n(\mathbf{r},t)=\sum_n a_n \exp(-iE_n t/\hbar)\psi_n(\mathbf{r})$$

is the solution to the time-dependent Schrödinger equation

(for the case where V does not vary in time)

with the initial condition

$$\Psi(\mathbf{r},0)=\psi(\mathbf{r})=\sum_n a_n \psi_n(\mathbf{r}) \qquad (3.18)$$

.

Hence,

***if we expand the spatial wavefunction in the energy eigenstates at* t = 0,**

we have solved for the time evolution of the state thereafter;

we have no further integration to do,

merely a calculation of the sum (3.17)

$$\Psi(\mathbf{r},t)=\sum_n a_n \Psi_n(\mathbf{r},t)=\sum_n a_n \exp(-iE_n t/\hbar)\psi_n(\mathbf{r})$$

at each time of interest to us.

Time-Dependent Schrödinger Equation - 2

Reading – Sections 3.6 – 3.7 up to Group velocity

Time evolution of superpositions

- **in an infinitely deep potential well**
- **in the harmonic oscillator**

Time evolution of wavepackets

- **concept of group velocity**

Examples of time-evolution of a linear superposition state – infinite quantum well and harmonic oscillator

Now we look at the time evolution for example cases where

the potential is fixed in time (i.e., $V(\mathbf{r},t) \equiv V(\mathbf{r})$) and

the system is in a superposition state.

Simple linear superposition in an infinite potential well

Harmonic oscillator

Simple linear superposition in an infinite potential well

Suppose we have an infinite potential well (i.e., one with infinitely high barriers), and that

the particle in that well is in a (normalized) linear superposition state

with equal parts of the first and second states of the well, e.g.,

$$\Psi(z,t) = \frac{1}{\sqrt{L_z}}\left[\exp\left(-i\frac{E_1}{\hbar}t\right)\sin\left(\frac{\pi z}{L_z}\right) + \exp\left(-i\frac{E_2}{\hbar}t\right)\sin\left(\frac{2\pi z}{L_z}\right)\right] \qquad (3.19)$$

Then the probability density is given by

$$\left|\Psi(z,t)\right|^2 = \frac{1}{L_z}\left[\sin^2\left(\frac{\pi z}{L_z}\right) + \sin^2\left(\frac{2\pi z}{L_z}\right) + 2\cos\left(\frac{E_2 - E_1}{\hbar}t\right)\sin\left(\frac{\pi z}{L_z}\right)\sin\left(\frac{2\pi z}{L_z}\right)\right] \qquad (3.20)$$

This probability density has a part that oscillates at an angular frequency

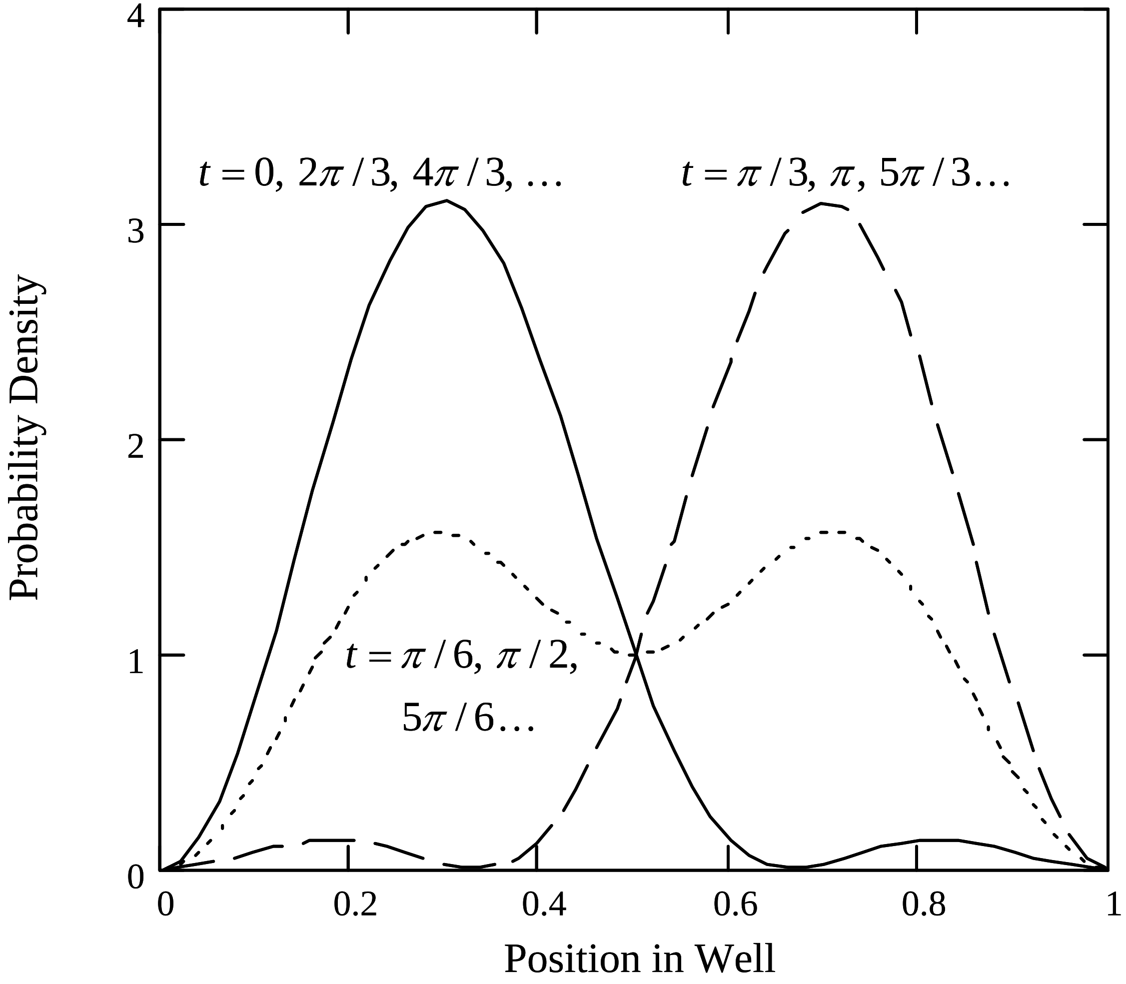
$$\omega_{21} = (E_2 - E_1)/\hbar = 3E_1/\hbar .$$

Note that the absolute energy origin does not matter here.

We could have added an arbitrary amount onto both of the two energies E_1 and E_2

without making any difference to the resulting oscillation.

Simple linear superposition in an infinite potential well



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Oscillation from the linear superposition of the first and second levels in a potential well with infinitely high barriers.

Here, the well has unit thickness, and

the unit of time is taken to be $\hbar / E_1$.

The oscillation angular frequency, ω_{21}, is 3 per unit time

because the energy separation of the first and second levels is $3E_1$

so the probability density oscillates back and forwards 3 times in 2π units of time.

Harmonic oscillator example

We construct a linear superposition state for the harmonic oscillator to see the time behavior.

For example, a superposition with equal parts of the first and second states.

Quite generally,

if we make a linear combination of two energy eigenstates with energies **E_a *and* E_b*,***

the resulting probability distribution will oscillate at the frequency $\omega_{ab} = \left| E_a - E_b \right| / \hbar$**.**

i.e., if we have a superposition wavefunction

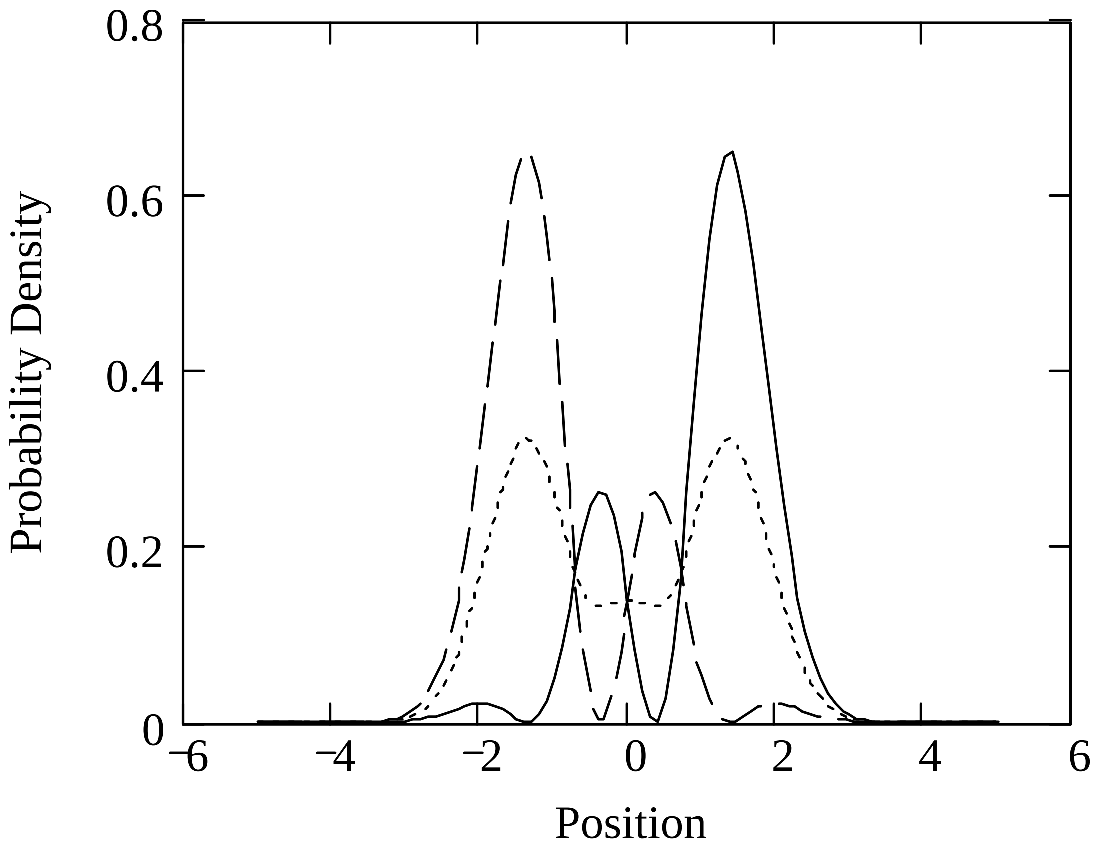
$$\Psi_{ab}\left(\mathbf{r},t\right) = c_a \exp\left(-iE_a t/\hbar\right)\psi_a\left(\mathbf{r}\right) + c_b \exp\left(-iE_b t/\hbar\right)\psi_b\left(\mathbf{r}\right) \tag{3.21}$$

then the probability distribution will be

$$\begin{aligned}\left|\Psi_{ab}\left(\mathbf{r},t\right)\right|^2 &= \left|c_a\right|^2\left|\psi_a\left(\mathbf{r}\right)\right|^2 + \left|c_b\right|^2\left|\psi_b\left(\mathbf{r}\right)\right|^2 \\ &\quad +2\left|c_a^*\psi_a^*\left(\mathbf{r}\right)c_b\psi_b\left(\mathbf{r}\right)\right|\cos\left[\frac{\left(E_a - E_b\right)t}{\hbar} - \theta_{ab}\right]\end{aligned} \tag{3.22}$$

where $\theta_{ab} = \arg\left(c_a\psi_a\left(\mathbf{r}\right)c_b^*\psi_b^*\left(\mathbf{r}\right)\right)$.

Harmonic oscillator – superposition of first two states



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Time evolution of an equal linear superposition of the first and second eigenstates of a harmonic oscillator.

The position is in dimensionless units (i.e., units $\sqrt{\hbar / m\omega}$ where *m* is the particle's mass).

This probability density oscillates at the (angular) frequency, ω, of the classical harmonic oscillator

Harmonic oscillator – “coherent state”

The linear superpositions that correspond best to our classical understanding of harmonic oscillators are known as “coherent states”.

The coherent state for a harmonic oscillator of frequency ω is

$$\Psi_N(\xi,t)=\sum_{n=0}^{\infty}c_{Nn}\exp\left[-i\left(n+\frac{1}{2}\right)\omega t\right]\psi_n(\xi) \tag{3.23}$$

where

$$c_{Nn}=\sqrt{\frac{N^n\exp(-N)}{n!}} \tag{3.24}$$

and the $\psi_n(\xi)$ are the harmonic oscillator eigenstates of Chapter 2

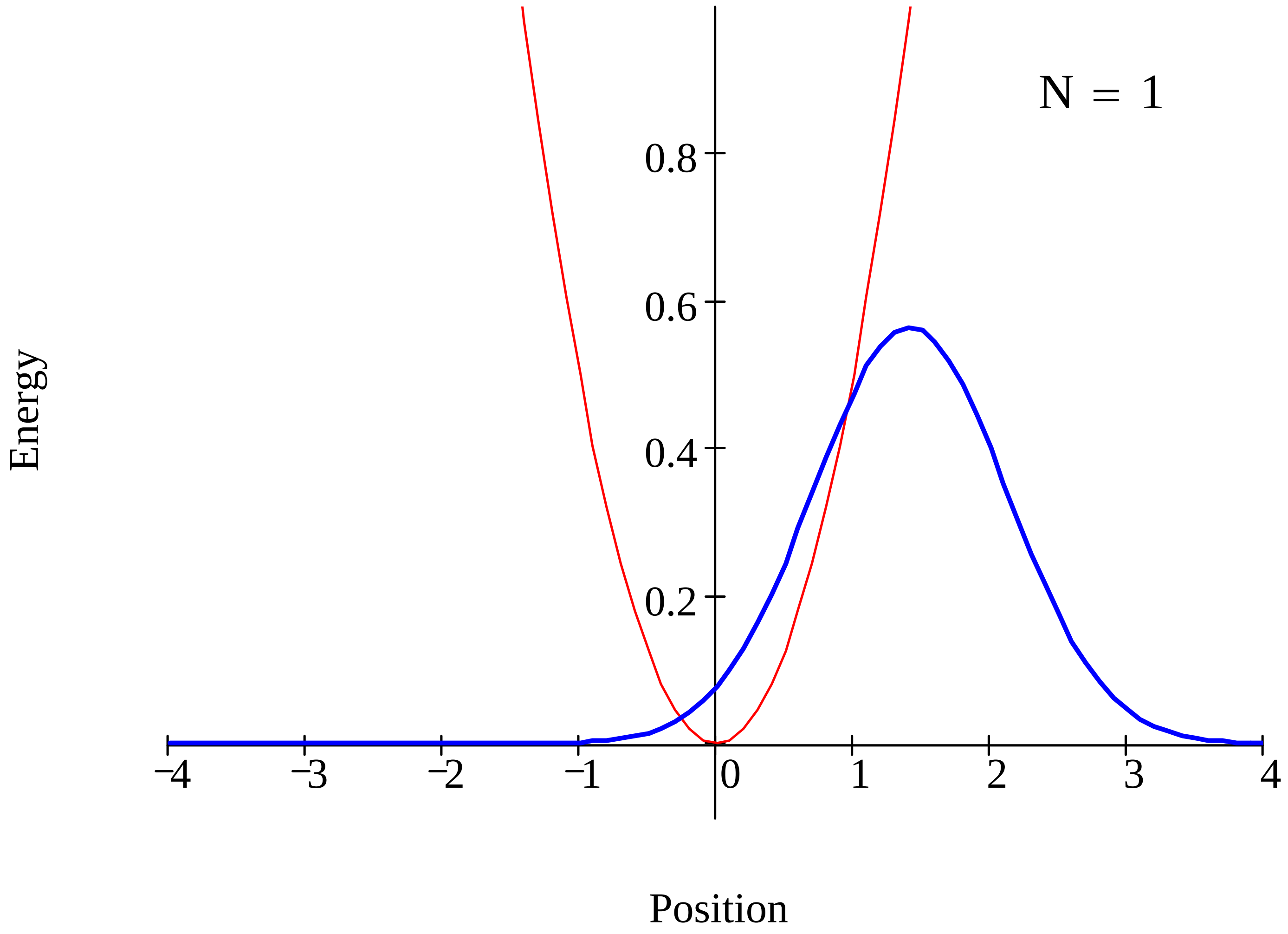
Incidentally, notice that

$$\left|c_{Nn}\right|^2=\frac{N^n\exp(-N)}{n!} \tag{3.25}$$

is the Poisson distribution from statistics, with mean N (and also standard deviation $\sqrt{N}$).

We can calculate the resulting probability density numerically by simply including a finite but sufficient number of terms in the series (3.23)

Harmonic oscillator in a coherent state for N = 1



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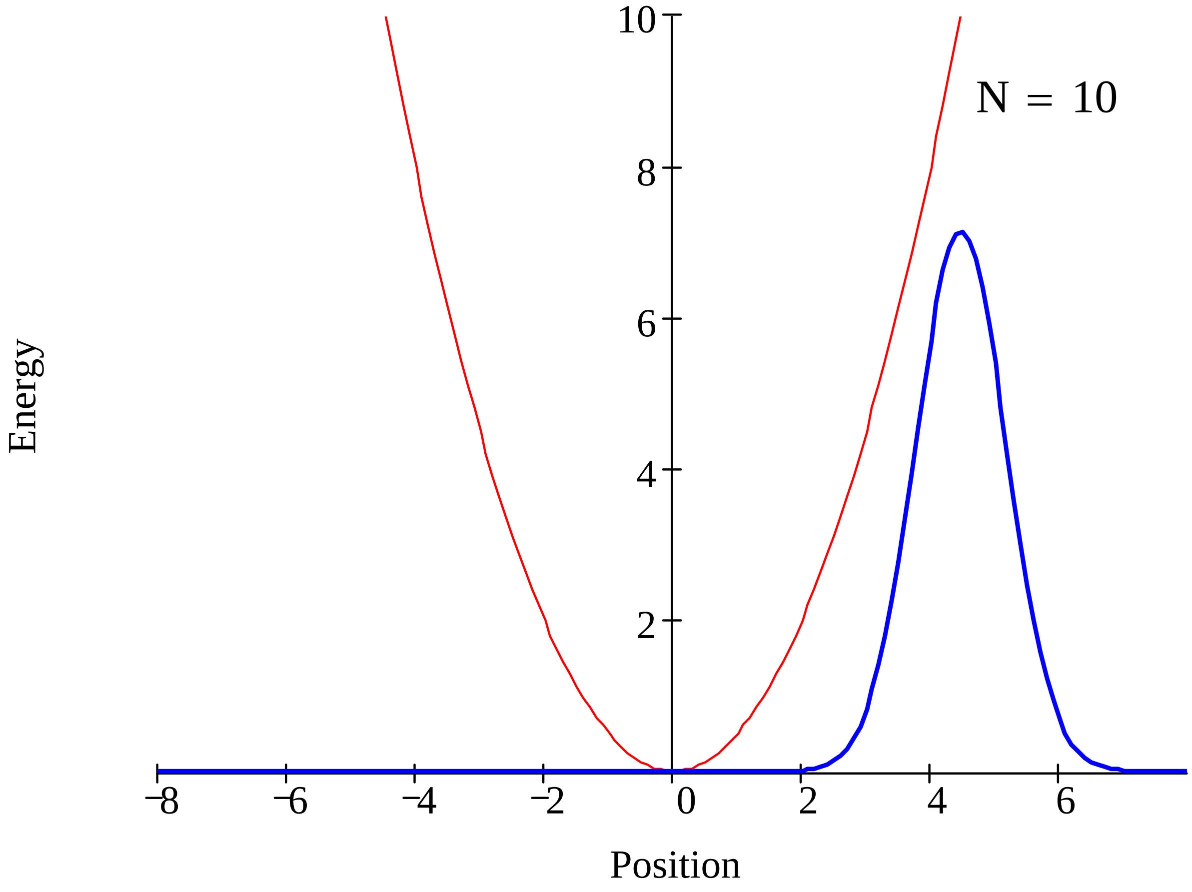
Probability distribution (not to scale vertically) for a coherent state of a harmonic oscillator with $N = 1$ at time $t = 0$. Also shown is the parabolic potential energy in this case.

Harmonic oscillator in a coherent state for N = 10



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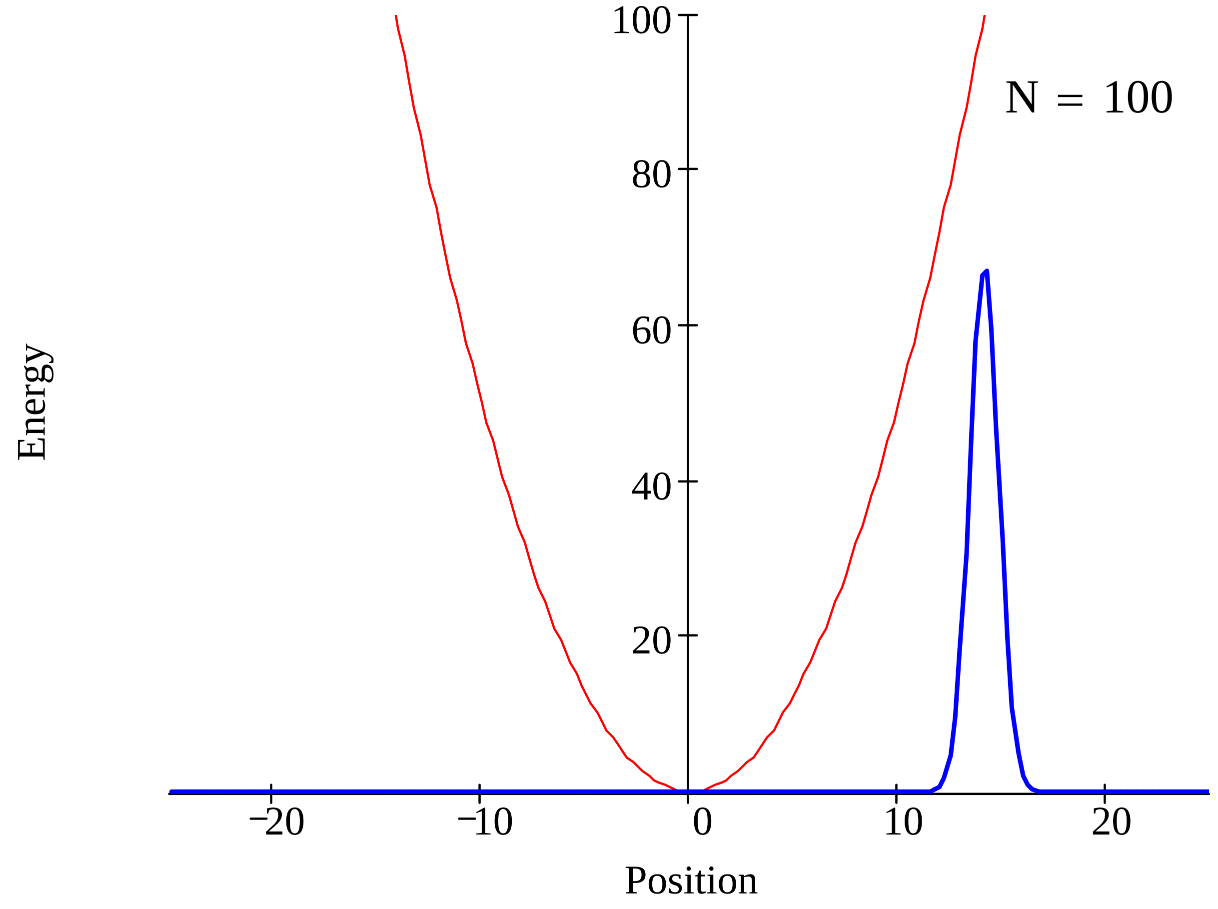
Probability distribution (not to scale vertically) for a coherent state of a harmonic oscillator with $N = 10$ at time $t = 0$. Also shown is the parabolic potential energy in this case.

Harmonic oscillator in a coherent state for N = 100



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Probability distribution (not to scale vertically) for a coherent state of a harmonic oscillator with $N = 100$ at time $t = 0$. Also shown is the parabolic potential energy in this case.

Harmonic oscillator in a coherent state

In each case,

- ***the probability distribution essentially oscillates back and forth from one side of the potential to the other,***
  - **with angular frequency ω,**
    - *retaining essentially the same shape as it does so.*

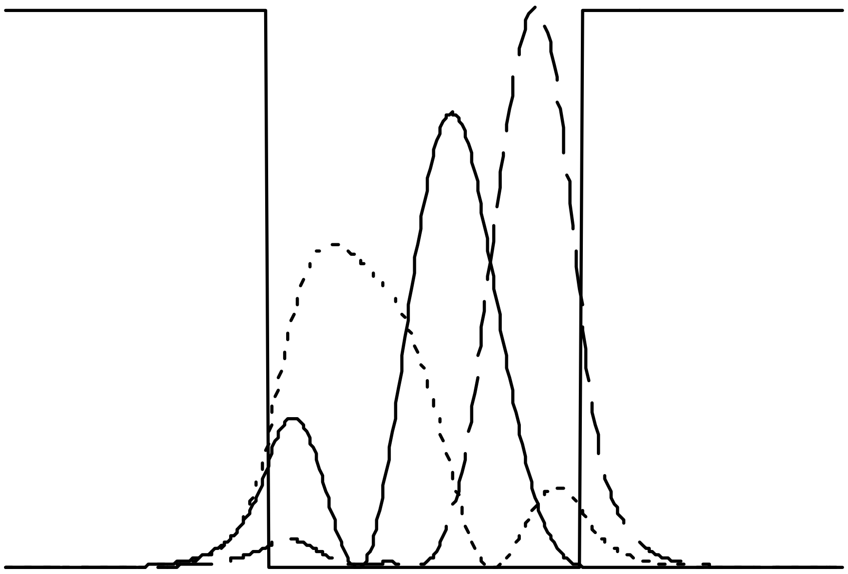
For higher N, the spatial width of the probability distribution becomes a smaller fraction of the oscillation amplitude,

- ***the probability distribution will appear to be very localized relative to the size of the oscillation***
  - **recovering the classical idea of oscillation**

In general, a system in a linear superposition of multiple energy eigenstates does not execute a simple harmonic motion like this harmonic oscillator does.

- ***That harmonic motion is a special consequence of the fact that all the energy levels are equally spaced in the harmonic oscillator case.***

Non-repetitive linear superposition in a finite well



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Probability density at three different times for an equal linear superposition of the first three levels of a finite potential well. (i) $t = 0$ (solid line); (ii) $t = \pi/2$ (dotted line); (iii) $t = \pi$ (dashed line). The time units are $\hbar / E_1^{\infty}$ where E_1^{∞} is the energy of the first level in a well of the same width but with infinitely high barriers.

Because the energy separations between the levels are not in integer ratios, the resulting probability density does not repeat in time.

Waves and particle motion - 1

Consider propagation of wave packets.

Imagine that the potential energy, V, is constant everywhere.

For simplicity, we could take V to be zero.

Then there is a solution of the time-independent Schrödinger equation possible for every energy E (greater than zero).

In fact there are two such solutions for every energy, a "right-propagating" one

$$\psi_{ER}(z) = \exp(ikz) \tag{3.26}$$

and a "left-propagating" one

$$\psi_{EL}(z) = \exp(-ikz) \tag{3.27}$$

where $k = \sqrt{2mE/\hbar^2}$ *as usual.*

The corresponding solutions of the time-dependent Schrödinger equation are

$$\Psi_{ER}(z,t) = \exp[-i(\omega t - kz)] \tag{3.28}$$

and

$$\Psi_{EL}(z,t) = \exp[-i(\omega t + kz)] \tag{3.29}$$

where $\omega = E/\hbar$.

Waves and particle motion - 2

We want to understand the correspondence between the movement of such a "free" particle

in the quantum mechanical description and

in the classical one.

We might at first ask for the "phase velocity" of the wave, which would be

$$v_p = \frac{\omega}{k} = \frac{E}{\hbar}\sqrt{\frac{\hbar^2}{2mE}} = \sqrt{\frac{E}{2m}} \qquad (3.30)$$

That would lead to a relation

$$E = 2mv_p^2,$$

which does not correspond with the classical relation between kinetic energy and velocity of

$$E = (1/2)mv^2.$$

Waves and particle motion - 3

If we examine the $\left|\Psi_{EL}(z,t)\right|^2$ or $\left|\Psi_{ER}(z,t)\right|^2$ associated with either of these waves,

$$\Psi_{ER}(z,t)=\exp\left[-i(\omega t-kz)\right] \text{ or } \Psi_{EL}(z,t)=\exp\left[-i(\omega t+kz)\right]$$

we will, however, find that they are uniform in space and time,

and it is not meaningful to ask if there is any movement associated with them.

To understand movement,

we have to construct a “wave-packet”

- **a linear superposition of waves that adds up to give a “packet” that is approximately localized in space at any given time.**

To understand what behavior we expect from such packets,

we have to introduce the concept of group velocity.

Time-Dependent Schrödinger Equation - 3

Reading – Section 3.7 starting from Group Velocity

Time evolution of wavepackets

freely propagating wave packets

wavepackets hitting a barrier

Waves and particle motion - group velocity - 1

Elementary wave theory says the velocity of the center of a wave packet or pulse is the "group velocity"

$$v_g = \frac{d\omega}{dk} \tag{3.31}$$

where ω is the frequency and k is the wavevector.

To understand this,

consider a total wave made up out of a superposition of two waves,

both propagating to the right,

one at frequency $\omega + \delta\omega$, with a wavevector $k + \delta k$,

and one at a frequency $\omega - \delta\omega$ and a wavevector $k - \delta k$.

Then the total wave is

$$f(z,t) = \exp\{-i[(\omega+\delta\omega)t - (k+\delta k)z]\} + \exp\{-i[(\omega-\delta\omega)t - (k-\delta k)z]\} \tag{3.32}$$

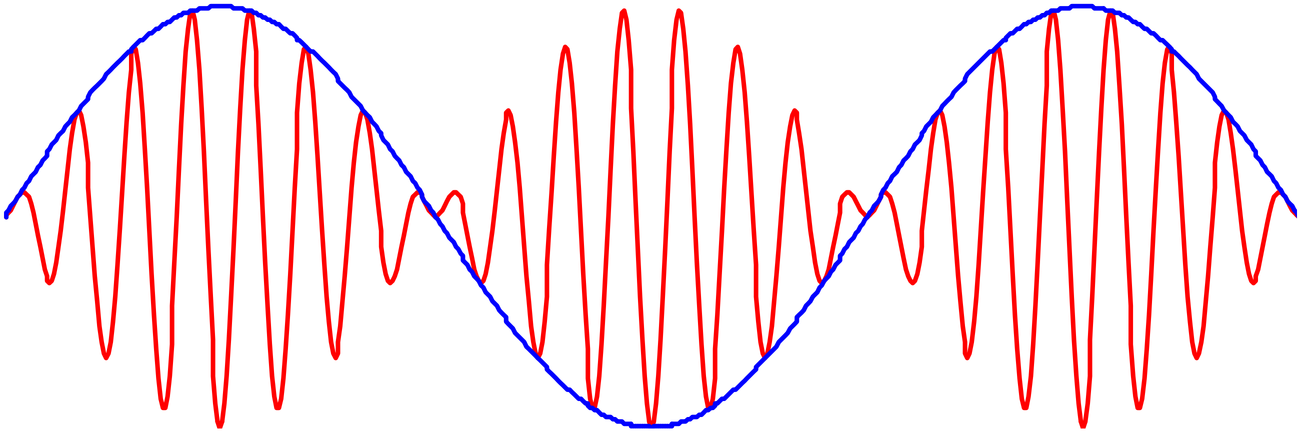
Waves and particle motion - group velocity - 2

We can rewrite this as

$$f(z,t) = 2\cos(\delta\omega t - \delta kz)\exp\left[-i(\omega t - kz)\right] \qquad (3.33)$$

which can be viewed as

an underlying wave $\exp\left[-i(\omega t - kz)\right]$



modulated by an envelope $\cos(\delta\omega t - \delta kz)$.

This envelope can be seen to move at a the "group velocity"

$$v_g = \frac{\delta\omega}{\delta k} \qquad (3.34)$$

or, in the limit of very small $\delta\omega$ and δk,

$$v_g = \frac{d\omega}{dk} \qquad (3.31)$$

Group velocity and dispersion for light

Often, for waves such as

light waves in free space, or sound waves in ordinary air in a room,

the velocity of the waves does not depend substantially on the frequency

so $d\omega / dk = \omega / k$***, and phase and group velocities are equal.***

When ω **is not proportional to *k*, we have "dispersion", e.g.,**

(1) near to some optical absorption line, such as in an atomic vapor,

the refractive index changes quite rapidly with frequency,

the variation of refractive index with frequency

known as material dispersion

is not negligible, and the group and phase velocities are no longer the same.

(2) in waveguides, different modes propagate with different velocities,

so there is dispersion from the geometry of the structure

a structural dispersion.

In long optical fibers,

the effects of dispersion and of group velocity are not negligible

(3) any structure whose physical properties,

such as refractive index,

change on a scale comparable to the wavelength

will show structural dispersion.

Group velocity for a free electron - 1

For a particle such as an electron,

phase velocity and group velocity of quantum mechanical waves are almost never the same.

For the simple free electron,

the frequency ω is not proportional to the wavevector magnitude k.

the time-independent Schrödinger equation tells us that,

for any wave component $\psi(z) \propto \exp(\pm ikz)$

In fact (for zero potential energy),

$$\frac{-\hbar^2}{2m_o}\frac{d^2\psi}{dz^2} = E\psi \tag{3.35}$$

i.e.,

$$E = \frac{\hbar^2 k^2}{2m_o} \tag{3.36}$$

So

$$\omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m_o}, \text{ i.e., } \omega \propto k^2 \tag{3.37}$$

Group velocity for a free electron - 2

We see then that the propagation of the electron wave is always highly dispersive.

Hence, we have a velocity for a wavepacket made up out of a linear superposition of waves of energies near E*,*

$$v_g = \frac{1}{dk/d\omega} = \frac{1}{\hbar dk/dE} = \sqrt{\frac{2E}{m}} \tag{3.38}$$

so that

$$E = \frac{1}{2} m v_g^2 \tag{3.39}$$

Hence,

the quantum mechanical description in terms of propagation as a superposition of waves

leading to wavepackets propagating at the group velocity

does correspond to the same velocity as we would have expected from a classical particle of the same energy.

Examples of motion of wavepackets

Here we examine two examples of wavepacket propagation

Freely propagating wave packet

Wavepacket arriving at a barrier

Freely propagating wave packet

There are many form of linear superposition that could give a wavepacket.

One common example - a Gaussian wavepacket, e.g.,

for a wavepacket propagating in the positive *z* direction we could have

$$\Psi_G(z,t) \propto \sum_k \exp\left[-\left(\frac{k-\bar{k}}{2\Delta k}\right)^2\right] \exp\left\{-i\left[\omega(k)t - kz\right]\right\} \tag{3.40}$$

where

$\bar{k}$ is the value at the center of the distribution of *k* values, and

the parameter Δk is a width parameter for the Gaussian function.

The sum here runs over all possible values of k, presumed evenly spaced

wavepackets made from finite sums of evenly spaced k values are useful for simulations.

It is useful also to introduce the idea of integration rather than summation when we are dealing with parameters that are continuous.

Instead of (3.40) above, we could choose to write

$$\Psi_G(z,t) \propto \int_k \exp\left[-\left(\frac{k-\bar{k}}{2\Delta k}\right)^2\right] \exp\left\{-i\left[\omega(k)t - kz\right]\right\} dk \tag{3.41}$$

Though this is now an integral rather than a sum,

it is still just a linear combination of eigenfunctions of the time-dependent Schrödinger equation.

Motion of a Gaussian wavepacket - 1

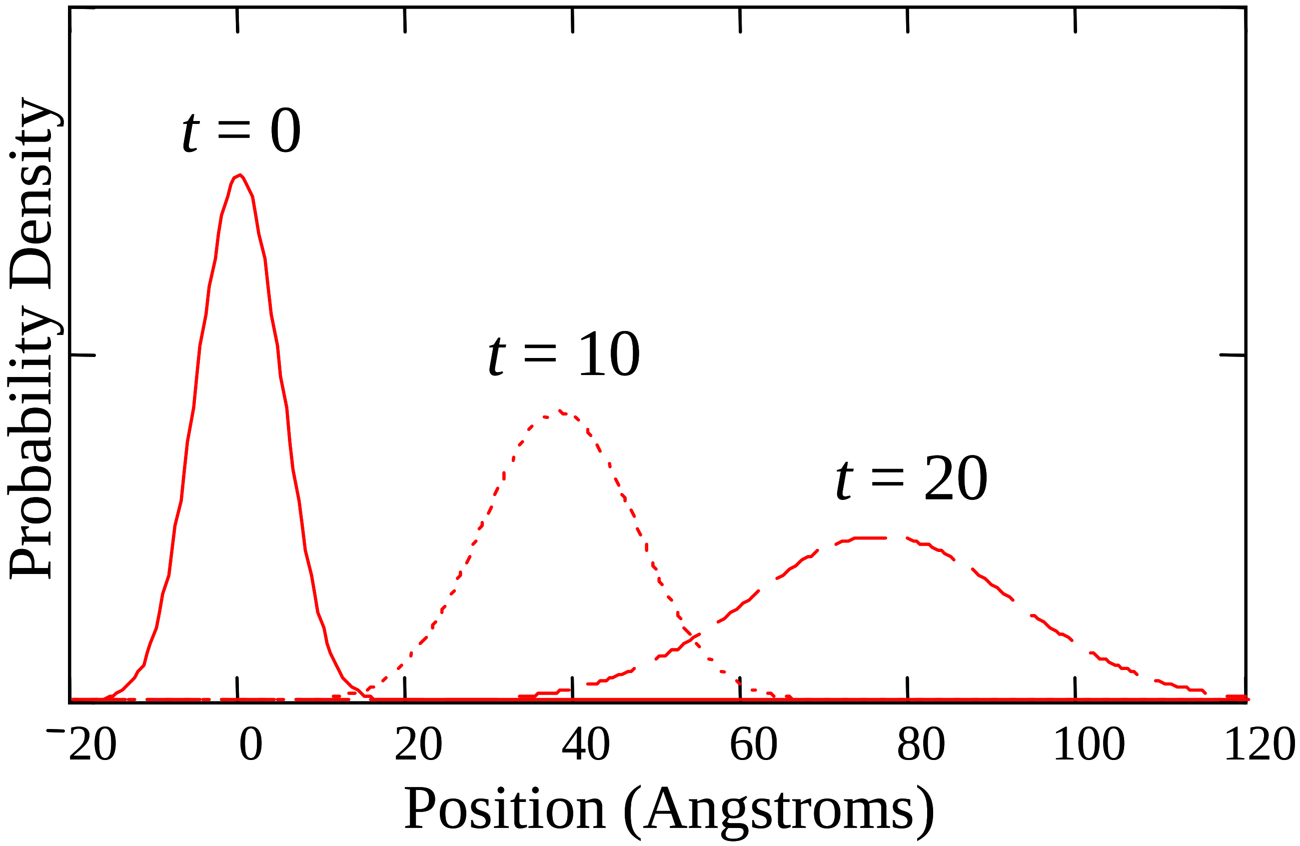


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Illustration of a wavepacket propagating in free space. The wavepacket is a Gaussian wavepacket in *k*-space, centered round a wavevector $\bar{k}$ = 0.5 Å^{-1}, which corresponds to an energy of ~ 0.953 eV, with a Gaussian width parameter Δ*k* of 0.14 Å^{-1}. The units of time are $\hbar/e \simeq 0.66\,\text{fs}$.

Motion of a Gaussian wavepacket - 2

We see first of all that

the wavepacket does move to the right as we expect,

with the center moving linearly in time.

We also see that

the wavepacket gets broader in time.

This increase in width is because

the group velocity itself is not even the same for different wave components in the wave packet,

a phenomenon called group-velocity dispersion.

There will be group velocity dispersion

if $d\omega / dk$ *is not a constant over the region of wavevectors of interest,*

i.e., if $d^2\omega / dk^2 \neq 0$, which is certainly the case for our free electron, for which

$$\frac{dv_g}{dk} = \frac{d^2\omega}{dk^2} = \frac{\hbar}{m_o} \tag{3.42}$$

Wavepacket hitting a barrier - 1

A more complex example is a wavepacket hitting a finite barrier.

- ***We can start by solving for the wavefunction of the time-independent Schrödinger equation***
  - **in the presence of a finite barrier for the situation**
    - *where there is no wave incident from the right.*

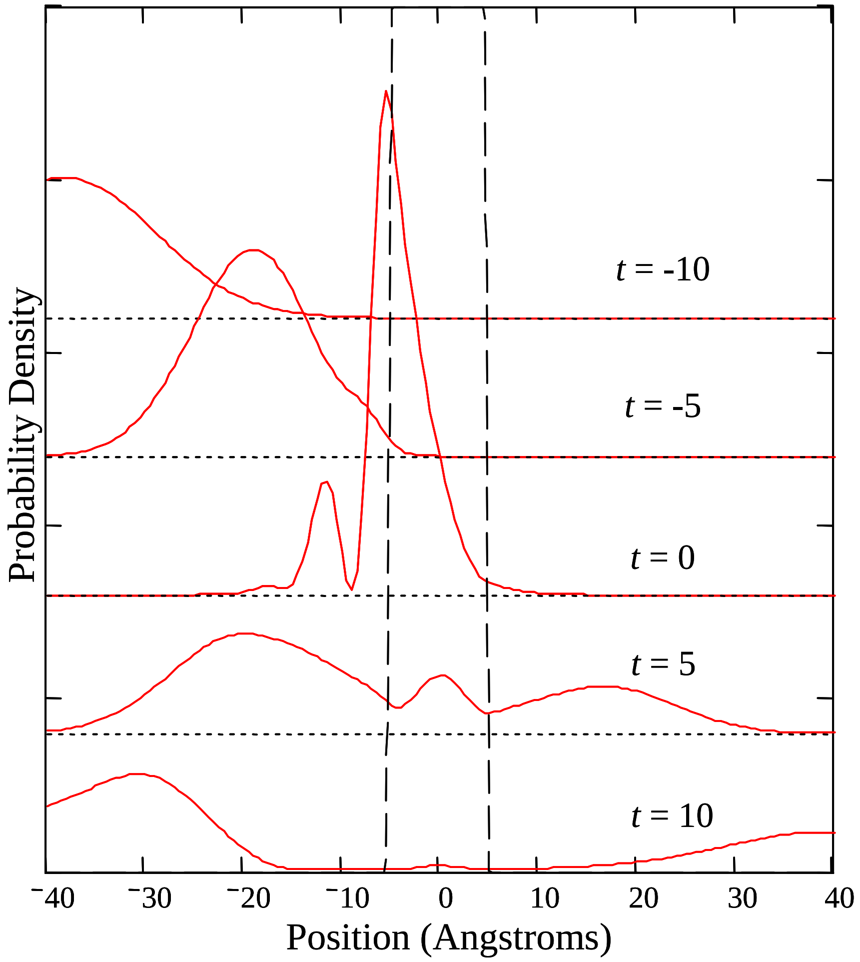
We find that there are solutions for every energy.

- ***Each of these solutions contains***
  - **a forward (right) propagating wave on the left of the barrier,**
    - *as well as a reflected wave there,*
  - **forward and backward waves within the barrier**
    - *(which may be exponentially growing and decaying for energies below the top of the barrier), and*
  - **a forward wave on the right.**

We then form a superposition of these solutions with Gaussian weights.

- ***The procedure is identical to that of (3.40) except the waves are these more complex solutions.***

Wavepacket hitting a barrier - 2



Click on the image for animation

Simulation of an electron wavepacket hitting a barrier. The barrier is 1 eV high and 10 Å thick, and is centered around the zero position. The wavepacket is a Gaussian wavepacket in *k*-space, centered round a wavevector $\bar{k}$ = 0.5 Å^{-1}, which corresponds to an energy of ~ 0.953 eV, with a Gaussian width parameter Δk of 0.14 Å^{-1}. The units of time are $\hbar/e \simeq 0.66\,\text{fs}$.

Wavepacket hitting a barrier - 3

Click here for animation
at an energy of 1.372 eV

Simulating at a higher energy, such as the one corresponding to the first resonance above the barrier at an energy ~ 1.37 eV, shows similar kinds of behaviors, but has a larger transmission and a smaller reflection.

Wavepacket hitting a barrier - 3

First the wavepacket approaches the barrier at times t = -10 and t = -5.

Near t = 0, we see strong interference effects.

At time t = 5 and t = 10,

we see a pulse propagating to the right on the right side of the barrier,

corresponding to a pulse that has propagated through the barrier

(in this case mostly by tunneling),

as well as a reflected pulse propagating backwards.

All of these phenomena in the time dependent behavior arise from

the interference of the various energy eigenstates of the problem,

with the time dependence itself arising from

the change in phase in time between the various components as the $\exp(-iEt/\hbar)$ *phase factors evolve in time.*

With the energy eigenstates already calculated for the problem, the time behavior arises simply from

a linear sum of these different components

with their time-dependent phase factors.

Time-Dependent Schrödinger Equation - 4

Reading – Sections 3.8 – 3.11

Quantum mechanical measurement and expectation values

- **Stern-Gerlach experiment**

The Hamiltonian

Operators and expectation values

Time evolution and the Hamiltonian operator

Quantum mechanical measurement and expectation values

Probabilities and expansion coefficients

When a normalized wavefunction is expanded in an orthonormal set, e.g.,

$$\Psi(\mathbf{r},t)=\sum_n c_n(t)\psi_n(\mathbf{r}) \tag{3.43}$$

then the normalization integral requires that

$$\int_{-\infty}^{\infty}\left|\Psi(\mathbf{r},t)\right|^2 d^3\mathbf{r}=\int_{-\infty}^{\infty}\left[\sum_n c_n^*(t)\psi_n^*(\mathbf{r})\right]\times\left[\sum_m c_m(t)\psi_m(\mathbf{r})\right]d^3\mathbf{r}=1 \tag{3.44}$$

If we look at the integral over the sums,

we see that because of the orthogonality of the basis functions,

the only terms that will survive after integration will be for $n=m$,

and because of the orthonormality of the basis functions,

the result from any such term in the integration will simply be $\left|c_n(t)\right|^2$.

Hence, we have

$$\sum_n \left|c_n\right|^2=1 \tag{3.45}$$

Quantum mechanical measurement

In quantum mechanics,

when we make a measurement on a small system with a large measuring apparatus,

of some quantity such as energy,

we find the following behavior,

which is sometimes elevated to a postulate or hypothesis in quantum mechanics:

On measurement, the system collapses into an eigenstate of the quantity being measured, with probability

$$P_n = |c_n|^2 \tag{3.46}$$

where c_n is the expansion coefficient in the (orthonormal) eigenfunctions of the quantity being measured.

(Our conclusion (3.45) [$\sum_n |c_n|^2 = 1$] is certainly consistent with using the $|c_n|^2$ as probabilities, since they add up to one.)

Measurement theory

This statement of

collapse into an eigenstate of the quantity being measured

is problematic if we consider it as anything other than

an empirical observation for measurements by large systems on small ones.

Resolving these difficulties has been a major activity in quantum mechanics up to the present day

modern pictures of these resolutions are much different from those originally envisaged in the early days of quantum mechanics.

The branch of quantum mechanics that deals with these problems is known as measurement theory,

the core problem is known as the measurement problem.

Expectation value of the energy

Suppose we measure the energy of our system in such an experiment.

We could repeat the experiment many times, and get a statistical distribution of results.

Given the probabilities, the average value of energy E that we would measure would be

$$\langle E \rangle = \sum_n E_n P_n = \sum_n E_n |c_n|^2 \qquad (3.47)$$

where we are using the notation $\langle E \rangle$ to denote the average value of E,

a quantity we call the "expectation value of E" in quantum mechanics.

Energy expectation value example

For example, for the coherent state discussed above with parameter N, we have

$$\begin{aligned}\langle E\rangle &= \sum_{n=0}^{\infty} E_n \frac{N^n \exp(-N)}{n!} \\ &= \hbar\omega\left[\sum_{n=0}^{\infty} n \frac{N^n \exp(-N)}{n!}\right] + \frac{1}{2}\hbar\omega \\ &= \left(N + \frac{1}{2}\right)\hbar\omega\end{aligned} \tag{3.48}$$

We can show that having an energy $\approx N\hbar\omega$ for the large N implicit in a classical situation corresponds very well to our notions of energy, frequency and oscillation amplitude in a classical oscillator

Stern-Gerlach experiment - 1

An electron has another property,

- *in addition to having a mass and a charge*
  - “spin”.

Electron spin makes the electron behave like a very small bar magnet

- *with the same strength for all electrons.*

If we pass a bar magnet through a uniform magnetic field

- *nothing will happen to the position of the bar*
  - the North and South poles of the bar magnet are pulled with equal and opposite force

Stern-Gerlach experiment - 2

If the field is not uniform,

the pole in the stronger part of the field will experience more force,

and the bar magnet will be deflected

If the bar magnet's south pole faces up

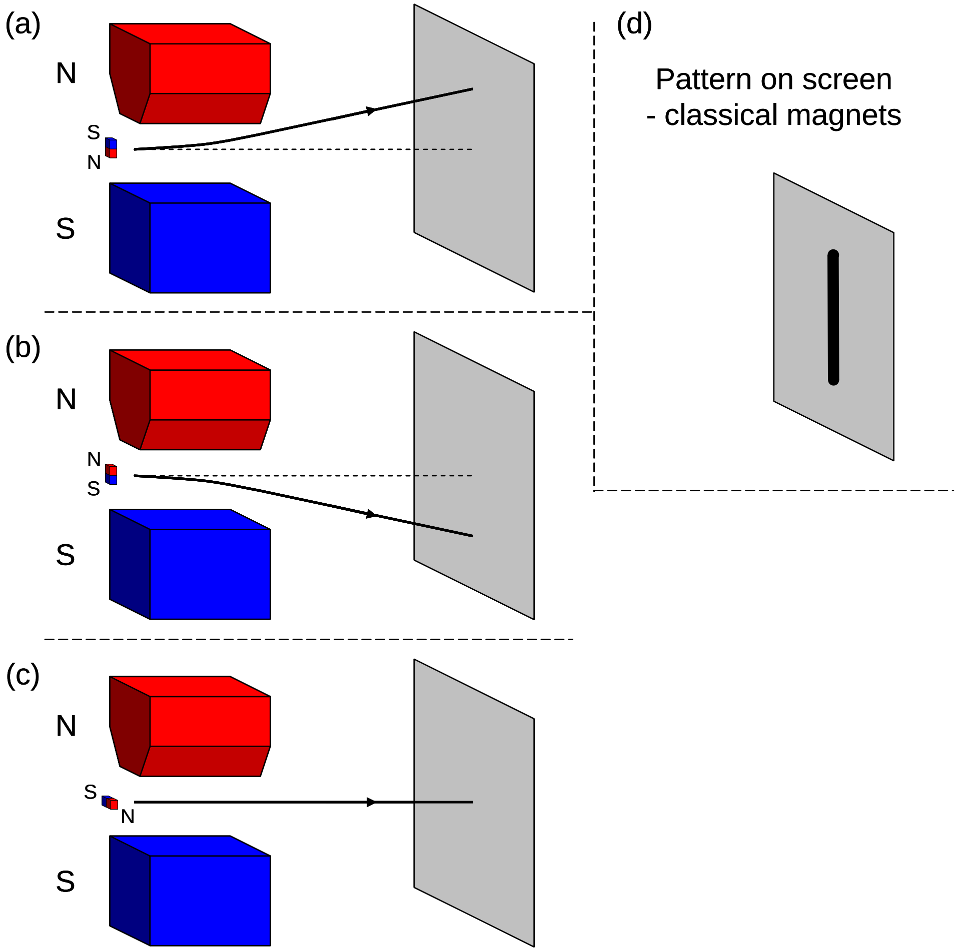
the magnet would be deflected upwards

If the bar magnet's north pole faces up

the magnet would be deflected downwards

If the bar magnet started out oriented in the horizontal plane

it would not be deflected at all



In any other orientation of the bar magnet, it would be deflected by some intermediate amount

expect to see a line of points where the magnets hit the screen

Stern-Gerlach experiment - 3

When we do this experiment with electrons

- *all the electrons land only at an upper position, or at a lower position*

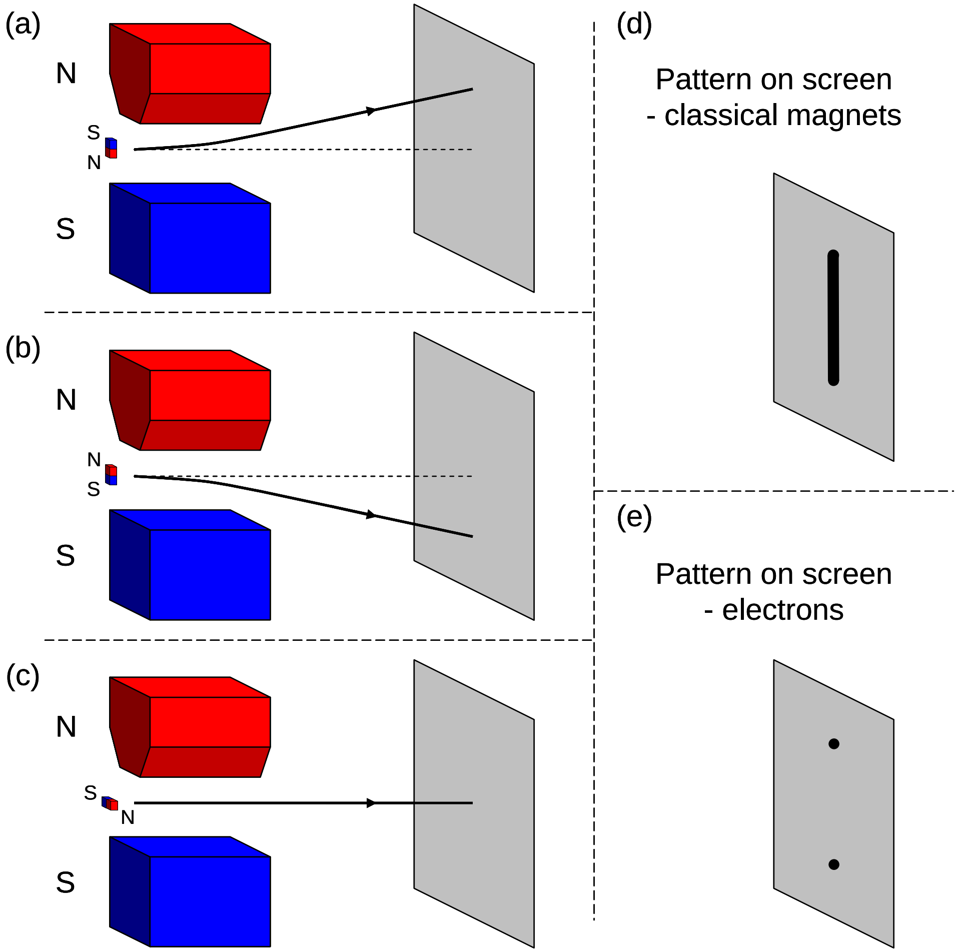
This is very surprising.

- *The electrons were not prepared in any way that always aligned their spins in the "up" or "down" directions.*

It also does not matter if we change the direction of the magnets

- *The pattern of two dots just rotates as we rotate the external magnets*

.



Stern-Gerlach experiment - 4

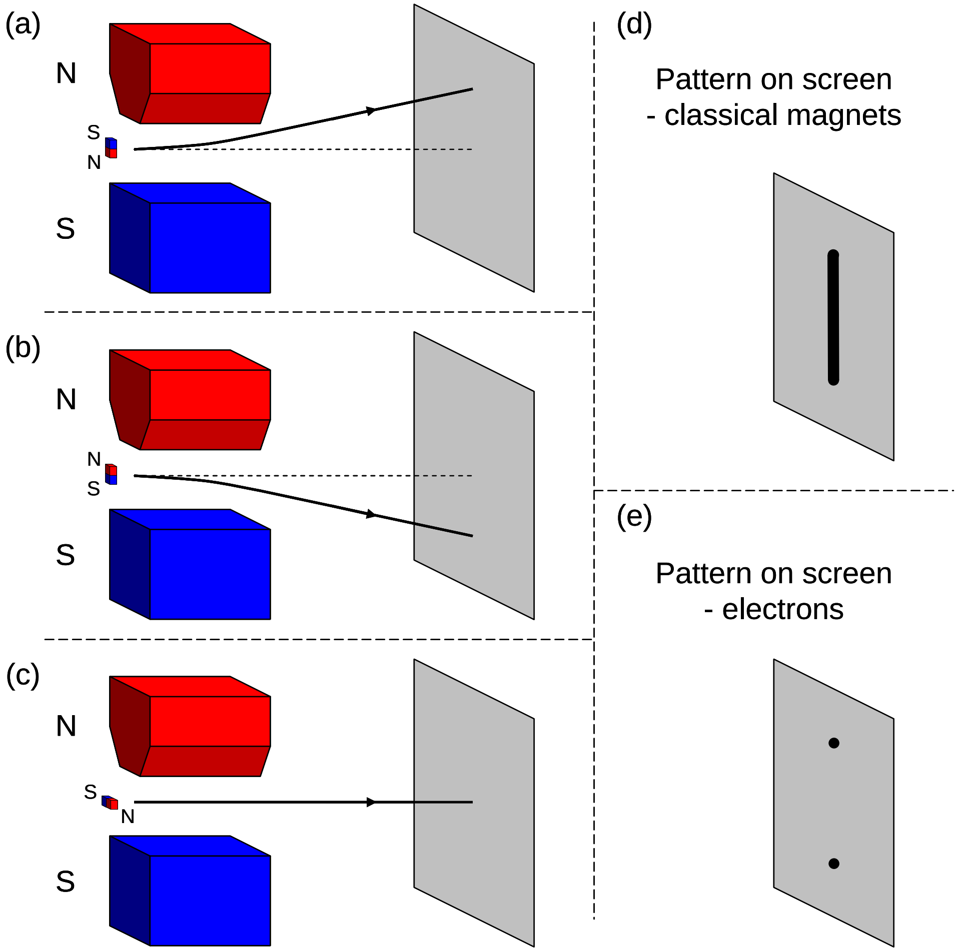
The quantum mechanical explanation is that

- *this apparatus "measures" the vertical component of the electron spin*

When we make a measurement

- *we "collapse" the state of the system into one of the eigen states*
  - here "spin up" or "spin down"
- *of the quantity being measured*
  - here the vertical electron spin component

This measurement behavior is truly strange, and totally counter to our classical intuition.



The Hamiltonian

An important concept in advanced descriptions of classical mechanics is the Hamiltonian,

a function, usually of positions and momenta, essentially representing the total energy in the system.

There are many formal links and correspondences between the Hamiltonian of classical mechanics and quantum mechanics.

In quantum mechanics that can be analyzed by Schrödinger's equation, we can define the entity

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) \tag{3.49}$$

so that we can write the time-dependent Schrödinger equation in the form

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} \tag{3.50}$$

or the time-independent Schrödinger equation as

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3.51}$$

(where $\psi(\mathbf{r})$ is now restricted to being an eigenfunction with associated eigenenergy E).

Hamiltonian operator

The entity $\hat{H}$ is not a number,

and it is not a function.

It is instead an "operator",

just like the entity d/dz is a spatial derivative operator.

We use the notation with a "hat" above the letter here to distinguish operators from functions and numbers.

The most general definition of an operator is

an entity that turns one function into another.

The particular operator $\hat{H}$ is called the Hamiltonian operator

because it is related to the total energy of the system.

The idea of the Hamiltonian operator extends beyond the specific definition here that applies to single, non-magnetic particles;

in general in non-relativistic quantum mechanics,

the Hamiltonian operator is the operator related to the total energy of the system.

Operators and expectation values - 1

We can now show an important but simple relation between

the Hamiltonian operator,

the wavefunction, and

the expectation value of the energy.

Consider the integral

$$I = \int \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)d^3\mathbf{r} \tag{3.52}$$

where $\Psi(\mathbf{r},t)$ ***is the wavefunction of some system of interest.***

We can expand this wavefunction in energy eigenstates, as in Eq.(3.43).

We know that, with $\psi_n(\mathbf{r})$ ***as the energy eigenstates (of the time-independent Schrödinger equation)***

$$\begin{aligned}\hat{H}\Psi(\mathbf{r},t) &= \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\sum_n c_n(t)\psi_n(\mathbf{r}) \\ &= \sum_n c_n(t)E_n\psi_n(\mathbf{r})\end{aligned} \tag{3.53}$$

and so

$$\int \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)d^3\mathbf{r} = \int_{-\infty}^{\infty}\left[\sum_m c_m^*(t)\psi_m^*(\mathbf{r})\right]\times\left[\sum_n c_n(t)E_n\psi_n(\mathbf{r})\right]d^3\mathbf{r} \tag{3.54}$$

Operators and expectation values - 2

Given the orthonormality of the $\psi_n(\mathbf{r})$, we have

$$\int \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)d^3\mathbf{r} = \sum_n E_n |c_n|^2 \tag{3.55}$$

But comparing to the result (3.47), we therefore have

$$\langle E \rangle = \int \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)d^3\mathbf{r} \tag{3.56}$$

This kind of relation between

the operator (here $\hat{H}$),

the quantum mechanical state (here $\Psi(\mathbf{r},t)$) and

the expected value of the quantity associated with the operator (here E)

is quite general in quantum mechanics.

Benefit of use of operator

Question:

if we already knew how to calculate $\langle E\rangle$ from Eq.(3.47),

$$\langle E\rangle = \sum_n E_n P_n = \sum_n E_n \left|c_n\right|^2$$

what is the benefit of this new relation, Eq. (3.56)?

$$\langle E\rangle = \int \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)\,d^3\mathbf{r}$$

Answer:

We do not have to solve for the eigenfunctions of the operator (here $\hat{H}$) to calculate the result.

We used the decomposition into eigenfunctions to prove the result (3.56),

but we do not have to do that decomposition to evaluate $\langle E\rangle$ from (3.56).

All we need is

the quantum mechanical state (here the wavefunction $\Psi(\mathbf{r},t)$),

and the operator associated with the quantity $\langle E\rangle$ (here $\hat{H}$).

Time evolution and the Hamiltonian operator - 1

Looking at Schrödinger's time-dependent equation in the form as in Eq. (3.50)

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

and rewriting it slightly as

$$\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{i\hat{H}}{\hbar}\Psi(\mathbf{r},t) \tag{3.57}$$

presuming that $\hat{H}$ does not depend on time (i.e., the potential $V(\mathbf{r})$ is constant in time),

it is tempting to wonder if it is "legal" and meaningful to integrate this equation directly to obtain

$$\Psi(\mathbf{r},t_1) = \exp\left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar}\right)\Psi(\mathbf{r},t_0) \tag{3.58}$$

Certainly if $\hat{H}$ were replaced by a constant number

a rather trivial case of an operator!

we could perform such an integration.

Time evolution and the Hamiltonian operator - 2

If it were legal and meaningful to do this for an actual time-independent Hamiltonian,

we would have an operator that,

in one operation,

gave us the state of the system at time t_1 *directly from its state at time* t_0.

To think about this "legality", first we note that,

because $\hat{H}$ ***is a linear operator, for any number*** a***,***

$$\hat{H}\left[a\Psi(\mathbf{r},t)\right] = a\hat{H}\Psi(\mathbf{r},t) \tag{3.59}$$

The operator $\hat{H}$ **"commutes" with the scalar quantity (i.e., the number)** a**.**

Because this relation holds for any function $\Psi(\mathbf{r},t)$***, we can write***

$$\hat{H}a = a\hat{H} \tag{3.60}$$

(Note that any time we have such an equation relating the operators themselves on either side, we are implicitly saying that this relation holds for these operators operating on any function in the space. I.e., the relation

$$\hat{A} = \hat{B} \tag{3.61}$$

for any two operators $\hat{A}$ **and** $\hat{B}$ **is really a shorthand for the statement**

$$\hat{A}\Psi = \hat{B}\Psi \tag{3.62}$$

where Ψ **is any arbitrary function in the space in question.)**

Time evolution and the Hamiltonian operator - 3

Next we have to define what we mean by an operator raised to a power.

By $\hat{H}^2$ we mean

$$\hat{H}^2\Psi(\mathbf{r},t) = \hat{H}\left[\hat{H}\Psi(\mathbf{r},t)\right] \tag{3.63}$$

Specifically, for example, for the energy eigenfunction $\psi_n(\mathbf{r})$

$$\hat{H}^2\psi_n(\mathbf{r}) = \hat{H}\left[\hat{H}\psi_n(\mathbf{r})\right] = \hat{H}\left[E_n\psi_n(\mathbf{r})\right] = E_n\hat{H}\psi_n(\mathbf{r}) = E_n^2\psi_n(\mathbf{r}) \tag{3.64}$$

We can proceed by an inductive process to define the meaning of all higher powers of an operator, i.e.,

$$\hat{H}^{m+1} \equiv \hat{H}\left[\hat{H}^m\right] \tag{3.65}$$

which will give, for the case of an energy eigenfunction

$$\hat{H}^m\psi_n(\mathbf{r}) = E_n^m\psi_n(\mathbf{r}) \tag{3.66}$$

Time evolution and the Hamiltonian operator - 4

Now let us look at the time evolution of some wavefunction $\Psi(\mathbf{r},t)$ between times t_0 and t_1.

Suppose the wavefunction at time t_0 is $\psi(\mathbf{r})$,

which we can expand in the energy eigenfunctions $\psi_n(\mathbf{r})$ as

$$\psi(\mathbf{r}) = \sum_n a_n \psi_n(\mathbf{r}) \tag{3.67}$$

Then we know

(see Eq.(3.17) $\Psi(\mathbf{r},t) = \sum_n a_n \Psi_n(\mathbf{r},t) = \sum_n a_n \exp(-iE_n t/\hbar)\psi_n(\mathbf{r})$**, for example)**

$$\Psi(\mathbf{r},t_1) = \sum_n a_n \exp\left[-\frac{iE_n(t_1 - t_0)}{\hbar}\right]\psi_n(\mathbf{r}) \tag{3.68}$$

We can write the exponential factors as power series, noting that

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{3.69}$$

so (3.68) can be written as

$$\Psi(\mathbf{r},t_1) = \sum_n a_n \left[1 + \left(-\frac{iE_n(t_1 - t_0)}{\hbar}\right) + \frac{1}{2!}\left(-\frac{iE_n(t_1 - t_0)}{\hbar}\right)^2 + \cdots\right]\psi_n(\mathbf{r}) \tag{3.70}$$

Time evolution and the Hamiltonian operator - 5

Because of Eq. (3.66),

everywhere we have $E_n^m \psi_n(\mathbf{r})$, *we can substitute* $\hat{H}^m \psi_n(\mathbf{r})$,

and so we have

$$\Psi(\mathbf{r},t_1) = \sum_n a_n \left[1 + \left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right) + \frac{1}{2!}\left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right)^2 + \cdots \right] \psi_n(\mathbf{r}) \qquad (3.71)$$

Because the operator $\hat{H}$, and all its powers as defined above, commute with scalar quantities (numbers), we can rewrite (3.71) as

$$\begin{aligned}\Psi(\mathbf{r},t_1) &= \left[1 + \left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right) + \frac{1}{2!}\left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right)^2 + \cdots \right] \sum_n a_n \psi_n(\mathbf{r}) \\ &= \left[1 + \left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right) + \frac{1}{2!}\left(-\frac{i\hat{H}(t_1 - t_0)}{\hbar} \right)^2 + \cdots \right] \Psi(\mathbf{r},t_0)\end{aligned} \qquad (3.72)$$

Time evolution and the Hamiltonian operator - 6

So, provided we define the exponential of the operator in terms of a power series, i.e.,

$$\exp\left[-\frac{i\hat{H}\left(t_1-t_0\right)}{\hbar}\right]\equiv\left[1+\left(-\frac{i\hat{H}\left(t_1-t_0\right)}{\hbar}\right)+\frac{1}{2!}\left(-\frac{i\hat{H}\left(t_1-t_0\right)}{\hbar}\right)^2+\cdots\right] \tag{3.73}$$

with powers of operators as given by (3.63) and (3.65),

we can indeed write Eq. (3.58).

$$\Psi\left(\mathbf{r},t_1\right)=\exp\left(-\frac{i\hat{H}\left(t_1-t_0\right)}{\hbar}\right)\Psi\left(\mathbf{r},t_0\right)$$

Hence we have established that

there is a well-defined operator that,

given the quantum mechanical wavefunction or "state" at time t_0,

will tell us what the state is at a time t_1.

The particular operator we have derived here is valid for situations where the Hamiltonian is not explicitly dependent on time

which usually means that the potential V does not depend on time.

It is possible to derive operators that deal with more complex situations, though we will not consider those here.

Time-Dependent Schrödinger Equation - 5

Reading – Sections 3.12 – 3.15

Momentum operator

Position operator

The Uncertainty Principle

Particle current

Momentum and the momentum operator - 1

Thus far, the only operator we have considered has been

the Hamiltonian $\hat{H}$

associated with

the energy E**.**

In quantum mechanics,

we can construct operators associated with many other measurable quantities.

Here we consider the momentum operator, which we will write as $\hat{p}$**.**

For $\hat{p}$**, we postulate the operator**

$$\hat{p} \equiv -i\hbar\nabla \tag{3.74}$$

with

$$\nabla \equiv \mathbf{x}_o \frac{\partial}{\partial x} + \mathbf{y}_o \frac{\partial}{\partial y} + \mathbf{z}_o \frac{\partial}{\partial z} \tag{3.75}$$

where $\mathbf{x}_o$, $\mathbf{y}_o$, and $\mathbf{z}_o$ are unit vectors in the *x*, *y*, and *z* directions.

Momentum and the momentum operator - 2

With this postulated form, $\hat{p} \equiv -i\hbar\nabla$ **(3.74), we find that**

$$\frac{\hat{p}^2}{2m} \equiv -\frac{\hbar^2}{2m}\nabla^2 \qquad (3.76)$$

and we have a correspondence between the classical notion of the energy E

$$E = \frac{p^2}{2m} + V \qquad (3.77)$$

and the corresponding Hamiltonian operator of the Schrödinger equation

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V = \frac{\hat{p}^2}{2m} + V \qquad (3.78)$$

The plane waves $\exp(i\mathbf{k}\cdot\mathbf{r})$ **are the eigenfunctions of the operator** $\hat{p}$**, since**

$$\hat{p}\exp(i\mathbf{k}\cdot\mathbf{r}) = \hbar\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad (3.79)$$

with eigenvalues $\hbar\mathbf{k}$***.***

We can therefore make the identification for these eigenstates that the momentum is

$$\mathbf{p} = \hbar\mathbf{k} \qquad (3.80)$$

Note that the $\mathbf{p}$ ***in Eq. (3.80) is a vector, with three components with scalar values, not an operator.***

Position and position operator

For the position operator,

the postulated operator is almost trivial when we are working with functions of position.

It is simply the position vector, $\mathbf{r}$, itself.

At least when we are working in a representation that is in terms of position,

we therefore typically do not write $\hat{\mathbf{r}}$*,*

though rigorously perhaps we should.

The operator for the z-component of position would, for example, also simply be z itself.

Uncertainty principle - 1

A commonly quoted form is to say that

we cannot simultaneously know both the position and momentum of a particle.

Classical mechanics implicitly assumes that knowing both position and momentum is possible.

Here we illustrate the position-momentum uncertainty principle by example.

We defined a Gaussian wavepacket above in Eq. (3.41)

$$\Psi_G(z,t) \propto \int_k \exp\left[-\left(\frac{k-\bar{k}}{2\Delta k}\right)^2\right] \exp\left\{-i\left[\omega(k)t - kz\right]\right\} dk$$

as

an integral over a set of waves with Gaussian weightings on their amplitudes about some central *k* value, $\bar{k}$.

We could rewrite Eq. (3.41) at time t = 0 as

$$\Psi(z,0) = \int_k \Psi_k(k)\exp(ikz)\,dk \tag{3.81}$$

where

$$\Psi_k(k) \propto \exp\left[-\left(\frac{k-\bar{k}}{2\Delta k}\right)^2\right] \tag{3.82}$$

Uncertainty principle - 2

$\Psi_k(k)$ **is the representation of the wavefunction in *k* space.**

$\left|\Psi_k(k)\right|^2$ ***is the probability* P$_k$ *(strictly, the probability density) that,***

if we measured the momentum of the particle (actually the z component of momentum),

it was found to have value $\hbar k$.

This probability would have a statistical distribution

$$P_k = \left|\Psi_k(k)\right|^2 \propto \exp\left[-\frac{\left(k-\bar{k}\right)^2}{2\left(\Delta k\right)^2}\right] \qquad (3.83)$$

The Gaussian in Eq. (3.83) corresponds to the statistical Gaussian probability distribution, with standard deviation Δk.

Uncertainty principle - 3

Note also that

Eq. (3.81) $\Psi(z,0) = \int_k \Psi_k(k)\exp(ikz)\,dk$

is simply the Fourier transform of $\Psi_k(k)$.

The Fourier transform of a Gaussian is a Gaussian.

Explicitly performing that Fourier transform, therefore, we can write

$$\Psi(z,0) \propto \exp\left[-(\Delta k)^2 z^2\right] \qquad (3.84)$$

Now considering the probability (or more strictly, the probability density) of finding the particle at point *z* at time *t* = 0 as $|\Psi(z,0)|^2$, we have

$$|\Psi(z,0)|^2 \propto \exp\left[-2(\Delta k)^2 z^2\right] \equiv \exp\left[-\frac{z^2}{2(\Delta z)^2}\right] \qquad (3.85)$$

where Δz *is chosen so that it is the standard deviation of the probability distribution in real space.*

Uncertainty principle - 4

From Eq. (3.85), we find the relation

$$\Delta k \Delta z = \frac{1}{2} \tag{3.86}$$

or, with momentum (here strictly the z component of momentum) $p = \hbar k$*,*

$$\Delta p \Delta z = \frac{\hbar}{2} \tag{3.87}$$

where $\Delta p = \hbar \Delta k$**.**

When the wavepacket propagated it got wider,

that is, Δz *became larger, though* Δk *had not changed*

the same Gaussian distribution of magnitudes of amplitudes of k **components remained,**

though their relative phases had now changed with time.

The Gaussian distribution and its Fourier transform have the minimum product $\Delta k \Delta z$ **of any distribution,**

and so we find the "uncertainty principle"

$$\Delta p \Delta z \geq \hbar / 2 \tag{3.88}$$

Uncertainty principle

Though demonstrated here only for a specific example,

this uncertainty principle is quite general.

It expresses the non-classical notion that,

if we know the position of a particle very accurately,

we cannot know its momentum very accurately.

Our modern understanding of quantum mechanics says that

it is not merely that we cannot simultaneously measure these two quantities,

or that quantum mechanics is only some incomplete statistical theory that does not tell us both momentum and position simultaneously even though they both exist to arbitrary accuracy.

Quantum mechanics is apparently a complete theory,

not merely a statistical "image" of some underlying deterministic theory;

a particle simply does not have simultaneously both a well defined position and a well defined momentum.

Uncertainty principles in other contexts

Uncertainty principles are well known in Fourier analysis.

One cannot simultaneously have both

a well defined frequency

and

a well defined time

for a signal.

If a signal is a short pulse,

it is necessarily made up out of a range of frequencies.

The shorter the pulse is,

the larger the range of frequencies that must be used to make it up, i.e.,

$$\Delta\omega\Delta t \geq \frac{1}{2} \tag{3.89}$$

The mathematics of this well-known Fourier analysis result is identical to that for the uncertainty principle discussed above.

Uncertainty principles in other contexts

Another common example is found in the diffraction angle of a beam,

- ***propagating, for example in the x direction,***
  - **emerging from a finite slit with some width in the *z* direction.**
    - *Smaller slits correspond to more tightly defined position in the z direction, and give rise to larger diffraction angles.*
      - The diffraction angle corresponds to the uncertainty in the z component of the wavevector.

If we think of light propagation as being due to momentum of photons,

- ***diffraction is understood as the uncertainty principle giving momentum uncertainty in the z direction for this example.***
  - **Specifically**
    - *propagation of Gaussian laser beams corresponds exactly to the above analysis if we define the beams with the correct parameters that correspond to the statistical definition of Gaussian distributions for the beam intensity.*

Particle current

Classical intuition leads us to expect that particles with kinetic energy must be moving,

and hence there will be particle currents or current densities (i.e., particles crossing unit area per unit time).

We have, however, apparently deduced from quantum mechanics that there are stationary states where the particle has energy exceeding the potential energy,

and we are now expecting that there may well be no current associated with such energy eigenstates.

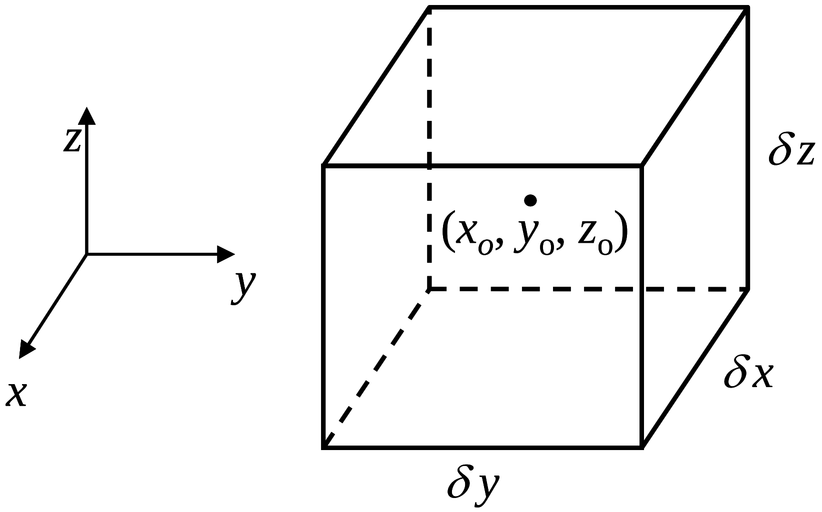
We need a meaningful way of calculating particle current in quantum mechanics so that we can check these notions.

Particle Current - 1

In general, if we are to conserve particles, we expect that we will have a relation of the form

$$\frac{\partial s}{\partial t} = -\nabla . \mathbf{j}_p \tag{3.90}$$

where s *is the particle density and* $\mathbf{j}_p$ *is the particle current density*



(We remember that divergence gives the net flow out of the faces of a small box. Eq. (3.90) is an example of a “continuity equation”)

In our quantum mechanical case, the particle density is $|\Psi(\mathbf{r},t)|^2$,

so we are looking for a relation of the form of Eq. (3.90) but with $|\Psi(\mathbf{r},t)|^2$ *instead of* s*.*

To do this requires a little algebra, and a clever substitution.

Particle Current - 2

We know that

$$\frac{\partial \Psi(\mathbf{r},t)}{\partial t} = \frac{1}{i\hbar}\hat{H}\Psi(\mathbf{r},t) \qquad (3.91)$$

which is simply Schrödinger's equation.

We can also take the complex conjugate of both sides, i.e.,

$$\frac{\partial \Psi^*(\mathbf{r},t)}{\partial t} = -\frac{1}{i\hbar}\hat{H}^*\Psi^*(\mathbf{r},t) \qquad (3.92)$$

Hence, we can write

$$\frac{\partial}{\partial t}\left[\Psi^*\Psi\right] + \frac{i}{\hbar}\left(\Psi^*\hat{H}\Psi - \Psi\hat{H}^*\Psi^*\right) = 0 \qquad (3.93)$$

If the potential is real and does not depend on time, then we can rewrite Eq. (3.93) as

$$\frac{\partial}{\partial t}\left[\Psi^*\Psi\right] + \frac{i\hbar}{2m}\left(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*\right) = 0 \qquad (3.94)$$

Now we use an algebraic "trick" to rearrange this, i.e.,

$$\begin{aligned}\Psi\nabla^2\Psi^* - \Psi^*\nabla^2\Psi &= \Psi\nabla^2\Psi^* + \nabla\Psi\nabla\Psi^* - \nabla\Psi\nabla\Psi^* - \Psi^*\nabla^2\Psi \\ &= \nabla\cdot\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right)\end{aligned} \qquad (3.95)$$

Particle Current - 3

Hence we have

$$\frac{\partial\left(\Psi^*\Psi\right)}{\partial t}=-\frac{i\hbar}{2m}\nabla\cdot\left(\Psi\nabla\Psi^*-\Psi^*\nabla\Psi\right) \tag{3.96}$$

which is an equation of the form of Eq. (3.90)

$$\frac{\partial s}{\partial t}=-\nabla.\mathbf{j}_p$$

if we identify

$$\mathbf{j}_p=\frac{i\hbar}{2m}\left(\Psi\nabla\Psi^*-\Psi^*\nabla\Psi\right) \tag{3.97}$$

as the particle current.

Hence we have found an expression for particle currents for situations where the potential does not depend on time.

Particle currents and stationary states

The expression Eq. (3.97) $\mathbf{j}_p = \frac{i\hbar}{2m}\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right)$ applies also for an energy eigenstate.

Explicitly presuming we are in the *n*th energy eigenstate, we have

$$\mathbf{j}_{pn}(\mathbf{r},t) = \frac{i\hbar}{2m}\left(\Psi_n(\mathbf{r},t)\nabla\Psi_n^*(\mathbf{r},t) - \Psi_n^*(\mathbf{r},t)\nabla\Psi_n(\mathbf{r},t)\right) \quad (3.98)$$

We can write out $\Psi_n(r,\mathrm{t})$ explicitly as

$$\Psi_n(\mathbf{r},t) = \exp\left(-i\frac{E_n}{\hbar}t\right)\psi_n(\mathbf{r}) \quad (3.99)$$

The gradient operator ∇ has no effect on the exponential time factor,

so the time factors in each term can be factored to the front of the expression,

and anyway multiply to unity because of the complex conjugation

$$\begin{aligned}\mathbf{j}_{pn}(\mathbf{r},t) &= \frac{i\hbar}{2m}\exp\left(-i\frac{E_n}{\hbar}t\right)\exp\left(i\frac{E_n}{\hbar}t\right)\left(\psi_n(\mathbf{r})\nabla\psi_n^*(\mathbf{r}) - \psi_n^*(\mathbf{r})\nabla\psi_n(\mathbf{r})\right) \\ &= \frac{i\hbar}{2m}\left(\psi_n(\mathbf{r})\nabla\psi_n^*(\mathbf{r}) - \psi_n^*(\mathbf{r})\nabla\psi_n(\mathbf{r})\right)\end{aligned} \quad (3.100)$$

Hence j_{pn} does not depend on time, i.e., for any energy eigenstate *n*

$$\mathbf{j}_{pn}(\mathbf{r},t) = \mathbf{j}_{pn}(\mathbf{r}) \quad (3.101)$$

Therefore particle current is constant in any energy eigenstate.

Electrical current density and radiation

For a particle such as an electron, the electrical current density is simply $e\mathbf{j}_p$.

A steady current does not radiate any electromagnetic radiation.

This means that an electron in an energy eigenstate does not radiate electromagnetic radiation.

Should a hydrogen atom in an energy eigenstate be radiating?

Classically, the electron orbiting round the nucleus would have a time varying current;

the electron in a classical orbit is continually being accelerated because its direction is changing all the time to keep it in its orbit, and so it would radiate electromagnetic energy.

This quantum mechanical result says that the atom in such a state does not radiate electromagnetic energy because there is no changing current.

The quantum mechanical picture agrees with the reality for hydrogen atoms in states,

and the classical picture does not.

Note also, when the spatial part of the energy eigenstate (i.e., ψ(r)) is real,

or can be written as a real function multiplied by a complex constant,

the right hand side of Eq. (3.100) is zero, and there is zero particle or electrical current.

Functions and Operators – 1

Reading – Section 4.1

Functions as vectors

Dirac bra-ket notation

Expansion coefficients in Dirac bra-ket notation

State vectors

Functions and Operators - 1

We have introduced quantum mechanics through

- ***the Schrödinger equation and***
- ***the spatial and temporal wavefunctions that are solutions to it.***

Quantum mechanics is much broader, however.

- ***E.g., photons are not described by this kind of Schrödinger equation***

We need a more general mathematical formalism to go much further.

- ***This formalism is mostly linear algebra, as in***
  - **matrix algebra,**
  - **Fourier transforms,**
  - **solutions of differential equations,**
  - **integral equations,**
  - **analysis of linear systems in general.**
- ***Here we assume at least the matrix version of linear algebra***

Functions and Operators - 2

The formalism of quantum mechanics is based on linear algebra

- ***because quantum mechanics is apparently absolutely linear in certain specific ways***
    - **i.e., in the quantum mechanical "amplitude"**

To generalize linear algebra for quantum mechanics,

- ***we introduce shorthand notations***
    - **especially Dirac's "bra-ket" notation**
- ***but the underlying concepts are standard for linear algebra***

The mathematical approach here is deliberately informal

- ***The emphasis is on grasping the core concepts and***
- ***ways of visualizing the mathematical operations***

The major goals of this mathematical approach are

- ***to visualizing quantum mechanics, and***
- ***to develop an intuitive understanding of quantum mechanics that extends to a broad range of problems.***

Functions as vectors - 1

A function, e.g., $f(x)$, is essentially

a mapping from one set of numbers

(the “argument”, x, of the function)

to another

(the “result” or “value”, $f(x)$, of the function).

The fundamentals of this concept are not changed

for functions of multiple variables, or

for functions with complex number or vector results.

We can imagine that

the set of possible values of the argument is a list of numbers, and

the corresponding set of values of the function is another list.

Functions as vectors - 2

One kind of list of arguments would be the list of all real numbers,

which we could list in order as

$x_1, x_2, x_3 \ldots$

and so on.

This is an infinitely long list,

and the adjacent values in the list are infinitesimally close together,

but we will regard these infinities as details!

If we presume that we know this list of possible arguments of the function,

we can write out the function as the corresponding list of values, and

we choose to write this list as a column vector, i.e.,

$$\begin{bmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ \vdots \end{bmatrix}$$

Functions as vectors - 3

For example,

we could specify the function at a discrete set of points spaced by some small amount δx***,***

with $x_2 = x_1 + \delta x$, $x_3 = x_2 + \delta x$ **and so on;**

We would do this

for sufficiently many values of x ***and***

over a sufficient range of x

to get a sufficiently useful representation for some calculation,

such as an integral.

The integral of $|f(x)|^2$ **could then be written as**

$$\int |f(x)|^2 dx \cong \begin{bmatrix} f^*(x_1) & f^*(x_2) & f^*(x_3) & \cdots \end{bmatrix} \begin{bmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ \vdots \end{bmatrix} \delta x \qquad (4.1)$$

Visualizing a function as a vector - 1

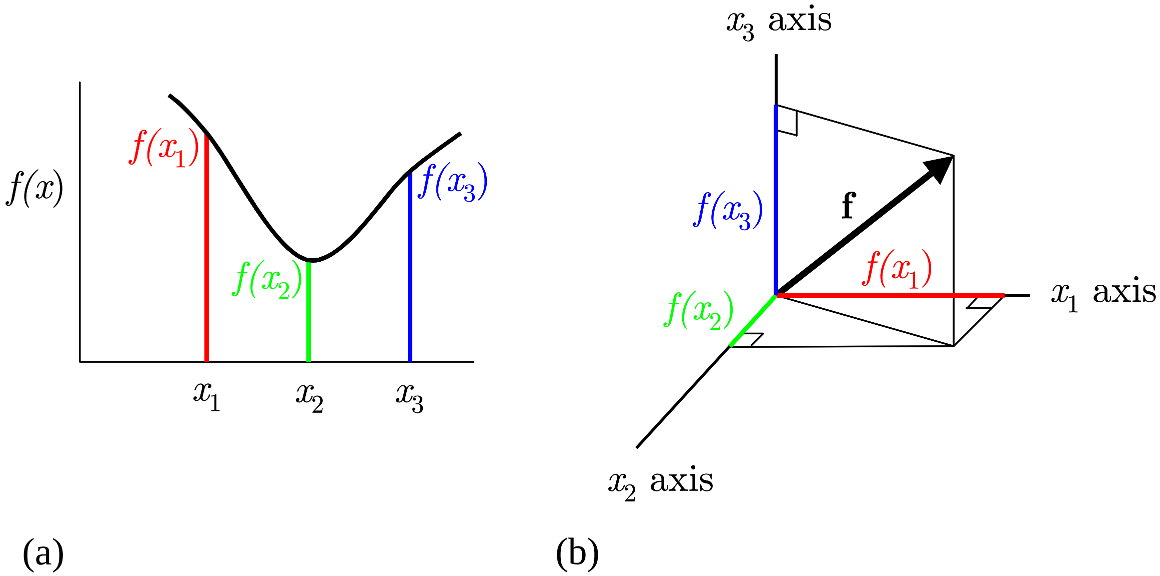
Suppose the function $f(x)$ is approximated by its values at three points,

x_1, x_2, **and** x_3,

and is represented as a vector

$$\mathbf{f} \equiv \begin{bmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \end{bmatrix}$$

Then we can visualize the function as a vector in normal geometrical space.



Visualizing a function as a vector - 2

Though the functions in quantum mechanics are complex, not merely real,

and, since there are many elements in the vector

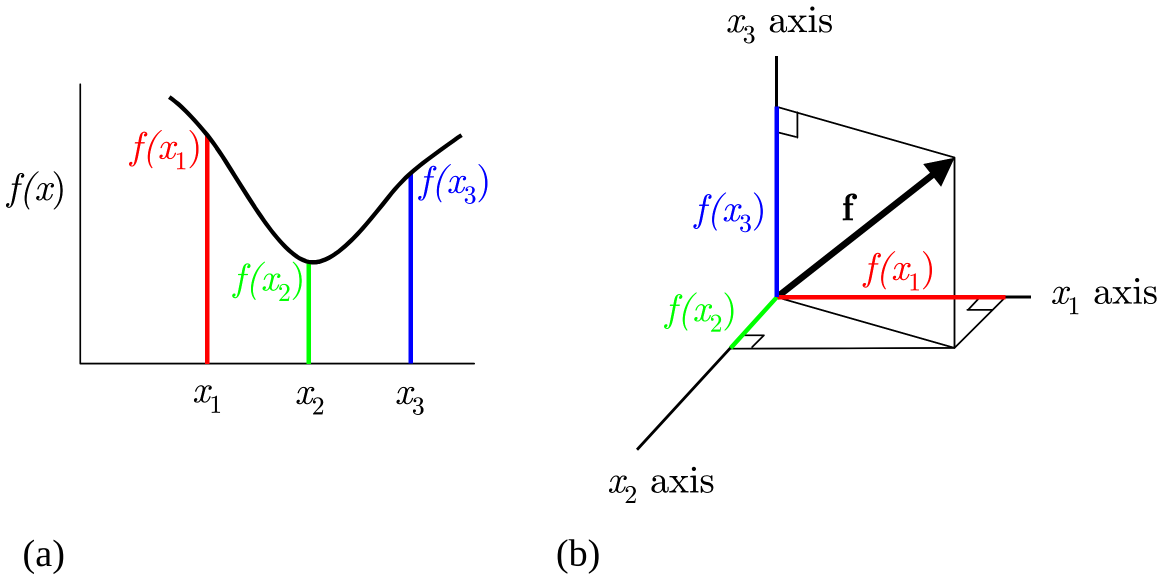
possibly an infinite number,

the space may need a very large (possibly infinite) number of dimensions

But we will still visualize the function

and, more generally, the quantum mechanical state

as a vector in a space.



Dirac bra-ket notation - 1

Now let us introduce the first part of the so-called Dirac "bra-ket" notation.

We will introduce the notation

$\left| f(x) \right\rangle$, **called a "ket",**

to refer to an appropriate form of our column vector.

For the case of our function $f(x)$,

one way to define the "ket" is

$$\left| f(x) \right\rangle \equiv \begin{bmatrix} f(x_1)\sqrt{\delta x} \\ f(x_2)\sqrt{\delta x} \\ f(x_3)\sqrt{\delta x} \\ \vdots \end{bmatrix} \qquad (4.2)$$

or, more strictly, the limit of this as $\delta x \to 0$.

We have incorporated $\sqrt{\delta x}$ into the vector to handle normalization

but the concept is still that the function is a vector list of numbers.

Dirac bra-ket notation - 2

We can similarly define the "bra" $\langle f(x)|$ to refer a row vector, in this case

$$\langle f(x)| \equiv \begin{bmatrix} f^*(x_1)\sqrt{\delta x} & f^*(x_2)\sqrt{\delta x} & f^*(x_3)\sqrt{\delta x} & \cdots \end{bmatrix} \tag{4.3}$$

where again we more strictly mean the limit of this as $\delta x \to 0$.

Note that, in our row vector, we take the complex conjugate of all the values.

The vector

$$\begin{bmatrix} a_1^* & a_2^* & a_3^* & \cdots \end{bmatrix}$$

is called, variously,

- **the Hermitian adjoint,**
- **the Hermitian transpose,**
- **the Hermitian conjugate,**
- **the adjoint,**

of the vector

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix}$$

Hermitian adjoint - 1

A common notation used to indicate the Hermitian adjoint is to use the character "†" as a superscript, i.e.,

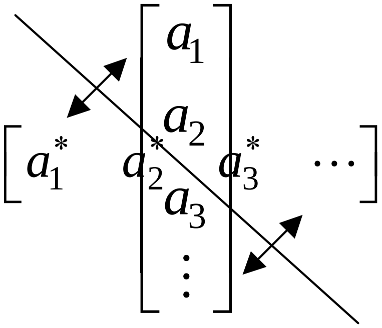
$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix}^\dagger = \begin{bmatrix} a_1^* & a_2^* & a_3^* & \cdots \end{bmatrix} \qquad (4.4)$$

Forming the Hermitian adjoint is like

reflecting about a -45º line,

then taking the complex conjugate of all the elements

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix}^\dagger \Rightarrow$$



$$= \begin{bmatrix} a_1^* & a_2^* & a_3^* & \cdots \end{bmatrix}$$

Hermitian adjoint - 2

The "bra" is the Hermitian adjoint of the "ket" and *vice versa*.

Note also that

$$\left(\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix}^\dagger\right)^\dagger = \begin{bmatrix} a_1^* & a_2^* & a_3^* & \cdots \end{bmatrix}^\dagger = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \qquad (4.5)$$

Bra-ket notation for functions

Considering $f(x)$ as a vector,

with the definitions (4.1), (4.2), and (4.3) we find

$$\int |f(x)|^2 dx \equiv \begin{bmatrix} f^*(x_1)\sqrt{\delta x} & f^*(x_2)\sqrt{\delta x} & f^*(x_3)\sqrt{\delta x} & \cdots \end{bmatrix} \begin{bmatrix} f(x_1)\sqrt{\delta x} \\ f(x_2)\sqrt{\delta x} \\ f(x_3)\sqrt{\delta x} \\ \vdots \end{bmatrix}$$

$$\equiv \sum_n f^*(x_n)\sqrt{\delta x}\, f(x_n)\sqrt{\delta x} \qquad (4.6)$$

$$\equiv \langle f(x) | f(x) \rangle$$

where again the strict equality applies in the limit when $\delta x \to 0$.

Writing this as a vector multiplication

eliminates the need to write a summation or integral

That is implicit in the vector multiplication.

Note the shorthand for the vector product of the "bra" and "ket"

$$\langle g | \times | f \rangle \equiv \langle g | f \rangle \qquad (4.7)$$

Bra-ket notation with different functions

This notation is also useful when we are dealing with integrals of two different functions,

i.e.,

$$\int g^*(x)f(x)dx \equiv \begin{bmatrix} g^*(x_1)\sqrt{\delta x} & g^*(x_2)\sqrt{\delta x} & g^*(x_3)\sqrt{\delta x} & \cdots \end{bmatrix} \begin{bmatrix} f(x_1)\sqrt{\delta x} \\ f(x_2)\sqrt{\delta x} \\ f(x_3)\sqrt{\delta x} \\ \vdots \end{bmatrix}$$

$$\equiv \sum_n g^*(x_n)\sqrt{\delta x}\, f(x_n)\sqrt{\delta x} \qquad (4.8)$$

$$\equiv \langle g(x) | f(x) \rangle$$

Inner product

In general this kind of "product"

$$\langle g | \times | f \rangle \equiv \langle g | f \rangle$$

is called an inner product in linear algebra.

The geometric vector dot product is an inner product,

the bra-ket "product" is an inner product,

and the "overlap integral" on the left of Eq. (4.8)

$$\int g^*(x) f(x) dx$$

is an inner product.

It is "inner" because

it takes two vectors and turns them into a number,

a "smaller" entity.

The bra-ket notation gives an inner "feel" to this multiplication

The special parentheses at either end give a "closed" look

Bra-ket notation and expansions on basis sets - 1

Suppose the function is not represented directly as a set of values for each point in ordinary geometrical space,

but instead as an expansion in a complete orthonormal basis set, $\psi_n(x)$***,***

$$f(x) = \sum_n c_n \psi_n(x) \tag{4.9}$$

We could also write the function as a vector or "ket"

(which would also in general have an infinite number of elements)

$$|f(x)\rangle \equiv \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \tag{4.10}$$

In this case, the "bra" becomes

$$\langle f(x)| \equiv \begin{bmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{bmatrix} \tag{4.11}$$

Bra-ket notation and expansions on basis sets - 2

When we write the function in this different form,

as a vector containing these expansion coefficients,

we say we have changed its “representation”.

The function $f(x)$ is still the same function as it was before,

and we visualize the vector $|f(x)\rangle$ as being the same vector in our space.

We have merely changed the axes in that space that we use to represent the function,

and hence the coordinates of the vector have changed

now they are the numbers c_1, c_2, $c_3 \ldots$.

Bra-ket notation and expansions on basis sets - 3

Just as before, we could evaluate

$$\begin{aligned}
\int \left| f(x) \right|^2 dx &\equiv \int f^*(x) f(x) dx \\
&\equiv \int \left[\sum_n c_n^* \psi_n^*(x) \right] \left[\sum_m c_m \psi_m(x) \right] dx \\
&\equiv \sum_{n,m} c_n^* c_m \int \psi_n^*(x) \psi_m(x) dx \\
&\equiv \sum_{n,m} c_n^* c_m \delta_{nm} \\
&\equiv \sum_n \left| c_n \right|^2 \\
&\equiv \begin{bmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \\
&\equiv \left\langle f(x) \middle| f(x) \right\rangle
\end{aligned} \tag{4.12}$$

Bra-ket notation and expansions on basis sets - 4

Similarly, with

$$g(x) = \sum_n d_n \psi_n(x) \tag{4.13}$$

we have

$$\int g^*(x) f(x) dx \equiv \begin{bmatrix} d_1^* & d_2^* & d_3^* & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \tag{4.14}$$

$$\equiv \langle g(x) | f(x) \rangle$$

with similar intermediate algebraic steps to those of Eq. (4.12).

Bra-ket expressions

Note that the result of a bra-ket expression like

$$\left\langle f(x) \middle| f(x) \right\rangle \text{ or } \left\langle g(x) \middle| f(x) \right\rangle$$

is simply a number (in general a complex one),

which is easy to see if we think of this as a vector multiplication.

Note too that

this number is not changed as we change the representation,

as we would expect by analogy with the dot product of two vectors,

which is independent of the coordinate system.

Expansion coefficients

Evaluating the c_n in Eq. (4.9) (or the d_n in Eq. (4.13)) is simple

because we choose the set of functions $\psi_n(x)$ to be orthonormal.

Since $\psi_n(x)$ is just another function,

we can also write it as a ket.

To evaluate the coefficient *c*$_m$, we premultiply by the bra $\langle\psi_m|$

$$\langle\psi_m(x)|f(x)\rangle = \sum_n c_n \langle\psi_m(x)|\psi_n(x)\rangle = c_m \tag{4.15}$$

Using bra-ket notation, we can write (4.9) ($f(x) = \sum_n c_n \psi_n(x)$) as

$$\begin{aligned} |f(x)\rangle &= \sum_n c_n |\psi_n(x)\rangle = \sum_n |\psi_n(x)\rangle c_n \\ &= \sum_n |\psi_n(x)\rangle\langle\psi_n(x)|f(x)\rangle \end{aligned} \tag{4.16}$$

Because c_n is just a number, it can be moved about in the product

(formally, multiplication of a vector and a number is *commutative*, though, or course, multiplication of vectors or matrices generally is not.)

Often in using the bra-ket notation, we may drop arguments like *x*.

Then we can write Eq. (4.16) as

$$|f\rangle = \sum_n |\psi_n\rangle\langle\psi_n|f\rangle \tag{4.17}$$

Reason for bra-ket notation

Here we see a key reason for introducing the Dirac bra-ket notation;

- ***it is a generalized shorthand way of writing the underlying linear algebra operations we need to perform,***
  - **and can be used whether we are thinking about representing functions as**
    - *continuous functions in some space, or as*
    - *summations over basis sets.*

- ***It will also continue to be useful as we consider other quantum mechanical attributes***
  - **ones that are not represented as functions in normal geometric space;**
    - *an example (to which we will return much later) is the "spin" of an electron, a magnetic property of the electron.*

State vectors

In quantum mechanics

- *where the function f represents the state of the quantum mechanical system*
  - **(for example, it might be the wavefunction),**
- *the set of numbers represented by the bra ($\langle f|$) or ket ($|f\rangle$) vector represents the state of the system, and*
  - **hence we refer to the ket vector that represents *f* as the “state vector” of the system,**
  - **and the corresponding bra vector as the (Hermitian) adjoint of that state vector.**

In quantum mechanics,

- *the bra or ket always represents either*
  - **the quantum mechanical state of the system**
    - *(such as the spatial wavefunction $\psi(x)$),*
  - **or some state that the system could be in**
    - *(such as one of the basis states $\psi_n(x)$).*

Convention for symbols inside bra and ket vectors - 1

The convention for what symbols we put inside the bra or ket is loose,

and usually one deduces from the context what exactly is being meant.

For example,

if it is obvious what basis we were working with,

we might use the notation $|n\rangle$ to represent the *n*th basis function (or basis "state")

rather than the notation $|\psi_n(x)\rangle$ or $|\psi_n\rangle$.

In general,

the symbols inside the bra or ket should be enough to make it clear what state we are discussing in a given context

There are otherwise essentially no rules for the notation inside the bra or ket.

Convention for symbols inside bra and ket vectors - 1

For example,

We could write

$$\left|\begin{array}{l}\text{The state where the electron has the lowest}\\ \text{possible energy in a harmonic oscillator with}\\ \text{potential energy } 0.375x^2\end{array}\right\rangle$$

but since we likely already know we are discussing such a harmonic oscillator,

it will save us time and space simply to write

$$|0\rangle$$

with the zero representing the quantum number of that state.

Either would be correct mathematically.

Functions and Operators – 2

Reading – Section 4.2 – 4.5

Vector space

Operators

Linear operators as matrices

Evaluating matrix elements for operators

Vector space - 1

We need a "space" in which our vectors exist.

For a vector with three components

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix}$$

we imagine a conventional three dimensional Cartesian space.

The vector can be visualized as a line in that space, starting from the origin,

with projected lengths a_1, a_2, *and* a_3 *along the* x, y, *and* z *axes respectively,*

with each of these axes being at right angles to each other axis.

Vector space - 2

For a function expressed as its value at a set of points,

instead of 3 axes labeled x*,* y*, and* z*,*

we may have an infinite number of different, orthogonal axes,

labeled with the basis function with which they are associated,

e.g., ψ_n**.**

Just as we may label the axes in conventional space with unit vectors

(e.g., one notation is $\hat{\mathbf{x}}$*,* $\hat{\mathbf{y}}$*, and* $\hat{\mathbf{z}}$ *for the unit vectors),*

so also here we can label the axes with the kets associated with the basis functions, $|\psi_n\rangle$;

either notation is acceptable.

Mathematical properties of geometrical space and vector space

Inner product

The geometrical space has a vector dot product that defines both the orthogonality of the axes, e.g.,

$$\hat{\mathbf{x}} \cdot \hat{\mathbf{y}} = 0 \tag{4.18}$$

and defines the components of a vector along those axes, e.g.,

$$\mathbf{f} = f_x \hat{\mathbf{x}} + f_y \hat{\mathbf{y}} + f_z \hat{\mathbf{z}} \tag{4.19}$$

with

$$f_x = \mathbf{f} \cdot \hat{\mathbf{x}} \tag{4.20}$$

and similarly for the other components.

Our vector space has an inner product that defines both the orthogonality of the basis functions

$$\langle \psi_m | \psi_n \rangle = \delta_{nm} \tag{4.21}$$

as well as the components

$$c_m = \langle \psi_m | f \rangle \tag{4.22}$$

Mathematical properties of geometrical space and vector space

Addition of vectors

With respect to addition of vectors,

both spaces are commutative

$$\mathbf{a}+\mathbf{b}=\mathbf{b}+\mathbf{a} \tag{4.23}$$

$$|f\rangle+|g\rangle=|g\rangle+|f\rangle \tag{4.24}$$

and associative

$$\mathbf{a}+(\mathbf{b}+\mathbf{c})=(\mathbf{a}+\mathbf{b})+\mathbf{c} \tag{4.25}$$

$$|f\rangle+(|g\rangle+|h\rangle)=(|f\rangle+|g\rangle)+|h\rangle \tag{4.26}$$

Mathematical properties of geometrical space and vector space

Linearity

They are both linear

with respect to multiplying by constants, e.g.,

$$c(\mathbf{a}+\mathbf{b}) = c\mathbf{a} + c\mathbf{b} \tag{4.27}$$

$$c(|f\rangle + |g\rangle) = c|f\rangle + c|g\rangle \tag{4.28}$$

(The constants in the our vector space case are certainly allowed to be complex.)

The inner product is linear

both in multiplying by constants, e.g.,

$$\mathbf{a}.(c\mathbf{b}) = c(\mathbf{a}.\mathbf{b}) \tag{4.29}$$

$$\langle f|cg\rangle = c\langle f|g\rangle \tag{4.30}$$

and in superposition of vectors

$$\mathbf{a}.(\mathbf{b}+\mathbf{c}) = \mathbf{a}.\mathbf{b} + \mathbf{a}.\mathbf{c} \tag{4.31}$$

$$\langle f|(|g\rangle + |h\rangle) = \langle f|g\rangle + \langle f|h\rangle \tag{4.32}$$

Mathematical properties of geometrical space and vector space

Length of vector ("norm" of vector)

There is a well-defined "length" to a vector in both cases (formally, a norm)

$$\|\mathbf{a}\| = \sqrt{\mathbf{a}.\mathbf{a}} \tag{4.33}$$

$$\| f \| = \sqrt{\langle f \mid f \rangle} \tag{4.34}$$

Completeness and "compactness"

In both cases,

any vector in the space can be represented to an arbitrary degree of accuracy as a linear combination of the basis vectors

this is the completeness requirement on the basis set

In vector spaces, this property of the vector space is sometimes described as "compactness".

Mathematical properties of geometrical space and vector space

Inner product and commutativity

The inner products in geometrical space and our vector space differ slightly

In geometrical space the lengths a_1, a_2, and a_3 of a vector are real,

so there the inner product (vector dot product) is commutative, i.e.,

$$\mathbf{a}.\mathbf{b} = \mathbf{b}.\mathbf{a} \tag{4.35}$$

In working with complex coefficients rather than real lengths,

it is more useful to have an inner product (as we do) that has a complex conjugate relation

$$\langle f|g\rangle = \left(\langle g|f\rangle\right)^* \tag{4.36}$$

Such a relation ensures that $\langle f|f\rangle$ is real, even if we work with complex numbers,

as required for it to be a useful norm.

(The existence of a norm is formally required to prove properties like completeness or compactness by showing that the norm of the difference of two vectors can be as small as desired.)

Mathematical properties of geometrical space and vector space

Additional mathematical properties and requirements

Both spaces have a "null" or zero vector

Both spaces have an "antivector" that added to the vector gives the null vector

Linear vector spaces and Hilbert spaces

The elementary mathematical properties above, other than the inner product, are sufficient to define these two spaces as "linear vector spaces"

With the properties of the inner product,

these are what are called "Hilbert spaces".

The Hilbert space is the space in which the vector representation of the function exists,

just as normal Cartesian geometrical space is the space in which a geometrical vector exists.

The main differences between our vector space and geometrical space are

(i) our components can be complex numbers rather than only real ones,

(ii) we can have more dimensions (possibly an infinite number).

but we can use the idea of a geometrical space as a starting point for visualizing our vector space.

Our vector space can also be called a function space.

A vector in this space is a representation of a function.

The set of basis vectors (basis functions) that can be used to represent vectors in this space is said in linear algebra to "span" the space.

Operators - 1

A function turns one number (the argument) into another (the result).

An operator turns one function into another.

> ***In the vector space representation of a function, an operator turns one vector into another.***

Suppose that we are constructing the new function $g(y)$ **from the function** $f(x)$

> ***by acting on*** $f(x)$ ***with the operator*** $\hat{A}$***.***

The variables *x* and *y* might actually be the same kind of variable,

> ***as in the case where the operator corresponds to differentiation of the function, e.g.,***

$$g(x) = \left(\frac{d}{dx}\right) f(x) \tag{4.37}$$

or they might be quite different,

> ***as in the case of a Fourier transform operation where x might represent time and y might represent frequency, e.g.,***

$$g(y) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \exp(-iyx)\, dx \tag{4.38}$$

Operators - 2

A standard notation for writing such an operation on a function is

$$g(y) = \hat{A} f(x) \tag{4.39}$$

Note that this is not a multiplication of $f(x)$ by $\hat{A}$ in the normal algebraic sense,

but should be read as $\hat{A}$ operating on $f(x)$.

For $\hat{A}$ to be the most general operation possible,

it should be possible for the value of $g(y)$,

for example at some particular value of $y = y_1$,

to depend on the values of $f(x)$ for all values of the argument x.

This is the case, for example, in the Fourier transform operation of Eq. (4.38).

$$g(y) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \exp(-iyx)\, dx$$

Linear operators

We interested here solely in what are called linear operators.

They are the only ones we will use in quantum mechanics,

again because of the fundamental linearity of quantum mechanics.

A linear operator has the following characteristics,

$$\hat{A}\left[f(x)+h(x)\right]=\hat{A}f(x)+\hat{A}h(x) \tag{4.40}$$

$$\hat{A}\left[cf(x)\right]=c\hat{A}f(x) \tag{4.41}$$

for any complex number c.

Consequences of linearity for representation of operators - 1

Let us consider how, in the most general way,

we could have the function $g(y)$ at some specific value y_1 of its argument, i.e., $g(y_1)$, related to the values of $f(x)$ for possibly all values of x

and still retain the linearity implied by Eqs. (4.40) and (4.41).

Think of the function $f(x)$ as being represented by a list of values,

$$f(x_1),\ f(x_2),\ f(x_3),\ \ldots\ ,$$

just as we did when considering $f(x)$ as a vector.

Again,

we can take the values of *x* to be as closely spaced as we want,

and we believe that this representation can give us as accurate a representation of $f(x)$ as we need for any calculation we need to perform.

Consequences of linearity for representation of operators - 2

Then we propose that, for a linear operation, the value of $g(y_1)$ might be related to the values of $f(x)$ by a relation of the form

$$g(y_1) = a_{11} f(x_1) + a_{12} f(x_2) + a_{13} f(x_3) + \ldots \tag{4.42}$$

where the a_{ij} are complex constants.

This form certainly has the linearity of the form required by Eqs. (4.40) and (4.41),

i.e., if we were to replace $f(x)$ by $f(x)+h(x)$, then we would have

$$\begin{aligned} g(y_1) &= a_{11}\left[f(x_1)+h(x_1)\right] + a_{12}\left[f(x_2)+h(x_2)\right] + a_{13}\left[f(x_3)+h(x_3)\right] + \ldots \\ &= a_{11} f(x_1) + a_{12} f(x_2) + a_{13} f(x_3) + \ldots \\ &\quad + a_{11} h(x_1) + a_{12} h(x_2) + a_{13} h(x_3) + \ldots \end{aligned} \tag{4.43}$$

as required by Eq. (4.40),

and similarly if we were to replace $f(x)$ by $cf(x)$, we would have

$$\begin{aligned} g(y_1) &= a_{11} cf(x_1) + a_{12} cf(x_2) + a_{13} cf(x_3) + \ldots \\ &= c\left[a_{11} f(x_1) + a_{12} f(x_2) + a_{13} f(x_3) + \ldots\right] \end{aligned} \tag{4.44}$$

Generality of our proposed form

Now let us consider whether the form Eq. (4.42)

$$g(y_1) = a_{11} f(x_1) + a_{12} f(x_2) + a_{13} f(x_3) + \ldots$$

is the most general it could be.

We can see this by trying to add other powers and "cross terms" of $f(x)$.

Any more complicated function relating $g(y_1)$ to $f(x)$ could presumably be written as a power series in $f(x)$, possibly involving $f(x)$ for different values of x (i.e., cross terms).

If we were to add

higher powers of $f(x)$, such as $\left[f(x)\right]^2$,

or cross terms such as $f(x_1)f(x_2)$ into the series (4.42),

it would no longer have the required linear behavior of Eqs. (4.43) and (4.44).

We also cannot add a constant term to the series (4.42);

that would violate the second linearity condition, (4.41),

since the additive constant would not be multiplied by c.

Hence we conclude Eq. (4.42) is the most general form possible for the relation between $g(y_1)$ and $f(x)$ if this relation is to correspond to a linear operator.

Construction of the entire operator

To construct the entire function $g(y)$,

we should construct series like Eq. (4.42) for each value of y, i.e., y_2, y_3, …

If we write the functions $f(x)$ and $g(y)$ as vectors,

then this general linear operation that relates the function $g(y)$ to the function $f(x)$ can be written as a matrix-vector multiplication,

$$\begin{bmatrix} g(y_1) \\ g(y_2) \\ g(y_3) \\ \vdots \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots \\ a_{21} & a_{22} & a_{23} & \cdots \\ a_{31} & a_{32} & a_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ \vdots \end{bmatrix} \tag{4.45}$$

with the operator

$$\hat{A} \equiv \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots \\ a_{21} & a_{22} & a_{23} & \cdots \\ a_{31} & a_{32} & a_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{4.46}$$

Any linear operator can be represented this way.

At least in so far as we presume functions can be represented as vectors, then linear operators can be represented by matrices.

Bra-ket notation and operators

In bra-ket notation, we can write Eq. (4.39) ($g(y)=\hat{A}f(x)$) as

$$|g\rangle = \hat{A}|f\rangle \tag{4.47}$$

If we regard the ket as a vector,

we now regard the (linear) operator $\hat{A}$ as a matrix.

In the language of vector (function) spaces,

the operator takes one vector (function) and turns it into another.

All of the following linear mathematical operations can be described in this way:

differentiation,

rotation (and dilatation) of a vector,

all linear transforms (Fourier, Laplace, Hankel, z-transform, …),

convolutions,

Green's functions in integral equations,

linear integral equations generally.

Linear operators and quantum mechanics

In quantum mechanics,

such linear operators are used as operators associated with measurable variables such as

the Hamiltonian operator for energy, and

the momentum operator for momentum,

as operators corresponding to changing the representation of a function (changing the basis),

and for a few other specific purposes,

with the associated vectors representing quantum mechanical states.

Consequences of linear operator algebra

A very important consequence of the mathematical equivalence of matrices and linear operators is that the

algebra for such operators is identical to that of matrices.

In particular,

operators do not in general commute, i.e.,

$$\hat{A}\hat{B}\left|f\right\rangle \text{ is not in general equal to } \hat{B}\hat{A}\left|f\right\rangle \tag{4.48}$$

for any arbitrary $\left|f\right\rangle$.

If we understand that we are considering the operators to be operating on an arbitrary vector in the space,

we can drop the vector itself,

and write relations between operators,

e.g., we can say, instead of Eq. (4.48)

$$\hat{A}\hat{B} \text{ is not in general equal to } \hat{B}\hat{A} \tag{4.49}$$

which we would regard as an obvious statement if we are thinking of the operators as matrices.

Whether or not operators commute is also of central importance in quantum mechanics.

Generalization to expansion coefficients

We presented the argument above for functions of a variable *x* or *y*

but we could instead talk about expansion coefficients on basis sets.

For example, we had expanded $f(x)$ on a basis set in Eq. (4.9)

$$f(x)=\sum_n c_n \psi_n(x)$$

We similarly had expanded $g(x)$ on a basis set in Eq. (4.13)

$$g(x)=\sum_n d_n \psi_n(x)$$

We could follow an argument as above, requiring that each expansion coefficient d_i depend linearly on all the expansion coefficients c_n,

obtaining a matrix vector statement of the same form, i.e.,

$$\begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & \cdots \\ A_{21} & A_{22} & A_{23} & \cdots \\ A_{31} & A_{32} & A_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \tag{4.50}$$

and the bra-ket statement of the relation between f, g, and $\hat{A}$, Eq.(4.47), $|g\rangle = \hat{A}|f\rangle$, remains unchanged.

Evaluating the elements of the matrix associated with an operator - 1

Suppose we start with $f(x) = \psi_j(x)$, or equivalently

$$|f\rangle = |\psi_j\rangle \tag{4.51}$$

i.e., we choose $f(x)$ to be the jth basis function.

In the expansion Eq. (4.9)

$$f(x) = \sum_n c_n \psi_n(x)$$

this means we are choosing $c_j = 1$ and setting all the other c's to be zero.

Now we operate on this $|f\rangle$ with $\hat{A}$ as in Eq. (4.47)

$$|g\rangle = \hat{A}|f\rangle$$

to get the resulting function $|g\rangle$.

Suppose we want to know specifically what the resulting coefficient d_i is of the ith basis function in the expansion of this function

i.e., as in Eq.(4.13).

$$g(x) = \sum_n d_n \psi_n(x)$$

Evaluating the elements of the matrix associated with an operator - 2

It is obvious from the matrix form, Eq.(4.50),

$$\begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & \cdots \\ A_{21} & A_{22} & A_{23} & \cdots \\ A_{31} & A_{32} & A_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

of the operation of $\hat{A}$ on this $|f\rangle$,

with the choice $c_j = 1$ and all other c's zero, that

$$d_i = A_{ij} \tag{4.52}$$

For example, for the specific case of $j = 2$, we would have

$$\begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{12} \\ A_{22} \\ A_{32} \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & \cdots \\ A_{21} & A_{22} & A_{23} & \cdots \\ A_{31} & A_{32} & A_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix} \tag{4.53}$$

and so

$$d_3 = A_{32}\,. \tag{4.54}$$

Evaluating the elements of the matrix associated with an operator - 3

But, from the expansions for $|f\rangle$ and $|g\rangle$ we have, for the specific case of $|f\rangle = |\psi_j\rangle$,

$$|g\rangle = \sum_n d_n |\psi_n\rangle = \hat{A}|\psi_j\rangle \qquad (4.55)$$

To extract d_i from this expression, we multiply by $\langle\psi_i|$ on both sides to obtain

$$d_i = \langle\psi_i|\hat{A}|\psi_j\rangle \qquad (4.56)$$

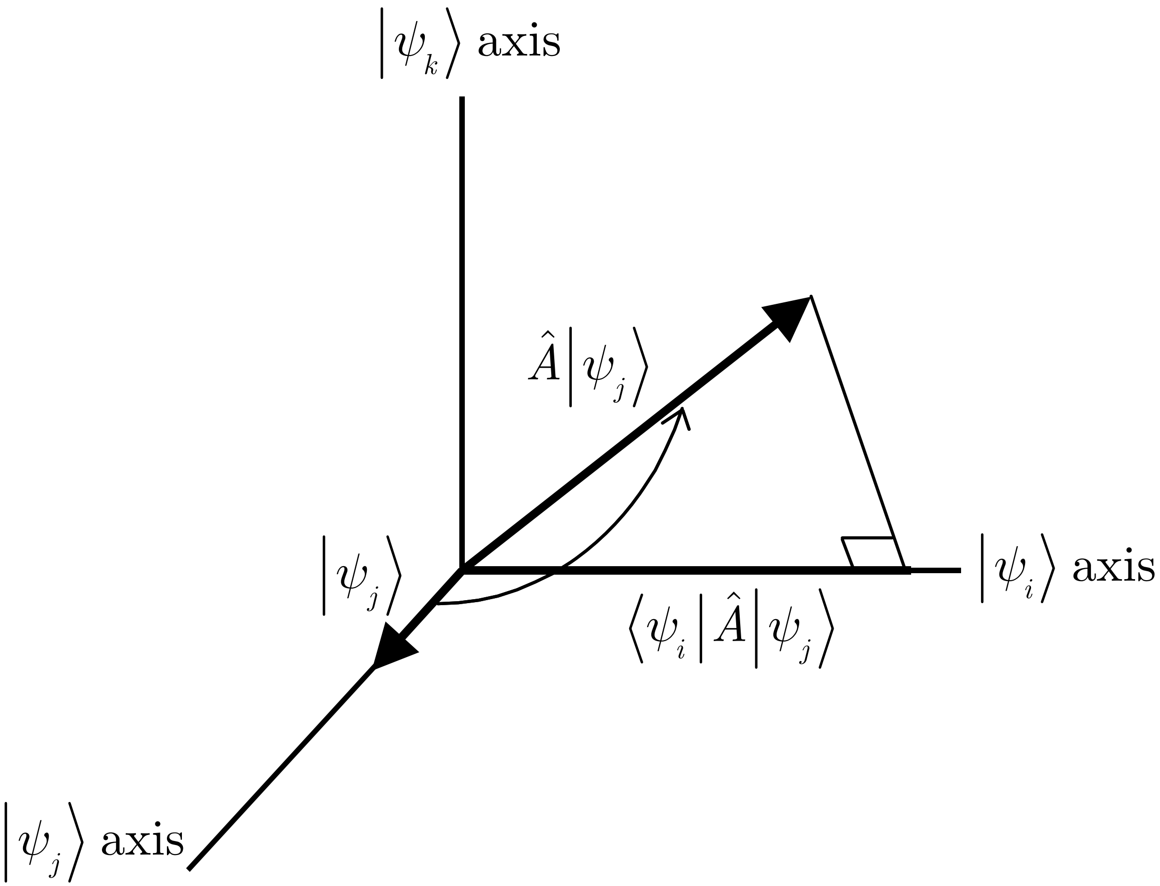
and hence we conclude, from Eq. (4.52) ($d_i = A_{ij}$)

$$A_{ij} = \langle\psi_i|\hat{A}|\psi_j\rangle \qquad (4.57)$$

If we now think back to integrals considered as vector-vector multiplications, then we can see that the matrix elements corresponding to the operator $\hat{A}$ are

$$A_{ij} = \int \psi_i^*(x)\hat{A}\psi_j(x)\,dx \qquad (4.58)$$

Visualization of a matrix element in Hilbert space



Operator $\hat{A}$ acting on the unit vector $|\psi_j\rangle$, generates the vector $\hat{A}|\psi_j\rangle$, which in general has a different length and direction from the original vector $|\psi_j\rangle$.

The matrix element $A_{ij} \equiv \langle\psi_i|\hat{A}|\psi_j\rangle$ is the projection of the vector $\hat{A}|\psi_j\rangle$ onto the $|\psi_i\rangle$ axis.

Evaluating the elements of the matrix associated with an operator - 4

We can if we wish write out the matrix explicitly for the operator $\hat{A}$, obtaining, with the notation of Eq. (4.57)

$$\hat{A} \equiv \begin{bmatrix} \langle\psi_1|\hat{A}|\psi_1\rangle & \langle\psi_1|\hat{A}|\psi_2\rangle & \langle\psi_1|\hat{A}|\psi_3\rangle & \cdots \\ \langle\psi_2|\hat{A}|\psi_1\rangle & \langle\psi_2|\hat{A}|\psi_2\rangle & \langle\psi_2|\hat{A}|\psi_3\rangle & \cdots \\ \langle\psi_3|\hat{A}|\psi_1\rangle & \langle\psi_3|\hat{A}|\psi_2\rangle & \langle\psi_3|\hat{A}|\psi_3\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{4.59}$$

We have therefore deduced how to set up both

the function as a vector in function space and

a linear operator as a matrix that operates on those vectors in the function space.

Functions and Operators – 3

Reading – Section 4.6 – 4.10 up to "Use of unitary operators to change basis sets for representing vectors"

Bilinear expansion of operators

Specific types of linear operators

- **Identity operator**
- **Inverse operators**
- **Unitary operators**
  - *conservation of length and inner product under unitary transformations*

Bilinear expansion of linear operators - 1

We know that we can expand functions in a basis set,

as in Eqs. (4.9), $f(x)=\sum_n c_n \psi_n(x)$*, or Eq.(4.16),* $\left| f(x)\right\rangle = \sum_n c_n \left|\psi_n(x)\right\rangle$.

What is the equivalent form of expansion for an operator?

We can deduce this from our matrix representation above.

Considering an arbitrary function *f*, written in ket form as $\left| f \right\rangle$,

from which a function g (written as the ket $\left| g \right\rangle$***) can be calculated***

by acting with a specific operator $\hat{A}$**, i.e.,**

$$\left| g \right\rangle = \hat{A} \left| f \right\rangle \tag{4.60}$$

Bilinear expansion of linear operators - 2

We presume that *g* and *f* are expanded on the basis set ψ_i,

i.e., in function space we have

$$|g\rangle = \sum_i d_i |\psi_i\rangle \qquad (4.61)$$

$$|f\rangle = \sum_j c_j |\psi_j\rangle \qquad (4.62)$$

From our matrix representation, Eq. (4.50), of the expression (4.60) ($|g\rangle = \hat{A}|f\rangle$), we know that

$$d_i = \sum_j A_{ij} c_j \qquad (4.63)$$

and, by definition of the expansion coefficient, we know that

$$c_j = \langle \psi_j | f \rangle \qquad (4.64)$$

Hence, (4.63) becomes

$$d_i = \sum_j A_{ij} \langle \psi_j | f \rangle \qquad (4.65)$$

Bilinear expansion of linear operators - 3

Substituting $d_i = \sum_j A_{ij} \langle \psi_j | f \rangle$ back into (4.61) ($|g\rangle = \sum_i d_i |\psi_i\rangle$),

$$|g\rangle = \sum_{i,j} A_{ij} \langle \psi_j | f \rangle |\psi_i\rangle \tag{4.66}$$

Remember that $\langle \psi_j | f \rangle \equiv c_j$ is simply a number, so we can move it within the multiplicative expression.

Hence we have

$$|g\rangle = \sum_{i,j} A_{ij} |\psi_i\rangle \langle \psi_j | f \rangle \tag{4.67}$$

But $|f\rangle$ represents an arbitrary function in the space,

so we therefore conclude that the operator $\hat{A}$ can be represented as

$$\hat{A} \equiv \sum_{i,j} A_{ij} |\psi_i\rangle \langle \psi_j | \tag{4.68}$$

This form, Eq. (4.68), is referred to as

a "bilinear expansion" of the operator,

and is analogous to the linear expansion of a vector.

Bilinear expansion of linear operators - 4

In integral notation for functions of a simple variable, we have, analogously, the relation

$$g(x) = \int \hat{A} f(x_1)\, dx_1 \tag{4.69}$$

which leads to the analogous form of the bilinear expansion

$$\hat{A} \equiv \sum_{i,j} A_{ij} \psi_i(x) \psi_j^*(x_1) \tag{4.70}$$

Note that these bilinear expansions can completely represent any linear operator that operates within the space,

i.e., for which the result of operating on a vector (function) with the operator is always a vector (function) in the same space.

Outer product

An expression of the form of Eq. (4.68)

$$\hat{A} \equiv \sum_{i,j} A_{ij} |\psi_i\rangle\langle\psi_j| \qquad (4.68)$$

contains an outer product of two vectors.

An inner product expression of the form $\langle g|f\rangle$ results in a single, complex number,

An outer product expression of the form $|g\rangle\langle f|$ generates a matrix, e.g.,

$$|g\rangle\langle f| = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \end{bmatrix} \begin{bmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{bmatrix} = \begin{bmatrix} d_1c_1^* & d_1c_2^* & d_1c_3^* & \cdots \\ d_2c_1^* & d_2c_2^* & d_2c_3^* & \cdots \\ d_3c_1^* & d_3c_2^* & d_3c_3^* & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \qquad (4.71)$$

The specific summation in Eq. (4.68) is actually, then, a sum of matrices,

with the matrix $|\psi_i\rangle\langle\psi_j|$ having the element in the ith row and the jth column being one, and all other elements being zero

Such outer product expressions for operators are very common in quantum mechanics.

Specific important types of linear operators

In the use of Hilbert spaces, there are specific important types of linear operators that are very important. Four of those are

(i) the identity operator,

important for operator algebra

(ii) inverse operators,

finding these often solves a physical problem mathematically, and they are also important in operator algebra

(iii) unitary operators,

very useful for changing the basis for representing the vectors, and describing the evolution of quantum mechanical systems

(iv) Hermitian operators.

used to represent measurable quantities in quantum mechanics, and they have some very powerful mathematical properties

Identity operator - 1

The identity operator $\hat{I}$ is that operator that, when it operates on a vector (function), leaves it unchanged.

In matrix form, the identity operator is, obviously,

$$\hat{I} = \begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \qquad (4.72)$$

In bra-ket form, the identity operator can be written in the form

$$\hat{I} = \sum_i |\psi_i\rangle\langle\psi_i| \qquad (4.73)$$

where the $|\psi_i\rangle$ form a complete basis for the function space of interest.

Identity operator - 2

Let us prove the statement Eq. (4.73) ($\hat{I} = \sum_i |\psi_i\rangle\langle\psi_i|$).

Consider the arbitrary function

$$|f\rangle = \sum_i c_i |\psi_i\rangle \qquad (4.74)$$

By definition we know that

$$c_m = \langle\psi_m|f\rangle \qquad (4.75)$$

so, explicitly

$$|f\rangle = \sum_i \langle\psi_i|f\rangle|\psi_i\rangle \qquad (4.76)$$

Now consider $\hat{I}|f\rangle$ where we use the definition of $\hat{I}$ we proposed in Eq. (4.73)

$$\hat{I}|f\rangle = \sum_i |\psi_i\rangle\langle\psi_i|f\rangle \qquad (4.77)$$

But $\langle\psi_i|f\rangle$ is simply a number, and so can be moved in the product. Hence

$$\hat{I}|f\rangle = \sum_i \langle\psi_i|f\rangle|\psi_i\rangle \qquad (4.78)$$

and hence, using Eq. (4.76), we have proved that, for arbitrary $|f\rangle$,

$$\hat{I}|f\rangle = |f\rangle \qquad (4.79)$$

and so our proposed representation of the identity operator, Eq.(4.73), is correct.

Identity operator - 3

Why prove Eq.(4.73) ($\hat{I} = \sum_i |\psi_i\rangle\langle\psi_i|$)?

The statement Eq. (4.73)

$$\hat{I} = \sum_i |\psi_i\rangle\langle\psi_i|$$

is trivial if $|\psi_i\rangle$ is the basis being used to represent the space.

Then

$$|\psi_1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix}, \; |\psi_2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix}, \; |\psi_3\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{bmatrix}, \; \cdots \qquad (4.80)$$

so that

$$|\psi_1\rangle\langle\psi_1| = \begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \; |\psi_2\rangle\langle\psi_2| = \begin{bmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \; |\psi_3\rangle\langle\psi_3| = \begin{bmatrix} 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \qquad (4.81)$$

and obviously $\sum_i |\psi_i\rangle\langle\psi_i|$ gives the identity matrix of Eq.(4.73).

Identity operator - 4

Note, however,

the statement Eq. (4.73) is true

even if the basis being used to represent the space is not $\left|\psi_i\right\rangle$. In that case,

$\left|\psi_i\right\rangle$ *is not a simple vector with the* i*th element equal to one and all other elements zero,*

and the matrix $\left|\psi_i\right\rangle\left\langle\psi_i\right|$ in general has possibly all of its elements non-zero.

Nonetheless, the sum of all of those matrices $\left|\psi_i\right\rangle\left\langle\psi_i\right|$ ***still leads to the identity matrix of Eq.(4.72).***

The important point is that we can choose **any** ***convenient complete basis to write the identity operator in the form Eq. (4.73).***

Identity operator - 5

We can understand why the identity operator can be written this way for an arbitrary complete set of basis vectors (functions) $|\psi_i\rangle$.

In an expression

$$|f\rangle = \sum_i |\psi_i\rangle\langle\psi_i|f\rangle \tag{4.82}$$

the bra $\langle\psi_i|$ projects out the component, c_i, of the vector (function) $|f\rangle$ of interest,

and multiplying by the ket $|\psi_i\rangle$ adds into the resulting vector (function) on the left an amount c_i of the vector (function) $|\psi_i\rangle$.

Adding up all such components in the sum merely reconstructs the entire vector (function) $|f\rangle$.

Identity operator and coordinate axes

An important point is that

the vector is the same vector regardless of which set of coordinate axes we choose to use to represent it.

If we think about the identity operator in terms of vectors,

then the identity operator is that operator that leaves any vector unchanged.

Looked at that way,

it is obvious that the identity operator is independent of what coordinate axes we use in the space.

Our algebra here is merely showing that we have set up the rules for the vector space so that we get the behavior we wanted to have.

Trace of an operator - 1

The identity matrix can be very useful in formal proofs.

The tricks are,

first, that we can insert it, expressed on any convenient basis, within other expressions, and,

second, we can often rearrange expressions to find identity operators buried within them that we can then eliminate to simplify the expressions.

A good illustration of this is the proof that the sum of the diagonal elements of an operator is independent of the basis on which we represent the operator;

that sum of diagonal elements is called the "trace" of the operator, and is written as $Tr(\hat{A})$**.**

The trace itself can be quite useful in various situations related to operators, and some of these will occur below.

Trace of an operator - 2

Let us consider the sum, S, of the diagonal elements of an operator $\hat{A}$, on some complete orthonormal basis $|\psi_i\rangle$, i.e.,

$$S = \sum_i \langle \psi_i | \hat{A} | \psi_i \rangle \tag{4.83}$$

Now let us suppose we have some other complete orthonormal basis, $|\phi_m\rangle$.

We can therefore write the identity operator as

$$\hat{I} = \sum_m |\phi_m\rangle\langle\phi_m| \tag{4.84}$$

We can insert an identity operator just before the operator $\hat{A}$ in Eq. (4.83),

which makes no difference to the result, since $\hat{I}\hat{A} = \hat{A}$,

so we have

$$S = \sum_i \langle \psi_i | \hat{I}\hat{A} | \psi_i \rangle = \sum_i \langle \psi_i | \left(\sum_m |\phi_m\rangle\langle\phi_m| \right) \hat{A} | \psi_i \rangle \tag{4.85}$$

Trace of an operator - 3

Rearranging $S = \sum_i \langle \psi_i | \hat{I}\hat{A} | \psi_i \rangle = \sum_i \langle \psi_i | \left(\sum_m | \phi_m \rangle \langle \phi_m | \right) \hat{A} | \psi_i \rangle$ **gives**

$$\begin{aligned} S &= \sum_m \sum_i \langle \psi_i | \phi_m \rangle \langle \phi_m | \hat{A} | \psi_i \rangle \\ &= \sum_m \sum_i \langle \phi_m | \hat{A} | \psi_i \rangle \langle \psi_i | \phi_m \rangle \qquad (4.86) \\ &= \sum_m \langle \phi_m | \hat{A} \left(\sum_i | \psi_i \rangle \langle \psi_i | \right) | \phi_m \rangle \end{aligned}$$

where, between the first and second lines, we have used the fact that $\langle \psi_i | \phi_m \rangle$ and $\langle \phi_m | \hat{A} | \psi_i \rangle$ are simply numbers and so can be swapped.

Now we see that we have another identity operator inside an expression in the bottom line, i.e.,

$$\hat{I} = \sum_i | \psi_i \rangle \langle \psi_i | \qquad (4.87)$$

and so, since $\hat{A}\hat{I} = \hat{A}$, we can remove this operator from the expression, leaving

$$S = \sum_m \langle \phi_m | \hat{A} | \phi_m \rangle \qquad (4.88)$$

Trace of an operator - 4

Hence, from Eqs. (4.83) ($S = \sum_i \langle \psi_i | \hat{A} | \psi_i \rangle$) and (4.88) ($S = \sum_m \langle \phi_m | \hat{A} | \phi_m \rangle$), we have proved that the sum of the diagonal elements,

i.e., the trace, of an operator is independent of the basis used to represent the operator,

which is why the trace can be a useful property of an operator.

Inverse operator

If we consider an operator $\hat{A}$ operating on an arbitrary function $|f\rangle$,

then the inverse operator,

if it exists,

is that operator $\hat{A}^{-1}$ such that

$$|f\rangle = \hat{A}^{-1}\hat{A}|f\rangle \qquad (4.89)$$

Since the function $|f\rangle$ is arbitrary, we can therefore identify

$$\hat{A}^{-1}\hat{A} = \hat{I} \qquad (4.90)$$

The operator $\hat{A}$ takes an "input" vector and, in general, stretches it and reorients it.

The inverse operator does exactly the opposite, restoring the original input vector.

Since the operator can be represented by a matrix,

finding the inverse of the operator reduces to finding the inverse of a matrix.

Existence of inverse operators

Just as in matrix theory, not all operators have inverses.

For example, the projection operator

$$\hat{P} = |f\rangle\langle f| \tag{4.91}$$

in general has no inverse,

because it projects all input vectors onto only one axis in the space,

the one corresponding to the vector $|f\rangle$*.*

This is a "many to one" mapping in vector space,

and there is no way of knowing anything about the specific input vector other than its component along this axis.

Hence in general we cannot go backwards to the original input vector starting from this information alone.

Unitary operators

A unitary operator, $\hat{U}$, is one for which

$$\hat{U}^{-1} = \hat{U}^{\dagger} \tag{4.92}$$

that is,

its inverse is its Hermitian transpose (or adjoint).

The Hermitian transpose of a matrix is formed by reflecting the matrix about its diagonal, and taking the complex conjugate.

$$\begin{bmatrix} u_{11} & u_{12} & u_{13} & \cdots \\ u_{21} & u_{22} & u_{23} & \cdots \\ u_{31} & u_{32} & u_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}^{\dagger} = \begin{bmatrix} u_{11}^{*} & u_{21}^{*} & u_{31}^{*} & \cdots \\ u_{12}^{*} & u_{22}^{*} & u_{32}^{*} & \cdots \\ u_{13}^{*} & u_{23}^{*} & u_{33}^{*} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{4.93}$$

Conservation of length and inner product under unitary transformations - 1

When a unitary operator operates on a vector,

it does not change the length of the vector.

This is consistent with the “unit” part of the term “unitary”.

In fact, more generally, when we operate on two vectors with the same unitary operator,

it does not change their inner product

the conservation of length follows from this as a special case, as we will show.

Conservation of length and inner product under unitary transformations - 2

Consider the unitary operator $\hat{U}$ and the two vectors $\left|f_{old}\right\rangle$ and $\left|g_{old}\right\rangle$.

We form two new vectors by operating with $\hat{U}$,

$$\left|f_{new}\right\rangle = \hat{U}\left|f_{old}\right\rangle \tag{4.94}$$

and

$$\left|g_{new}\right\rangle = \hat{U}\left|g_{old}\right\rangle \tag{4.95}$$

In conventional matrix (or matrix-vector) multiplication with real matrix elements, we know that

$$(AB)^T = B^T A^T \tag{4.96}$$

where the superscript "T" indicates the transpose (reflection about the diagonal).

In matrix or operator multiplication with complex elements, we obtain

$$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{4.97}$$

and, explicitly, for matrix-vector multiplication

$$\left(\hat{A}|h\rangle\right)^\dagger = \langle h|\hat{A}^\dagger \tag{4.98}$$

Conservation of length and inner product under unitary transformations - 3

Hence, with our definitions $\left|f_{new}\right\rangle = \hat{U}\left|f_{old}\right\rangle$ and $\left|g_{new}\right\rangle = \hat{U}\left|g_{old}\right\rangle$ from above

$$\begin{aligned}\left\langle g_{new}\middle|f_{new}\right\rangle &= \left\langle g_{old}\middle|\hat{U}^\dagger\hat{U}\middle|f_{old}\right\rangle \\ &= \left\langle g_{old}\middle|\hat{U}^{-1}\hat{U}\middle|f_{old}\right\rangle \\ &= \left\langle g_{old}\middle|\hat{I}\middle|f_{old}\right\rangle \\ &= \left\langle g_{old}\middle|f_{old}\right\rangle\end{aligned} \quad (4.99)$$

so, as promised,

the inner product is not changed if both vectors are transformed this way.

In particular,

$$\left\langle f_{new}\middle|f_{new}\right\rangle = \left\langle f_{old}\middle|f_{old}\right\rangle \quad (4.100)$$

i.e., the length of a vector is not changed by a unitary operator.

Functions and Operators – 4

Reading – Sections 4.10 “Use of unitary operators to change basis sets for representing vectors” - 4.13

Specific types of linear operators

- **Identity operator**
- **Inverse operators**
- **Unitary operators**
  - *conservation of length and inner product under unitary transformations*
  - *use of unitary operators to change basis sets for representing vectors*
  - *use of unitary operators for changing the representation of operators*
  - *unitary operators that change the state vector*
- **Hermitian operators**
- **Matrix form of derivative operators**
- **Matrix corresponding to multiplying by a function**

Unitary operators to change representations of vectors - 1

One major use of unitary operators is to change basis sets

or, equivalently, representations or coordinate axes.

Suppose that we have a vector (function) $\left|f_{old}\right\rangle$ that is represented,

when we express it as an expansion on the functions $\left|\psi_n\right\rangle$,

as the mathematical column vector

$$\left|f_{old}\right\rangle = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \tag{4.101}$$

These numbers c_1, c_2, c_3, … are the projections of $\left|f_{old}\right\rangle$

on the orthogonal coordinate axes in the vector space labeled with $\left|\psi_1\right\rangle$, $\left|\psi_2\right\rangle$, $\left|\psi_3\right\rangle$ … .

Unitary operators to change representations of vectors - 2

Suppose we want to represent this vector on a new set of orthogonal axes,

which we will label $|\phi_1\rangle$, $|\phi_2\rangle$, $|\phi_3\rangle$, … .

Changing the axes,

which is equivalent to changing the basis set of functions,

does not, of course, change the vector we are representing,

but it does change the column of numbers used to represent the vector.

For example, suppose the original vector was actually the first basis vector in the old basis, $|\psi_1\rangle$.

Then in this new representation,

the elements in the column of numbers would be the projections of this vector on the various new coordinate axes,

each of which is simply $\langle\phi_m|\psi_1\rangle$,

i.e., under this coordinate transformation (or change of basis),

$$\begin{bmatrix}1\\0\\0\\\vdots\end{bmatrix} \Rightarrow \begin{bmatrix}\langle\phi_1|\psi_1\rangle\\\langle\phi_2|\psi_1\rangle\\\langle\phi_3|\psi_1\rangle\\\vdots\end{bmatrix} \tag{4.102}$$

Unitary operators to change representations of vectors - 3

We could write out similar transformations for each basis vectors $|\psi_n\rangle$.

We get the correct transformation if we define a matrix

$$\hat{U} = \begin{bmatrix} u_{11} & u_{12} & u_{13} & \cdots \\ u_{21} & u_{22} & u_{23} & \cdots \\ u_{31} & u_{32} & u_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \qquad (4.103)$$

where

$$u_{ij} = \left\langle \phi_i \middle| \psi_j \right\rangle \qquad (4.104)$$

and define our new column of numbers $|f_{new}\rangle$ as

$$\left| f_{new} \right\rangle = \hat{U} \left| f_{old} \right\rangle \qquad (4.105)$$

Unitary operators to change representations of vectors - 4

Note incidentally that $\left| f_{old} \right\rangle$ and $\left| f_{new} \right\rangle$ are the same vector in the vector space;

- ***it is only the representation (the coordinate axes), and, consequently***
  - **the column of numbers,**
- ***that have changed,***
  - **not the vector itself.**

Suppose we have a sculpture of an arrow sticking at an angle up out of the floor.

- ***We could write down a representation of the arrow's length and direction***
  - **e.g., the tip of the arrow is 2.5 m above the floor, leaning 50 cm to the left and 20 cm back toward us**
- ***If we move to another position,***
  - **the representation we write down changes,**
    - *though the arrow remains the same*

Unitary operators to change representations of vectors - 5

Now we can prove that $\hat{U}$ is unitary.

Writing the matrix multiplication in its sum form, we have

$$\begin{aligned}\left(\hat{U}^{\dagger}\hat{U}\right)_{ij} &= \sum_m u_{mi}^{*} u_{mj} = \sum_m \left\langle \phi_m \middle| \psi_i \right\rangle^{*} \left\langle \phi_m \middle| \psi_j \right\rangle \\ &= \sum_m \left\langle \psi_i \middle| \phi_m \right\rangle \left\langle \phi_m \middle| \psi_j \right\rangle = \left\langle \psi_i \middle| \left(\sum_m \left| \phi_m \right\rangle \left\langle \phi_m \right| \right) \middle| \psi_j \right\rangle \\ &= \left\langle \psi_i \middle| \hat{I} \middle| \psi_j \right\rangle = \left\langle \psi_i \middle| \psi_j \right\rangle \\ &= \delta_{ij}\end{aligned} \tag{4.106}$$

so

$$\hat{U}^{\dagger}\hat{U} = \hat{I} \tag{4.107}$$

and hence $\hat{U}$ is unitary since its Hermitian transpose is therefore its inverse (Eq. (4.92)).

Hence any change in basis can be implemented with a unitary operator.

We can also say that

any such change in representation to a new orthonormal basis is a unitary transform.

Note also, incidentally, that

$$\hat{U}\hat{U}^{\dagger} = \left(\hat{U}^{\dagger}\hat{U}\right)^{\dagger} = \hat{I}^{\dagger} = \hat{I} \tag{4.108}$$

Unitary operators to change representations of vectors - 6

Given that we concluded above that a unitary transform did not change any inner product,

we can now also conclude that a transformation to a new orthonormal basis does not change any inner product.

Again, this is as we would have expected from thinking about the inner product being like a vector dot product of two geometrical vectors;

of course such an inner product does not depend on the coordinate axes,

only on the directions and lengths of the vectors themselves.

Unitary operators to change representations of operators

What happens to the matrix of an operator when we change the basis?

Consider an expression such as

$$\begin{aligned}\left\langle g_{new}\middle|\hat{A}_{new}\middle|f_{new}\right\rangle &= \left(\left|g_{new}\right\rangle\right)^{\dagger}\hat{A}_{new}\left|f_{new}\right\rangle \\ &= \left(\hat{U}\left|g_{old}\right\rangle\right)^{\dagger}\hat{A}_{new}\left(\hat{U}\left|f_{old}\right\rangle\right) = \left\langle g_{old}\middle|\hat{U}^{\dagger}\hat{A}_{new}\hat{U}\middle|f_{old}\right\rangle\end{aligned} \quad (4.109)$$

where the vectors $\left|f\right\rangle$ and $\left|g\right\rangle$ are arbitrary.

Note here also that the subscripts new ***and*** old ***refer to the representations, not the vectors (or operators).***

The actual vectors and operators are not changed by the change of representation,

only the sets of numbers that represent them are changed.

Hence this result should not be changed by changing the representation.

So we believe that

$$\left\langle g_{new}\middle|\hat{A}_{new}\middle|f_{new}\right\rangle = \left\langle g_{old}\middle|\hat{A}_{old}\middle|f_{old}\right\rangle \quad (4.110)$$

Consequently, we can deduce that

$$\hat{A}_{old} = \hat{U}^{\dagger}\hat{A}_{new}\hat{U} \quad (4.111)$$

or, equivalently $$\hat{U}\hat{A}_{old}\hat{U}^{\dagger} = \left(\hat{U}\hat{U}^{\dagger}\right)\hat{A}_{new}\left(\hat{U}\hat{U}^{\dagger}\right) = \hat{A}_{new} \quad (4.112)$$

Unitary operators that change the state vector

Operators that change the quantum mechanical state are also unitary.

Such operators are not changing the basis set –

they are actually changing the state of the quantum mechanical system,

and are changing the vector's orientation in vector space.

Why such operators arise in quantum mechanics is simple.

If we are working, for example, with a single particle,

then the sum of all the occupation probabilities of all possible states is unity.

I.e., if the quantum mechanical state $|\psi\rangle$ is expanded on the basis $|\psi_n\rangle$,

$$|\psi\rangle = \sum_n a_n |\psi_n\rangle \tag{4.113}$$

then $\sum_n |a_n|^2 = 1$, and if the particle is to be conserved

then this sum is retained as the quantum mechanical system evolves in time.

But this sum is just the square of the length of the vector $|\psi\rangle$.

Hence a unitary operator, which conserves length,

is an appropriate operator for describing changes that conserve the particle.

For example, the time-evolution operator for a system where the Hamiltonian does not change in time, $\exp\left(-i\hat{H}t/\hbar\right)$*, can be shown to be unitary.*

Hermitian operators - 1

A Hermitian operator is one that is its own Hermitian adjoint, i.e.,

$$\hat{M}^{\dagger} = \hat{M} \tag{4.114}$$

We can also equivalently say that a Hermitian operator is self-adjoint.

Expressed in matrix terms, we have, with

$$\hat{M} = \begin{bmatrix} M_{11} & M_{12} & M_{13} & \cdots \\ M_{21} & M_{22} & M_{23} & \cdots \\ M_{31} & M_{32} & M_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{4.115}$$

that

$$\hat{M}^{\dagger} = \begin{bmatrix} M_{11}^{*} & M_{21}^{*} & M_{31}^{*} & \cdots \\ M_{12}^{*} & M_{22}^{*} & M_{31}^{*} & \cdots \\ M_{13}^{*} & M_{23}^{*} & M_{33}^{*} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{4.116}$$

so the Hermiticity condition, Eq. (4.114), implies

$$M_{ij} = M_{ji}^{*} \tag{4.117}$$

for all i and j, from which we can also conclude that the diagonal elements of a Hermitian operator must be real.

Hermitian operators - 2

To understand what the Hermiticity statement (4.114) means for actions on functions in general,

we can examine the result

$$\langle g|\hat{M}|f\rangle.$$

We can consider the Hermitian adjoint of this result,

$$\left(\langle g|\hat{M}|f\rangle\right)^{\dagger},$$

using the rules for the adjoints of the products of matrices

(and vectors as special cases of matrices),

specifically the relation Eq. (4.97) ($\left(\hat{A}\hat{B}\right)^{\dagger}=\hat{B}^{\dagger}\hat{A}^{\dagger}$).

Of course, in the specific case of the result $\langle g|\hat{M}|f\rangle$,

the resulting matrix is a “one-by-one” matrix that can also be considered as simply a number, and so

$$\left(\langle g|\hat{M}|f\rangle\right)^{\dagger}\equiv\left(\langle g|\hat{M}|f\rangle\right)^{*} \qquad (4.118)$$

Hermitian operators - 3

Hence we have, using the rule for the adjoint of products of matrices, for any functions *f* and *g*,

$$\begin{aligned}\left(\langle g|\hat{M}|f\rangle\right)^* &\equiv \left(\langle g|\hat{M}|f\rangle\right)^\dagger = \left[\langle g|\left(\hat{M}|f\rangle\right)\right]^\dagger \\ &= \left(\hat{M}|f\rangle\right)^\dagger \left(\langle g|\right)^\dagger = \left(|f\rangle\right)^\dagger \hat{M}^\dagger \left(\langle g|\right)^\dagger \\ &= \langle f|\hat{M}^\dagger|g\rangle\end{aligned} \tag{4.119}$$

Now we use the Hermiticity of $\hat{M}$, $\hat{M}^\dagger = \hat{M}$ (Eq. (4.114)), and obtain

$$\langle f|\hat{M}|g\rangle = \left(\langle g|\hat{M}|f\rangle\right)^* \tag{4.120}$$

which could be regarded as the most complete and general way of stating the Hermiticity of an operator $\hat{M}$.

Note this is true even if $|f\rangle$ and $|g\rangle$ are not orthogonal.

The statement for the matrix elements, Eq. (4.117), is just a special case.

Hermitian operators - 4

In integral form, for functions $f(x)$ and $g(x)$,

the statement Eq. (4.120) of the Hermiticity of $\hat{M}$ can be written

$$\int g^*(x)\hat{M}f(x)\,dx = \left[\int f^*(x)\hat{M}g(x)\,dx\right]^* \qquad (4.121)$$

We can rewrite the right hand side using the property

$$(ab)^* = a^*b^*$$

of complex conjugates to obtain

$$\int g^*(x)\hat{M}f(x)\,dx = \int f(x)\left\{\hat{M}g(x)\right\}^* dx \qquad (4.122)$$

and a simple rearrangement leads to

$$\int g^*(x)\hat{M}f(x)\,dx = \int \left\{\hat{M}g(x)\right\}^* f(x)\,dx \qquad (4.123)$$

Authors who prefer to introduce Hermitian operators in the integral form often use the form Eq. (4.123) to define the operator $\hat{M}$ as Hermitian.

The forms Eqs. (4.114), $\hat{M}^\dagger = \hat{M}$,

(4.117), $M_{ij} = M_{ji}^*$,

(4.120), $\langle f|\hat{M}|g\rangle = \left(\langle g|\hat{M}|f\rangle\right)^*$,

and, for functions of a continuous variable, (4.123), can all be regarded as equivalent statements of the Hermiticity of the operator $\hat{M}$.

Bra-ket and integral notations

Note that the bra-ket notation is more elegant than the integral notation in one important way.

In the bra-ket notation,

the operator can also be considered to operate to the left –

$\langle g|\hat{A}$ *is just as meaningful a statement as the statement* $\hat{A}|f\rangle$*,*

and it does not matter how we group the multiplications in the bra-ket notation, i.e.,

$$\langle g|\hat{A}|f\rangle \equiv \left(\langle g|\hat{A}\right)|f\rangle \equiv \langle g|\left(\hat{A}|f\rangle\right) \qquad (4.124)$$

because of the associativity of matrix multiplication.

Conventional operators in the notation used in integration,

such as a differential operator, d/dx,

do not have any meaning when they operate "to the left",

hence we end up with the somewhat clumsy form Eq. (4.123)

$$\int g^*(x)\hat{M}f(x)\,dx = \int \left\{\hat{M}g(x)\right\}^* f(x)\,dx$$

for Hermiticity in this notation.

Properties of Hermitian operators

The eigenvalues and eigenvectors of Hermitian operators have some special properties, some of which are very easily proved.

The important properties are

Reality of eigenvalues

Orthogonality of eigenfunctions with different eigenvalues

Completeness of the set of eigenfunctions

Reality of eigenvalues

Suppose $|\psi_n\rangle$ is a normalized eigenvector of the Hermitian operator $\hat{M}$ with eigenvalue μ_n.

Then, by definition,

$$\hat{M}|\psi_n\rangle = \mu_n|\psi_n\rangle \tag{4.125}$$

Therefore

$$\langle\psi_n|\hat{M}|\psi_n\rangle = \mu_n\langle\psi_n|\psi_n\rangle = \mu_n \tag{4.126}$$

But from the Hermiticity of $\hat{M}$ we know

$$\langle\psi_n|\hat{M}|\psi_n\rangle = \left(\langle\psi_n|\hat{M}|\psi_n\rangle\right)^* = \mu_n^* \tag{4.127}$$

and hence μ_n must be real.

This suggests that such an operator may be useful for representing a quantity that is real, such as a measurable quantity.

Orthogonality of eigenfunctions for different eigenvalues

The eigenfunctions of a Hermitian operator corresponding to different eigenvalues are orthogonal, as can easily be proved in bra-ket notation.

Trivially,

$$0 = \langle\psi_m|\hat{M}|\psi_n\rangle - \langle\psi_m|\hat{M}|\psi_n\rangle \tag{4.128}$$

So, by associativity and the rule Eq. (4.97) (**$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger$**)

$$0 = \left(\langle\psi_m|\hat{M}\right)|\psi_n\rangle - \langle\psi_m|\left(\hat{M}|\psi_n\rangle\right) = \left(\hat{M}^\dagger|\psi_m\rangle\right)^\dagger|\psi_n\rangle - \langle\psi_m|\left(\hat{M}|\psi_n\rangle\right) \tag{4.129}$$

Now, using

the Hermiticity of $\hat{M}$ ***(***$\hat{M} = \hat{M}^\dagger$***),***

the Hermitian adjoint of a complex number is its complex conjugate

and the fact that the eigenvalues of a Hermitian operator are real anyway,

we have

$$0 = \mu_m\langle\psi_m|\psi_n\rangle - \mu_n\langle\psi_m|\psi_n\rangle = (\mu_m - \mu_n)\langle\psi_m|\psi_n\rangle \tag{4.130}$$

But, by assumption, μ_m **and** μ_n **are different,**

and hence

$$\langle\psi_m|\psi_n\rangle = 0 \tag{4.131}$$

and we have proved that the eigenfunctions associated with different eigenvalues of a Hermitian operator are orthogonal.

Degeneracy

It is quite possible

> *and actually common in problems that are highly symmetric in some way or another*

to have more than one eigenfunction associated with a given eigenvalue.

This situation is known as *degeneracy*.

It is provable that

> *the number of such degenerate solutions for a given finite eigenvalue is itself finite.*

Completeness of sets of eigenfunctions

A very important result for compact Hermitian operators is that,

provided the operator is bounded,

that is, it gives a resulting vector of finite length when it operates on any finite input vector,

the set of eigenfunctions is complete,

i.e., it spans the space on which the operator is compact.

The proof of this result is understandable with effort,

but requires setting up a mathematical framework for functional analysis that is beyond what we can justify here.

This result means in practice that we can use the eigenfunctions of any bounded Hermitian operator to expand functions.

This greatly increases the available basis sets beyond the simple spatial or Fourier transform sets.

For many problems, it means we can greatly simplify the description of them.

Hermitian operators and quantum mechanics

Bounded Hermitian operators have the attractive properties of having

real eigenvalues,

orthogonal eigenfunctions, and

complete sets of eigenfunctions.

As far as we know,

the physically measurable quantities in quantum mechanics can be represented by bounded Hermitian operators.

Some state this as an axiom of quantum mechanics.

We have already seen

momentum and

energy (Hamiltonian) operators.

We will encounter several other such operators corresponding to other physical quantities as we get further into quantum mechanics

with the same algebra and properties as discussed here, and

we hence have a very general, sound, and useful mathematical methodology for discussing quantum mechanics.

Matrix form of derivative operators - 1

So far, we have not related matrices to the differential operators,

such as d^2/dx^2 ***or*** d/dx***,***

that we have used in actual quantum mechanics,

as in the Schrödinger equation or the momentum operator,

and it may not be immediately obvious that those can be described as matrices.

It is usually more convenient to handle such operators using the integral form of inner products and matrix elements.

We merely wish to show matrix forms for conceptual completeness.

Matrix form of derivative operators - 2

If we return to our original discussion of functions as vectors,

we can postulate that an appropriate form for the differential operator d/dx ***would be***

$$\frac{d}{dx} \equiv \begin{bmatrix} \ddots & & & & & \\ \cdots & -\frac{1}{2\delta x} & 0 & \frac{1}{2\delta x} & 0 & \cdots \\ \cdots & 0 & -\frac{1}{2\delta x} & 0 & \frac{1}{2\delta x} & \cdots \\ & & & & \ddots & \end{bmatrix} \tag{4.132}$$

where as usual we are presuming we can take the limit as $\delta x \to 0$**.**

Matrix form of derivative operators - 3

If we were to multiply the column vector whose elements are the values of the function $f(x)$ at a set of values spaced by an amount δx, then we would obtain

$$
\begin{bmatrix}
\ddots & & & & & \\
\cdots & -\frac{1}{2\delta x} & 0 & \frac{1}{2\delta x} & 0 & \cdots \\
\cdots & 0 & -\frac{1}{2\delta x} & 0 & \frac{1}{2\delta x} & \cdots \\
 & & & & & \ddots
\end{bmatrix}
\begin{bmatrix}
\vdots \\
f(x_i-\delta x) \\
f(x_i) \\
f(x_i+\delta x) \\
f(x_i+2\delta x) \\
\vdots
\end{bmatrix}
$$

$$
=\begin{bmatrix}
\vdots \\
\dfrac{f(x_i+\delta_x)-f(x_i-\delta x)}{2\delta x} \\
\dfrac{f(x_i+2\delta_x)-f(x_i)}{2\delta x} \\
\vdots
\end{bmatrix}
=\begin{bmatrix}
\vdots \\
\left.\dfrac{df}{dx}\right|_{x_i} \\
\left.\dfrac{df}{dx}\right|_{x_i+\delta x} \\
\vdots
\end{bmatrix}
\qquad (4.133)
$$

where again we understand that we are taking the limit as $\delta x \to 0$.

Hence we have a way of representing a derivative as a matrix.

Matrix form of derivative operators - 4

Note that we have postulated a form that has a symmetry about the matrix diagonal.

In this case the matrix is antisymmetric in reflection about the diagonal.

This matrix is not, however, Hermitian,

which reflects the fact that the operator d/dx *is not a Hermitian operator,*

as can be verified from any of the definitions above of Hermiticity.

We can see from this matrix representation, by contrast, that

the operator id/dx *(or, for that matter,* $-id/dx$*)*

would be Hermitian,

and hence that the momentum operator,

such as its x *component* $p_x = -i\hbar d/dx$

would be Hermitian.

It is left as an exercise for the reader to show how the second derivative, for example, $d^2/dx^2 \equiv \lim_{\delta x \to 0}\left[\left(f\left(x+\delta x\right)-2f\left(x\right)+f(x+\delta x)\right)/(\delta x)^2\right]$ *can be represented as a matrix, and that the corresponding matrix is Hermitian.*

Matrix corresponding to multiplying by a function

We can formally "operate" on the function $f(x)$ by multiplying it by the function $V(x)$ to generate another function $g(x) = V(x)f(x)$.

Since the function $V(x)$ is performing the role of an operator (even though it is a particularly simple form of operator),

we can if we wish represent it as a matrix,

and in that case, it is a simple diagonal matrix whose elements are the values of the function at each of the different points.

If the function is real,

the corresponding matrix is Hermitian

(though it is not if the function is complex).

Hence, one can conclude that the Hamiltonian as used in Schrödinger's equation,

being the sum of two Hermitian matrices,

e.g., in the one dimensional case, one corresponding to the Hermitian operator $\left(-\hbar^2/2m\right)\partial^2/\partial x^2$ and the other corresponding to the "operator" $V(x)$

is Hermitian.

Operators and quantum mechanics - 1

Reading – Sections 5.1 – 5.2

Commutation of operators

Commuting operators and sets of eigenfunctions

General form of the uncertainty principle

Position-momentum uncertainty principle

Energy time uncertainty principle

Operators and quantum mechanics

A postulate of quantum mechanics

all measurable quantities can be associated with a Hermitian operator.

e.g.,

energy

momentum

also will see

position

"orbital" angular momentum

spin angular momentum

Now we examine some of the important properties of operators associated with measurable quantities.

Note: some operators that are useful in quantum mechanics are not Hermitian;

for example,

non-Hermitian creation and annihilation operators that are used extensively in quantum optics.

Commutation of operators - 1

A very important property of Hermitian operators representing physical variables is whether they commute,

i.e., whether

$$\hat{A}\hat{B} = \hat{B}\hat{A} \tag{5.1}$$

where $\hat{A}$ and $\hat{B}$ are two Hermitian operators.

Remember that,

because these linear operators obey the same algebra as matrices,

in general operators do not commute.

For quantum mechanics, we formally define an entity

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{5.2}$$

This entity is called the commutator.

An equivalent statement to Eq. (5.1) is then

$$\left[\hat{A}, \hat{B}\right] = 0 \tag{5.3}$$

Commutation of operators - 2

If the operators do not commute,

then Eq. (5.3) ($\left[\hat{A},\hat{B}\right]=0$) does not hold,

and in general we can choose to write

$$\left[\hat{A},\hat{B}\right]=i\hat{C} \tag{5.4}$$

where $\hat{C}$ is sometimes referred to as

the remainder of commutation or

the commutation rest.

Commuting operators and sets of eigenfunctions

Operators that commute share the same set of eigenfunctions, and operators that share the same set of eigenfunctions commute.

We will now prove both of these statements.

Operators that commute share the same set of eigenfunctions

Suppose that operators $\hat{A}$ and $\hat{B}$ commute,

and suppose the $|\psi_n\rangle$ are the eigenfunctions of $\hat{A}$ with eigenvalues A_i.

Then

$$\hat{A}\hat{B}|\psi_i\rangle = \hat{B}\hat{A}|\psi_i\rangle = \hat{B}A_i|\psi_i\rangle = A_i\hat{B}|\psi_i\rangle \qquad (5.5)$$

i.e.,

$$\hat{A}\left[\hat{B}|\psi_i\rangle\right] = A_i\left[\hat{B}|\psi_i\rangle\right] \qquad (5.6)$$

But this means that the vector $\hat{B}|\psi_i\rangle$ is also the eigenvector $|\psi_i\rangle$ or is proportional to it,

i.e., for some number B_i

$$\hat{B}|\psi_i\rangle = B_i|\psi_i\rangle \qquad (5.7)$$

This kind of relation holds for all the eigenfunctions $|\psi_i\rangle$,

so these eigenfunctions are also the eigenfunctions of the operator $\hat{B}$,

with associated eigenvalues B_i.

Hence we have proved the first statement that operators that commute share the same set of eigenfunctions.

Note that the eigenvalues A_i and B_i are not in general equal to one another.

Operators that share the same set of eigenfunctions commute

Suppose that the Hermitian operators $\hat{A}$ and $\hat{B}$ share the same complete set

of eigenfunctions $|\psi_n\rangle$

with associated sets of eigenvalues A_n and B_n respectively.

Then

$$\hat{A}\hat{B}|\psi_i\rangle = \hat{A}B_i|\psi_i\rangle = A_i B_i|\psi_i\rangle \tag{5.8}$$

and similarly

$$\hat{B}\hat{A}|\psi_i\rangle = \hat{B}A_i|\psi_i\rangle = B_i A_i|\psi_i\rangle \tag{5.9}$$

Hence, for any function $|f\rangle$, which can always be expanded in this complete set of functions

$$|f\rangle = \sum_i c_i|\psi_i\rangle \tag{5.10}$$

we have

$$\hat{A}\hat{B}|f\rangle = \sum_i c_i A_i B_i|\psi_i\rangle = \sum_i c_i B_i A_i|\psi_i\rangle = \hat{B}\hat{A}|f\rangle \tag{5.11}$$

Since we have proved this for an arbitrary function $|f\rangle$, we have proved that the operators commute, hence proving the second statement.

Equivalence of commutation and shared eigenvectors

This equivalence has an important quantum mechanical consequence.

- ***Suppose the commuting operators represent different measurable quantities.***
  - **An example of such a situation is the case of a free particle, i.e., one for which the potential is constant everywhere;**
    - *in this case, the energy operator (Hamiltonian) and the momentum operator have the same eigenfunctions (plane waves)*
      - and the operators for energy and momentum commute with one another.
  - **In this case, if the particle is in an energy eigenstate, then it is also in a momentum eigenstate,**
    - *and the particle in this case can simultaneously have both a well-defined energy and a well-defined momentum.*
      - We can measure both of these quantities and get perfectly well-defined values for both.

What happens when the operators do not commute?

General form of the uncertainty principle - 1

First, we need to set up the concepts of the mean and variance of an expectation value.

Using $\bar{A}$ to denote the mean value of a quantity A,

we have, in the bra-ket notation,

for a measurable quantity associated with the Hermitian operator $\hat{A}$ when the state of the system is $|f\rangle$

$$\bar{A} = \langle A \rangle = \langle f | \hat{A} | f \rangle \qquad (5.12)$$

Let us define a new operator $\Delta\hat{A}$ associated with the difference between the measured value of *A* and its average value, i.e.,

$$\Delta\hat{A} = \hat{A} - \bar{A} \qquad (5.13)$$

Now, $\bar{A}$ is just a real number, and so this operator is also Hermitian.

So that we can examine the variance of the quantity A,

we examine the expectation value of the operator $(\Delta\hat{A})^2$.

Expanding the arbitrary function $|f\rangle$ on the basis of the eigenfunctions, $|\psi_i\rangle$, of $\hat{A}$, i.e., $|f\rangle = \sum_i c_i |\psi_i\rangle$,

we can formally evaluate the expectation value of $(\Delta\hat{A})^2$.

General form of the uncertainty principle - 2

We have

$$\begin{aligned}\left\langle (\Delta\hat{A})^2 \right\rangle &= \left(\sum_i c_i^* \langle \psi_i |\right)\left(\hat{A}-\bar{A}\right)^2\left(\sum_j c_j |\psi_j\rangle\right)\\ &= \left(\sum_i c_i^* \langle \psi_i |\right)\left(\hat{A}-\bar{A}\right)\left(\sum_j c_j \left(A_j-\bar{A}\right)|\psi_j\rangle\right)\\ &= \left(\sum_i c_i^* \langle \psi_i |\right)\left(\sum_j c_j \left(A_j-\bar{A}\right)^2|\psi_j\rangle\right)\\ &= \sum_i |c_i|^2\left(A_i-\bar{A}\right)^2\end{aligned} \qquad (5.14)$$

Because the $|c_i|^2$ are the probabilities that the system is found, on measurement, to be in the state i (or, equivalently, $|\psi_i\rangle$),

and the quantity $\left(A_i-\bar{A}\right)^2$ simply represents the squared deviation of the value of the quantity A from its average value,

then by definition

$$\overline{(\Delta A)^2} \equiv \left\langle \left(\Delta\hat{A}\right)^2 \right\rangle = \left\langle \left(\hat{A}-\bar{A}\right)^2 \right\rangle = \left\langle f \middle| \left(\hat{A}-\bar{A}\right)^2 \middle| f \right\rangle \qquad (5.15)$$

is the mean squared deviation we will find for the quantity A on repeatedly measuring the system prepared in state $|f\rangle$.

General form of the uncertainty principle - 3

In statistical language, this quantity $\overline{(\Delta A)^2}$ is called the variance,

and the square root of the variance, which we can write as

$$\Delta A \equiv \sqrt{\overline{(\Delta A)^2}} \tag{5.16}$$

is the standard deviation.

The standard deviation gives a well-defined measure of the width of a distribution.

We can also consider some other quantity B associated with the Hermitian operator $\hat{B}$,

$$\overline{B} = \langle B \rangle = \langle f | \hat{B} | f \rangle \tag{5.17}$$

and, with similar definitions

$$\overline{(\Delta B)^2} \equiv \left\langle \left(\Delta \hat{B}\right)^2 \right\rangle = \left\langle \left(\hat{B} - \overline{B}\right)^2 \right\rangle = \left\langle f \left| \left(\hat{B} - \overline{B}\right)^2 \right| f \right\rangle \tag{5.18}$$

(5.15) and (5.18), give us ways of calculating the uncertainty in the measurements of the quantities *A* and *B* when the system is in a state $|f\rangle$.

Now we use these in our general proof of the uncertainty principle.

General form of the uncertainty principle - 4

Suppose that the two Hermitian operators $\hat{A}$ and $\hat{B}$ do not commute,

and have a commutation rest $\hat{C}$ as defined in Eq. (5.4) ($\left[\hat{A},\hat{B}\right]=i\hat{C}$) above.

Consider, for some arbitrary real number α, the number

$$G(\alpha)=\left\langle\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)f\middle|\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)f\right\rangle\geq 0 \qquad (5.19)$$

By $\left|\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)f\right\rangle$, we simply mean the vector $\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)|f\rangle$,

but we wrote it in this form to emphasize that it is simply a vector,

and as a result has a positive inner product with itself,

which must be greater than or equal to zero,

as in this equation (5.19).

Now we rearrange (5.19) to obtain

$$\begin{aligned}G(\alpha)&=\langle f|\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)^{\dagger}\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)|f\rangle\\&=\langle f|\left(\alpha\Delta\hat{A}^{\dagger}+i\Delta\hat{B}^{\dagger}\right)\left(\alpha\Delta\hat{A}-i\Delta\hat{B}\right)|f\rangle\end{aligned} \qquad (5.20)$$

General form of the uncertainty principle - 5

By Hermiticity of the operators, we have then

$$\begin{aligned}G(\alpha) &= \left\langle f \middle| \left(\alpha\Delta\hat{A} + i\Delta\hat{B}\right)\left(\alpha\Delta\hat{A} - i\Delta\hat{B}\right) \middle| f \right\rangle \\ &= \left\langle f \middle| \alpha^2\left(\Delta\hat{A}\right)^2 + \left(\Delta\hat{B}\right)^2 - i\alpha\left(\Delta\hat{A}\Delta\hat{B} - \Delta\hat{B}\Delta\hat{A}\right) \middle| f \right\rangle \\ &= \left\langle f \middle| \alpha^2\left(\Delta\hat{A}\right)^2 + \left(\Delta\hat{B}\right)^2 - i\alpha\left[\Delta\hat{A}, \Delta\hat{B}\right] \middle| f \right\rangle \\ &= \left\langle f \middle| \alpha^2\left(\Delta\hat{A}\right)^2 + \left(\Delta\hat{B}\right)^2 + \alpha\hat{C} \middle| f \right\rangle\end{aligned}$$

i.e.

$$\begin{aligned}G(\alpha) &= \alpha^2\overline{(\Delta A)^2} + \overline{(\Delta B)^2} + \alpha\bar{C} \\ &= \overline{(\Delta A)^2}\left[\alpha + \frac{\bar{C}}{2\overline{(\Delta A)^2}}\right]^2 + \overline{(\Delta B)^2} - \frac{\left(\bar{C}\right)^2}{4\overline{(\Delta A)^2}} \geq 0\end{aligned} \qquad (5.21)$$

The last step is a simple though not very obvious rearrangement.

General form of the uncertainty principle - 6

But this relation (5.21) must be true for arbitrary α, and so it is true for the specific value

$$\alpha = -\frac{C}{2\overline{\left(\Delta A\right)^2}} \tag{5.22}$$

which sets the first term equal to zero in (5.21), and so we have

$$\overline{\left(\Delta A\right)^2}\,\overline{\left(\Delta B\right)^2} \geq \frac{\left(\bar{C}\right)^2}{4} \tag{5.23}$$

This is the general form of the uncertainty principle.

It tells us the relative minimum size of the uncertainties in two quantities if we perform a measurement.

Only if the operators associated with the two quantities commute

and hence give $\hat{C}$ *and therefore* $\bar{C} = 0$*)*

can there be no width to the distribution of results for both quantities.

This is a very non-classical result, and is one of the core results of quantum mechanics that differs fundamentally from classical mechanics.

Position-momentum uncertainty principle - 1

We now formally derive the position-momentum relation.

Consider the commutator of $\hat{p}_x$ and x. (We treat the function x as the operator for position.)

To be sure we are taking derivatives correctly, we consider this commutator operating on an arbitrary function $|f\rangle$.

$$\begin{aligned}[\hat{p},x]|f\rangle &= -i\hbar\left(\frac{d}{dx}x - x\frac{d}{dx}\right)|f\rangle \\ &= -i\hbar\left\{\frac{d}{dx}\left(x|f\rangle\right) - x\frac{d}{dx}|f\rangle\right\} \\ &= -i\hbar\left\{|f\rangle + x\frac{d}{dx}|f\rangle - x\frac{d}{dx}|f\rangle\right\} \\ &= -i\hbar|f\rangle\end{aligned} \tag{5.24}$$

So, since $|f\rangle$ is arbitrary, we can write

$$[\hat{p},x] = -i\hbar \tag{5.25}$$

and the commutation rest operator $\hat{C}$ is simply the number

$$\hat{C} = -\hbar \tag{5.26}$$

Position-momentum uncertainty principle - 2

Hence

$$\bar{C} = -\hbar \qquad (5.27)$$

and so, from (5.23) ($\overline{(\Delta A)^2}\,\overline{(\Delta B)^2} \geq \frac{(\bar{C})^2}{4}$) we have

$$(\Delta p_x)^2 (\Delta x)^2 \geq \frac{\hbar^2}{4} \qquad (5.28)$$

or, equivalently,

$$\Delta p_x \Delta x \geq \frac{\hbar}{2} \qquad (5.29)$$

Energy-time uncertainty principle

We can proceed to calculate a similar relation between energy uncertainty and time uncertainty.

The energy operator is the Hamiltonian, $\hat{H}$.

From Schrödinger's time-dependent equation, we know that

$$\hat{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle \tag{5.30}$$

for an arbitrary state $|\psi\rangle$.

If we take the time operator to be just the function t, then we have,

using essentially identical algebra to that used above for the momentum-position uncertainty principle,

$$\left[\hat{H}, t\right] = i\hbar\left(\frac{\partial}{\partial t}t - t\frac{\partial}{\partial t}\right) = i\hbar \tag{5.31}$$

and so, similarly we have

$$(\Delta E)^2(\Delta t)^2 \geq \frac{\hbar^2}{4} \tag{5.32}$$

or

$$\Delta E \Delta t \geq \frac{\hbar}{2} \tag{5.33}$$

which is the energy-time uncertainty principle.

Frequency-time uncertainty principle

We can relate this result mathematically to the frequency-time uncertainty principle that occurs in Fourier analysis.

Noting that $E = \hbar\omega$ ***in quantum mechanics, we have***

$$\Delta\omega\Delta t \geq \frac{1}{2} \tag{5.34}$$

Operators and quantum mechanics – 2

Reading – Sections 5.3 – 5.4 through “Delta function in 3 dimensions”

Transitioning from sums to integrals

Continuous eigenvalues and delta functions

- ***Dirac delta function***

Transitioning from sums to integrals - 1

We need to be able to transition from sums to integrals

we can do this transition when the different states involved are closely spaced in some parameter (e.g., momentum or energy),

and when all the terms in the sum vary smoothly with that parameter.

Imagine we have states,

indexed by an integer q***,***

and for each of those q**,**

some quantity has the value f_q*.*

Hence, summing all of those would give a result

$$S = \sum_q f_q \tag{5.35}$$

It could be that f_q **can also be written as a function of some parameter** u

that itself takes on some value for each q***, i.e.,***

$$f_q \equiv f\left(u_q\right)$$

For example, the different q **states could represent states of different momentum** $\hbar k_q$**,**

in which case u_q *could be the momentum,*

and f_q could be some matrix element that depended on momentum.

Transitioning from sums to integrals - 2

Then we could just as well write, instead of Eq. (5.35) ($S = \sum_q f_q$),

$$S = \sum_q f\left(u_q\right) \qquad (5.36)$$

Suppose now that the u_q and the f_q are very closely spaced as we change q,

and vary relatively smoothly with q.

We suppose that this smooth change of u_q with q is such that we can represent u as some smooth, and differentiable, function of q.

Hence,

$$u_{q+1} - u_q \simeq \frac{du}{dq} \qquad (5.37)$$

i.e., we are approximating $\delta u / \delta q$ by du / dq,

and we note that δq,

the separation in q between adjacent values of q

is just unity, since q is by choice an integer.

Transitioning from sums to integrals - 3

So, if we were to consider some range Δu,

the number of different terms in the sum that would lie within that range is $\Delta u / (du/dq)$,

or defining a "density of states"

$$g(u) = \frac{1}{(du/dq)} \tag{5.38}$$

the number of terms in the sum that lie within Δu is $g(u)\Delta u$.

Hence, instead of summing over q,

we could instead consider a range of values of u,

each separated by an amount Δu,

and write the sum over all those values, i.e.,

$$S = \sum_q f_q \equiv \sum_q f(u_q) \simeq \sum_u f(u) g(u) \Delta u \tag{5.39}$$

Finally, we can formally let Δu become very small, and approximate the sum by an integral, to obtain

$$S \simeq \int f(u) g(u) du \tag{5.40}$$

Transitioning from sums to integrals - 4

The rule, therefore, in going from a sum to an integral,

is to insert the density of states in the integration variable into the integrand, i.e.,

$$\sum_{q} \ldots \to \int \ldots g(u)\,du \tag{5.41}$$

Of course, the limits of the integral must correspond to the limits in the sum.

Continuous eigenvalues and delta functions - 1

At the beginning, we talked about plane waves as solutions of Schrödinger's wave equation in empty space;

such waves cannot be normalized in the way we have discussed so far.

E.g., for a plane wave in the *z* direction, such a wave can be written in the form

$$\psi_k(z) = C_k \exp(ikz) \tag{5.42}$$

Obviously

$$|\psi_k(z)|^2 = |C_k|^2 \tag{5.43}$$

and so, if we integrate $|\psi_k(z)|^2$ *over the infinite range of all possible* z*,*

we will get an infinite result for any finite value of C.

Hence we cannot define a normalization coefficient C ***in the same way we did before.***

Note these are the eigenfunctions of the momentum operator for the z **direction,**

$\hat{p}_z \equiv -i\hbar\, \partial/\partial z$***, with eigenvalues*** $\hbar k$

where the quantity k **can take on any real value.**

Continuous eigenvalues and delta functions - 2

This normalization problem is common when eigenvalues can take on any value within a continuous range, e.g.,

- ***energy eigenvalues of unbounded systems, such as***
  - **the states above the “top” of a finite potential well,**
  - **or states above the ionization energy of a hydrogen atom.**

The situation for energy eigenvalues can be resolved mathematically by

- ***putting the whole system within a large but finite box,***
  - **with infinitely high “walls”,**
    - *and letting the size of the box become arbitrarily large.*
      - That is not always mathematically convenient, however.

Furthermore, for the case of the momentum eigenfunctions,

- ***building a box with potential barriers may make no difference to the momentum eigenfunctions***
  - **the potential does not appear in the momentum eigenfunction equation**
    - *and the solutions to that mathematical problem are still infinite plane waves no matter what potential box we build.*

Solution

- ***introduce the Dirac delta function.***

Dirac delta function

The Dirac delta function, $\delta(x)$, is essentially a very narrow peak, of unit area, centered on $x = 0$.

it is infinitesimally wide, and infinitely high, but still with unit area.

It is not strictly a function because,

in the one place that it really matters ($x = 0$),

its value is not strictly defined.

The formal definition of the delta function is

$$\int_{-\infty}^{\infty} \delta(x)\,dx = 1,\ \delta(x) = 0 \text{ for } x \neq 0 \tag{5.44}$$

Its most important property is that, for any continuous function $f(x)$,

$$\int_{-\infty}^{\infty} f(x)\delta(x)\,dx = f(0) \tag{5.45}$$

This relation, Eq. (5.45), is an operational definition of the delta function, from which we can deduce

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a) \tag{5.46}$$

$\delta(x - a)$ ***is a very sharply peaked function round about $x = a$.***

I.e., it pulls the value $f(a)$ out of the integral.

Representing the delta function

The delta function in practice can be defined as

the limit of just about any symmetrical peaked function in the limit as

the width of the peak goes to zero and

the height goes to infinity,

provided we make sure the function retains unit area as we take the limit.

Sinc function representation

Based on the "sinc" function,

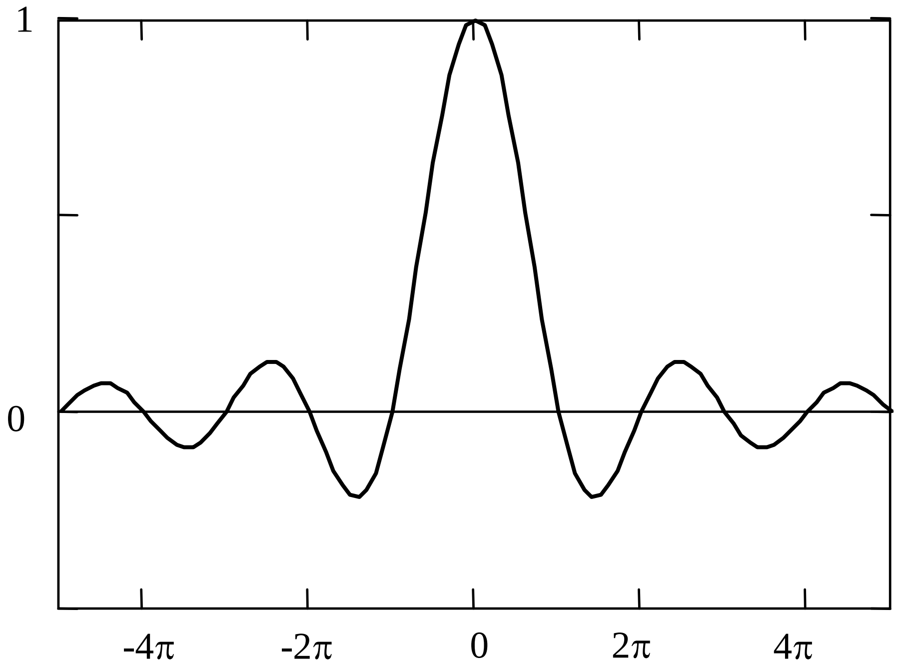
$$\frac{\sin x}{x} \equiv \operatorname{sinc} x \qquad (5.47)$$

we can write

$$\delta(x) = \lim_{L\to\infty} \frac{\sin Lx}{\pi x} \qquad (5.48)$$

where we have used the fact that

$$\int_{-\infty}^{\infty} \frac{\sin x}{x}\, dx = \pi \qquad (5.49)$$



Other representations

Exponential integral representation

A form that is very useful in formal evaluations of integrals is

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ixt)\, dt \qquad (5.50)$$

which can readily be proved using the result Eq. (5.49) ($\int_{-\infty}^{\infty} \frac{\sin x}{x} dx = \pi$) above.

Lorentzian representation

Based on the Lorentzian function,

common as, for example, a line shape in atomic spectra,

with a line width (half width at half maximum) of ε*, we have*

$$\delta(x) = \lim_{\varepsilon \to 0} \frac{1}{\pi\varepsilon} \frac{1}{1 + (x/\varepsilon)^2} \qquad (5.51)$$

where we have used the result

$$\int_{-\infty}^{\infty} \frac{1}{1 + x^2} dx = \pi \qquad (5.52)$$

Other representations

Gaussian representation

Based on the Gaussian function of 1/e half width w, we have

$$\delta(x) = \lim_{w\to 0} \frac{1}{w\sqrt{\pi}} \exp\left(-\frac{x^2}{w^2}\right) \tag{5.53}$$

where we have used the result

$$\int_{-\infty}^{\infty} \exp\left(-x^2\right) dx = \sqrt{\pi} \tag{5.54}$$

Square pulse representation

One of the simplest representations is that of a "square pulse" function that we could define as

$$s(x) = \begin{cases} 0, & x < -\eta/2 \\ 1/\eta, & -\eta/2 \le x \le \eta/2 \\ 0 & x > \eta/2 \end{cases} \tag{5.55}$$

which is a function of width η, and height $1/\eta$, centered at $x = 0$. With this square pulse function, we have

$$\delta(x) = \lim_{\eta\to 0} s(x) \tag{5.56}$$

Relation to Heaviside function

The square pulse function can be written in terms of the Heaviside function

i.e., the "unit step" function

$$\Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \tag{5.57}$$

in terms of which we have the square pulse from above

$$s(x) = \frac{\Theta(x+\eta/2) - \Theta(x-\eta/2)}{\eta} \tag{5.58}$$

In the limit as $\eta \to 0$, this is simply the definition of the derivative of Θ, and so we have also

$$\begin{aligned} \delta(x) &= \lim_{\eta\to 0} \frac{\Theta(x+\eta/2) - \Theta(x-\eta/2)}{\eta} \\ &= \frac{d\Theta(x)}{dx} \end{aligned} \tag{5.59}$$

From this, we can immediately conclude that the Heaviside function is the integral of the delta function, i.e.,

$$\Theta(x) = \int_{-\infty}^{x} \delta(x_1)\, dx_1 \tag{5.60}$$

Basis function representation and closure - 1

Another representation that is particularly general and useful is a representation in terms of any complete set.

Suppose we have a complete orthonormal set of functions, $\phi_i(x)$.

Then we can expand any function in this set, i.e.,

$$f(x) = \sum_n a_n \phi_n(x) \tag{5.61}$$

As usual, we find an expansion coefficient a_m by premultiplying by $\phi_m^*(x)$ and integrating over x, i.e.,

$$\int \phi_m^*(x) f(x) dx = \sum_n a_n \int \phi_m^*(x) \phi_n(x) dx = \sum_n a_n \delta_{nm} = a_m \tag{5.62}$$

Now we can use the far left of (5.62) to substitute for the expansion coefficients in (5.61), i.e., writing

$$a_n = \int \phi_n^*(x') f(x') dx' \tag{5.63}$$

we have

$$f(x) = \sum_n \left(\int \phi_n^*(x') f(x') dx' \right) \phi_n(x) \tag{5.64}$$

Interchanging the order of the integral and the sum, we have

$$f(x) = \int f(x') \left(\sum_n \phi_n^*(x') \phi_n(x) \right) dx' \tag{5.65}$$

Basis function representation and closure - 2

Comparing

Eq. (5.65) ($f(x) = \int f(x') \left(\sum_n \phi_n^*(x') \phi_n(x) \right) dx'$) to

Eq. (5.46) ($\int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a)$),

we see that this sum is performing exactly as the delta function, i.e.,

$$\sum_n \phi_n^*(x') \phi_n(x) = \delta(x'-x) \ \left(= \delta(x-x') \right) \tag{5.66}$$

Hence we have a general representation of the delta function in terms of any complete set. This can be formally useful.

This property, Eq. (5.66), of the set of functions is known as

closure,

and is a consequence of the completeness of the set.

Basis function representation and closure - 3

We can also see that Eq. (5.66)

$$\sum_n \phi_n^*(x')\phi_n(x) = \delta(x'-x) \ \left(= \delta(x-x')\right)$$

is simply the expansion of the delta function in the set $\phi_i(x)$,

with the expansion coefficients simply being the numbers $\phi_n^*(x')$.

Hence, e.g., the expansion of $\delta(x)$ would have expansion coefficients $\phi_n^*(0)$.

We can understand intuitively that,

if a set of functions can represent such an extreme function as a delta function,

then it can represent any other reasonable function,

and so we can understand how this property of closure is related to completeness.

Delta function in 3 dimensions

It is straightforward to construct delta functions in higher dimensions.

The result is merely the product of the various one-dimensional delta functions.

For example, using the short-hand $\delta(\mathbf{r})$ to represent the delta function for three dimensions, we can write

$$\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z) \tag{5.67}$$

Operators and quantum mechanics – 3

Reading – Section 5.4 from "Normalizing to a delta function"

Normalizing to a delta function

Using functions normalized to a delta function

Normalization of plane waves

Relation to Fourier transforms

Periodic boundary conditions

Position eigenfunctions

Change of basis

Normalizing to a delta function - 1

Now that we have introduced the delta function,

we can use it to perform a kind of normalization for these functions that are not normalizable in the previous sense.

e.g., momentum eigenfunctions discussed above (Eq. (5.42) $\psi_k(z) = C_k \exp(ikz)$).

Consider the "orthogonality" integral of two momentum eigenfunctions,

deliberately restricting the range of integration to a large range $\pm L$***, i.e.,***

$$\begin{aligned}\int_{-L}^{L} \psi_{k1}^*(z)\psi_k(z)\,dz &= C_{k1}^* C_k \int_{-L}^{L} \exp(-ik_1 z)\exp(ikz)\,dz \\ &= C_{k1}^* C_k \int_{-L}^{L} \exp\left[i(k-k_1)z\right]dz \\ &= 2C_{k1}^* C_k \frac{\sin\left[(k-k_1)L\right]}{(k-k_1)}\end{aligned} \tag{5.68}$$

Hence, taking the limit as L becomes very large, we have

$$\int_{-\infty}^{\infty} \psi_{k1}^*(z)\psi_k(z)\,dz = 2\pi C_{k1}^* C_k \delta(k-k_1) \tag{5.69}$$

where we have used the sinc function representation, Eq. (5.48) ($\delta(x) = \lim_{L\to\infty} \frac{\sin Lx}{\pi x}$), of the delta function.

Normalizing to a delta function - 2

So, if we choose

$$C_k = \frac{1}{\sqrt{2\pi}} \tag{5.70}$$

i.e., if we choose the momentum eigenfunctions to be defined as

$$\psi_k(z) = \frac{1}{\sqrt{2\pi}} \exp(ikz) \tag{5.71}$$

then we at least get a tidy form for the orthogonality integral.

Specifically, instead of Eq. (5.69), $\int_{-\infty}^{\infty} \psi_{k1}^*(z)\psi_k(z)dz = 2\pi C_{k1}^* C_k \delta(k-k_1)$**, we have**

$$\int_{-\infty}^{\infty} \psi_{k1}^*(z)\psi_k(z)dz = \delta(k-k_1) \tag{5.72}$$

This choice of normalization, Eq. (5.72) is called

"normalization to a delta function".

We can construct a viable mathematics for handling such "unnormalizable" functions if we normalize in this way.

Normalizing to a delta function - 3

Compare Eq. (5.72)

$$\int_{-\infty}^{\infty} \psi_{k1}^{*}(z)\psi_{k}(z)\,dz = \delta(k-k_1)$$

with the orthonormality relation for conventional normalizable functions, Eq. (2.35).

$$\int_{0}^{L_z} \psi_{n}^{*}(z)\psi_{m}(z)\,dz = \delta_{nm}$$

In that former case, the integral limits may be finite,

but the equations are otherwise essentially identical except that we now have

a Dirac delta function, $\delta(k-k_1)$*,*

instead of the Kronecker delta, δ_{nm}.

This substitution of

Dirac delta function for

Kronecker delta

is quite a general feature as we compare the results for the two classes of functions.

Using functions normalized to a delta function - 1

Functions normalized to a delta function can be handled

provided we work with integrals rather than sums,

with careful use of the density of states

Suppose we have an orthonormal basis set of functions $\psi_q(z)$,

and we expand some other function, $\phi(z)$, on this set

$$\phi(z) = \sum_q f_q \psi_q(z) \tag{5.73}$$

The sum of the squares of the expansion coefficients gives

$$\int |\phi(z)|^2 dz = \sum_{p,q} f_p^* f_q \int \psi_p^*(z) \psi_q(z) dz = \sum_q |f_q|^2 \tag{5.74}$$

so the normalization of the function is the same as that of the expansion coefficients

as usual.

Using functions normalized to a delta function - 2

Presume now there is a quantity u_q (such as momentum) associated with the q that allows us to write, instead of $\phi(z)=\sum_q f_q\psi_q(z)$, equivalently,

$$\phi(z)=\sum_q f(u_q)\psi(u_q,z) \qquad (5.75)$$

where $f(u_q)\equiv f_q$ ***and*** $\psi(u_q,z)\equiv\psi_q(z)$.

(Note, for any specific value of u_q, such as a value v, we can write

$$f(v)=\int\psi^*(v,z)\phi(z)\,dz \qquad (5.76)$$

in the usual way of evaluating expansion coefficients.)

Now, let us transform the sum, Eq. (5.75), into an integral,

using the density of states, $g(u)=1/(du/dq)$ ***as in Eqs. (5.38) (***$g(u)=\dfrac{1}{(du/dq)}$***)***

and (5.41) ($\sum_q\ldots\rightarrow\int\ldots g(u)\,du$***) above***

$$\phi(z)=\int f(u)\psi(u,z)g(u)\,du \qquad (5.77)$$

Using functions normalized to a delta function - 3

Now we can substitute this form of $\phi(z)=\int f(u)\psi(u,z)g(u)\,du$ **back into Eq. (5.76) (** $f(v)=\int \psi^*(v,z)\phi(z)\,dz$ **) to give**

$$f(v)=\int f(u)\left[\int \psi^*(v,z)\psi(u,z)g(u)\,dz\right]du \qquad (5.78)$$

from which we see, by the definition of the delta function, Eq. (5.46), **(** $\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a)$ ***) that***

the term in square brackets is performing as a delta function, i.e.,

$$\int \psi^*(v,z)\psi(u,z)g(u)\,dz=\delta(v-u) \qquad (5.79)$$

Using functions normalized to a delta function - 4

The functions so far are all presumed to be normalized conventionally.

Now, however, we have a way of choosing other functions

that works with the delta function normalization to give useful results.

First, we make the restriction that the density of states is a constant, i.e.,

$$g(u) \equiv g \tag{5.80}$$

e.g., for momentum eigenfunctions, or plane waves in a large box.

Now, let us define two new functions,

folding the square root of the density of states into each function, i.e.,

$$F(u) = \sqrt{g}\, f(u) \tag{5.81}$$

$$\Psi(u,z) = \sqrt{g}\,\psi(u,z) \tag{5.82}$$

Using functions normalized to a delta function - 5

Then with these new functions ($F(u)=\sqrt{g}\,f(u)$ and $\Psi(u,z)=\sqrt{g}\psi(u,z)$) we find,

first, that the $\Psi(u,z)$ are basis functions normalized to a delta function,

i.e., Eq. (5.79) ($\int\psi^*(v,z)\psi(u,z)g(u)dz=\delta(v-u)$) becomes

$$\int\Psi^*(v,z)\Psi(u,z)dz=\delta(v-u) \tag{5.83}$$

second, the expansion in functions normalized to a delta function,

i.e., Eq. (5.77) ($\phi(z)=\int f(u)\psi(u,z)g(u)du$) becomes

$$\phi(z)=\int F(u)\Psi(u,z)du \tag{5.84}$$

and we can also write for the expansion coefficient (or now expansion function), from (5.76) ($f(v)=\int\psi^*(v,z)\phi(z)dz$)

$$F(v)=\int\Psi^*(v,z)\phi(z)dz \tag{5.85}$$

third, $F(u)$ has a simple normalization

$$\int|\phi(z)|^2dz=\sum_q|f_q|^2=\int|f(u)|^2gdu=\int|F(u)|^2du \tag{5.86}$$

Using functions normalized to a delta function - 6

This use of functions normalized to delta functions

can be done any time the density of states is large and uniform.

The fact that the final results do not depend on the density of states

means that these expressions continue to be meaningful in the limit as the density of states becomes effectively infinite,

as is the case for momentum eigenfunctions.

The incorporation of the square root of the density of states into each of the expansion coefficients and the basis functions avoids two problems.

Otherwise, as the density of states increases,

the expansion coefficients themselves become very small,

as does the amplitude of the basis functions

The incorporation of the square root of the density of states into both expansion coefficients and basis functions

leaves them both quite finite, and

leaves us with a simple mathematics for handling the resulting functions,

without infinities or other singularities.

Box and delta function normalization

Now as an example we examine plane waves of the form $C_k \exp(ikz)$,

in two different approaches of "box" and delta function normalizations

In a box of length L,

normalizing such an exponential plane wave gives

$$\int_{-L/2}^{L/2} C_k^* \exp(-ikz) C_k \exp(ikz)\, dz = |C_k|^2 L = 1 \tag{5.87}$$

i.e.,

$$C_k = \frac{1}{\sqrt{L}} \tag{5.88}$$

so the box-normalized wavefunction is

$$\psi_k(z) \equiv \psi(k,z) = \frac{1}{\sqrt{L}} \exp(ikz) \tag{5.89}$$

To transform this to a wavefunction normalized to a delta function,

we multiply by the square root of the density of states.

Taking the density of states to be $g = L/2\pi$, corresponding to adjacent k values being spaced by $2\pi/L$ in such a box, we have

$$\Psi(k,z) = \sqrt{g}\,\psi(k,z) = \sqrt{\frac{L}{2\pi}} \frac{1}{\sqrt{L}} \exp(ikz) = \frac{1}{\sqrt{2\pi}} \exp(ikz) \tag{5.90}$$

as proposed before in Eq. (5.71) when considering plane waves normalized to a delta function.

Relation to Fourier transforms

When our basis functions are the plane waves,

$$\Psi(u,z) \equiv \frac{1}{\sqrt{2\pi}} \exp(-iuz) \qquad (5.91)$$

the expansion of the function $F(u)$ ***in those functions is exactly equivalent to the mathematics of the Fourier transform, i.e.,***

$$\phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(u) \exp(-iuz)\, dz \qquad (5.92)$$

where $\phi(z)$ **is the Fourier transform of the function** $F(u)$**.**

Note that then Eq. (5.86)

$$\int \left|\phi(z)\right|^2 dz = \int \left|F(u)\right|^2 du$$

is simply a statement of Parseval's theorem,

which in turn is saying that the Fourier transform is a transform that does not change the length of the vector in Hilbert space,

and it is a unitary transform.

Periodic boundary conditions

We like to work with exponential waves rather than sines and cosines

because the mathematics is easier to handle.

Putting exponential waves in a box causes a minor formal problem.

If we ask that the wavefunction reaches zero at the walls of the box,

then the allowed solutions are sine waves, not exponentials.

A mathematical trick is to pretend that the boundary conditions are periodic

with the length,* L*, of the box being the period, i.e., to pretend that

$$\exp(ikz) = \exp[ik(z+L)] \tag{5.93}$$

This leads to the requirement that

$$\exp(ikL) = 1 \tag{5.94}$$

which in turn means that

$$k = \frac{2m\pi}{L} \tag{5.95}$$

where m is a positive or negative integer or zero.

The allowed values of k are therefore spaced by $2\pi/L$,

and the density of states in k *(the number of states per unit* k*) is therefore*

$$g = \frac{L}{2\pi} \tag{5.96}$$

Position eigenfunctions - 1

Thus far the only quantum mechanical functions we have dealt with explicitly that are normalized to a delta function are plane waves,

which are also the momentum eigenfunctions.

There is another very simple example

the position eigenfunctions.

In the representation where functions are described in terms of position

the position operator is simply the position, z***, itself (in the one-dimensional case).***

What are the functions that,

when operated on by the position operator,

give results that are simply an eigenvalue (which should be a “value” of position) times the function?

Position eigenfunctions - 2

Answer - the position eigen functions are delta functions.

For example, consider the function

$$\psi_{z_o}(z) = \delta(z - z_o) \tag{5.97}$$

Then we can see that

$$\hat{z}\psi_{z_o}(z) = z_o\psi_{z_o}(z) \tag{5.98}$$

where we have explicitly written the position operator as $\hat{z}$.

The only value of z for which the eigen function is non-zero is the one $z = z_o$,

so in any expression involving $\hat{z}\psi_{z_o}(z)$ we can simply replace it by $z_o\psi_{z_o}(z)$.

Normalization of the delta function

The delta function itself is normalized to a delta function.

To see this consider the integral

$$\int \delta(z_1 - z)\delta(z_2 - z)dz = \delta(z_1 - z_2) \tag{5.99}$$

To understand why this integral itself evaluates to a delta function,

consider the first delta function as being one of its other representations,

such as a Gaussian as in Eq. (5.53),

before we have quite taken the limit.

Then by the definition of the delta function

$$\int \frac{1}{w\sqrt{\pi}} \exp\left(-\frac{(z_1 - z)^2}{w^2}\right)\delta(z_2 - z)\,dz = \frac{1}{w\sqrt{\pi}} \exp\left(-\frac{(z_1 - z_2)^2}{w^2}\right) \tag{5.100}$$

Then take the limit of large w *of the right hand side,*

which is the delta function on the right of Eq. (5.99).

Expansion of a function in position eigenfunctions

We expect that the position eigenfunctions form a complete set,

and so we can expand other functions in them.

Suppose that we have some set of expansion coefficients $F(z_o)$ that we use in an expansion of the form of Eq. (5.84), $\phi(z)=\int F(u)\Psi(u,z)dz$

as appropriate for expansion in functions normalized to a delta function.

Then we have, using the position eigenfunctions as in Eq. (5.97) above,

$$\phi(z)=\int F(z_o)\delta(z-z_o)dz_o \qquad (5.101)$$

Given the definition of the delta function, i.e., we have

$$\phi(z)=F(z) \qquad (5.102)$$

I.e., a function $\phi(z)$ of position is its own set of expansion coefficients in the expansion in position eigenfunctions.

Wavefunction amplitudes are just expansions on position eigenfunctions.

Our wavefunction normalization integrals, of the form $\int|\phi(z)|^2 dz$, are just the normalization, Eq. (5.86), $\int|\phi(z)|^2 dz=\int|F(u)|^2 du$, for expansions in functions normalized to a delta functions.

We have actually been using the concept of functions normalized to a delta function all along.

Change of basis for sets normalized to a delta function - 1

Consider changing between position and momentum basis sets,

an example that is the most common such transformation.

Presume we have function $\phi_{old}(z)$ expressed in the "old", position basis.

The "new" basis set,

also normalized to a delta function,

is the set of momentum eigenfunctions, $(1/2\pi)^{1/2}\exp(ikz)$, as in Eq. (5.90).

Then, according to our expansion formula for functions normalized to a delta function, Eq. (5.85),

$$F(v)=\int \Psi^{*}(v,z)\phi(z)\,dz\,,$$

we have

$$\phi_{new}(k)=\frac{1}{\sqrt{2\pi}}\int \phi_{old}(z)\exp(-ikz)\,dz \qquad (5.103)$$

Change of basis for sets normalized to a delta function - 2

We can if we wish formally write this transformation in terms of an (integral) operator

$$\hat{U} \equiv \frac{1}{\sqrt{2\pi}} \int \exp(-ikz)\, dz \tag{5.104}$$

Note that $\hat{U}$ is an operator. One can only actually perform the integral once this operator operates on a function of z.

In this form, we can then write Eq. (5.103),

$$\phi_{new}(k) = \frac{1}{\sqrt{2\pi}} \int \phi_{old}(z) \exp(-ikz)\, dz\,,$$

in the form we have used before for basis transformations, as

$$|\phi_{new}\rangle = \hat{U}\, |\phi_{old}\rangle \tag{5.105}$$

where in our notation we are anticipating that this operator $\hat{U}$ is unitary (a proof that is left to the reader).

Change of basis for sets normalized to a delta function - 3

Let us look at the specific case where the function $\phi_{old}(z)$ is actually the position basis function $|\phi_{old}\rangle = \delta(z - z_o)$.

Then we find that, in what is now the momentum representation, that basis function is now expressed as

$$|\phi_{new}\rangle = \frac{1}{\sqrt{2\pi}} \int \delta(z - z_o) \exp(-ikz)\,dz = \frac{1}{\sqrt{2\pi}} \exp(-ikz_o) \tag{5.106}$$

In other words,

a* position *eigenfunction

in the* momentum *representation

is $(1/2\pi)^{1/2} \exp(-ikz_o)$**,**

where k ***takes on an unrestricted range of values,***

just as for a specific value of $k = k_o$

the* momentum *eigenfunction

in the* position *representation

is $(1/2\pi)^{1/2} \exp(ik_o z)$

where z ***takes on an unrestricted range of values.***

Change of basis for sets normalized to a delta function - 4

The operator that will take us back to the position representation we can guess by the symmetry of this particular problem will be

$$\hat{U}^{\dagger} = \frac{1}{\sqrt{2\pi}} \int \exp(ikz)\, dk \qquad (5.107)$$

Note that in constructing this adjoint,

we have taken the complex conjugate,

and we have interchanged the roles of k and z,

which is analogous to the formation of an adjoint in our conventionally normalizable basis representations,

where we take the complex conjugate,

and interchange indices on the matrix elements or basis functions.

Change of basis for sets normalized to a delta function - 5

We can now formally transform the position operator into the momentum basis,

using the usual formula for such transformations,

i.e., formally operating on an arbitrary function $|f\rangle$

$$
\begin{aligned}
\hat{z}_{new}|f\rangle &= \hat{U}\hat{z}_{old}\hat{U}^{\dagger}|f\rangle \\
&= \frac{1}{2\pi}\int \exp(-ikz)\int z\exp(ik'z)\,f(k')\,dk'dz = \frac{1}{2\pi}\iint z\exp\left[-i(k-k')z\right]f(k')\,dk'dz \\
&= \frac{-1}{2\pi i}\frac{\partial}{\partial k}\iint \exp\left[-i(k-k')z\right]dzf(k')\,dk' = i\frac{\partial}{\partial k}\int \delta(k'-k)\,f(k')\,dk' \\
&= i\frac{\partial}{\partial k}f(k) \equiv i\frac{\partial}{\partial k}|f\rangle
\end{aligned}
\tag{5.108}
$$

Note we have used the algebraic trick $-iz\exp[-i(k-k')z] \equiv (\partial/\partial k)\exp[-i(k-k')z]$.

Since $|f\rangle$ is arbitrary, then we can write the position operator in the momentum representation as

$$\hat{z}_{new} = i\frac{\partial}{\partial k} \tag{5.109}$$

Note the symmetry between this and the z momentum operator in the position representation, which is $\hat{p}_z = (-i\hbar)(\partial/\partial z)$.

Approximation methods in quantum mechanics – 1

Reading – Sections 6.1 and 6.2. Also read Section 2.11 for background.

Approximation methods on quantum mechanics

- **for practical reasons of calculations**
- **for conceptual reasons – idea of processes**

Time-independent problems

- **Example problem**
  - *potential well with an electric field*
- **Use of finite matrices**

Approximation methods in quantum mechanics

For all the equations used in quantum mechanics, e.g.,

- ***Schrödinger's equation***
- ***extensions of Schrödinger's equation to include electron spin***
- ***relativistically correct quantum mechanical equations***
- ***equations appropriate for describing photons***

relatively few problems are simple enough to be solved exactly.

- ***Relatively few classical mechanics problems can be solved exactly either.***
  - **Problems with multiple bodies or interactions between multiple systems are often difficult to solve.**

It is useful,

- ***both from the practical point of view***
  - **i.e., we can actually do the problems ourselves**
- ***and the conceptual one***
  - **i.e., we can know what we are doing!**

to understand key approximation methods of quantum mechanics.

Approximation techniques

There are several techniques,

> ***and it is quite common to invent new techniques or variants of old ones to tackle particular problems.***

These techniques also often offer physical insight into the problem

Among the most common techniques are

- ***(i) use of finite basis subsets (finite matrices),***
- ***(ii) perturbation theory,***
  - **which comes in two flavors,**
    - *time-independent and*
    - *time-dependent,*
- ***(iii) the variational method***

Example problem – one-dimensional potential well with an electric field

To illustrate the methods, we analyze a particular problem,

> ***a one-dimensional, infinitely deep potential well for an electron with an applied electric field.***

This problem is solvable exactly analytically (see Section 2.11)

> ***though the solution functions are somewhat obscure (Airy functions).***

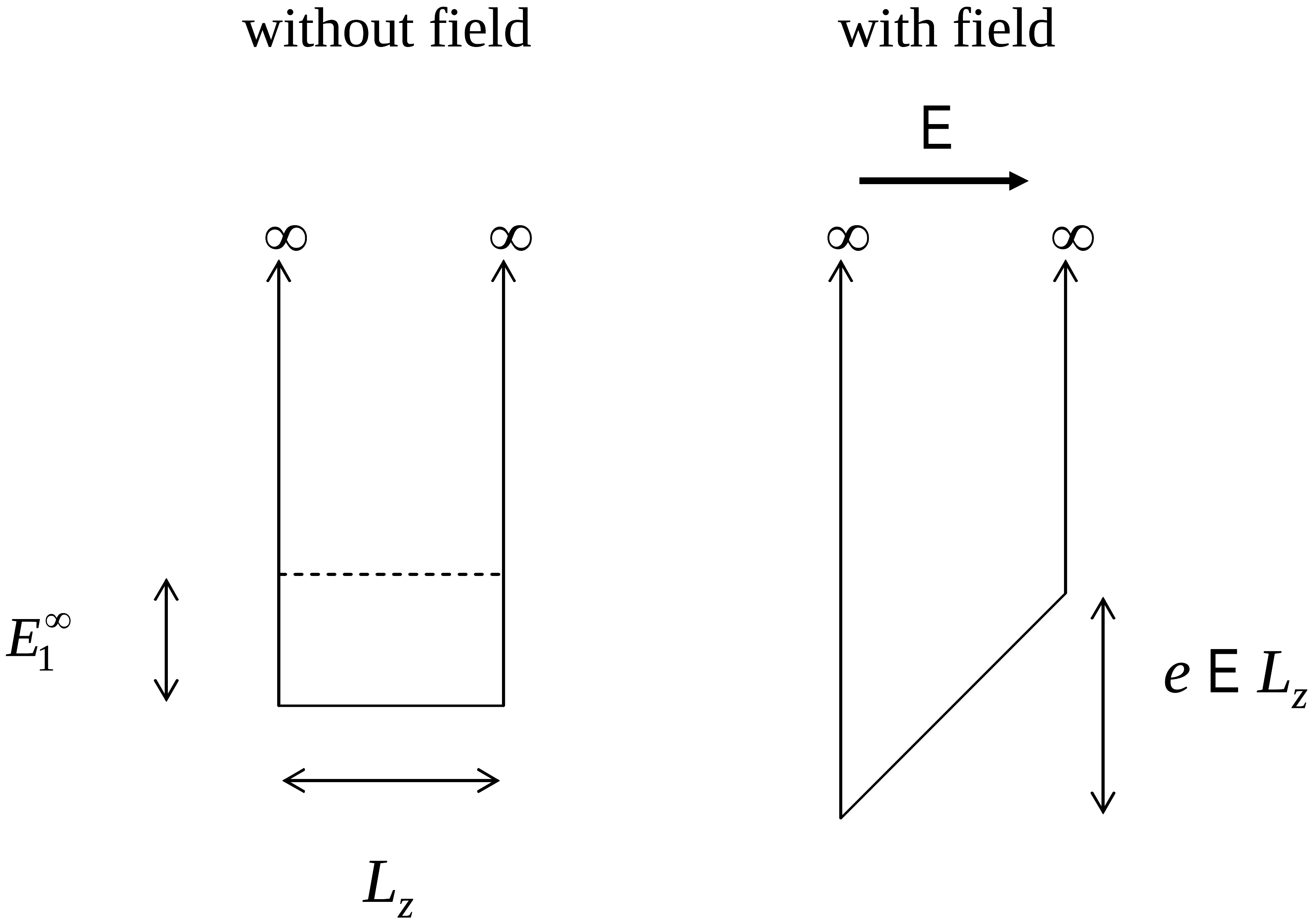
We can solve this problem by various approximation methods without using Airy functions

> ***these methods can be easier than evaluating the "exact" solutions.***

This problem has a specific practical application,

> ***in the design of quantum well electroabsorption modulators.***
>
> ***The shifts in the energy levels calculated here translate into***
>
> > **shifts in the optical absorption edge in semiconductor quantum well structures with applied electric fields.**
> >
> > > *This shift in turn is used to modulate the transmission of a light beam in high speed modulators in optical communications systems.*

Potential well with electric field



Construction of Hamiltonian - 1

The energy of an electron in an electric field E simply increases linearly with distance.

A positive electric field in the positive z direction pushes the electron in the negative z direction with a force of magnitude $e\mathsf{E}$,

and so the potential energy of the electron increases in the positive z direction with the form $e\mathsf{E}z$.

We choose the potential to be zero in the middle of the well.

Hence, within the well, the potential energy is

$$V(z) = e\mathsf{E}(z - L_z/2) \qquad (6.1)$$

and the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + e\mathsf{E}(z - L_z/2) \qquad (6.2)$$

Construction of Hamiltonian - 2

It is convenient to define dimensionless units for this problem.

A convenient unit of energy, E_1^∞, is the confinement energy of the first state of the original infinitely deep well, i.e.,

$$E_1^\infty = \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2$$

and in those units the eigenenergy of the nth state will be

$$\eta_n = \frac{E_n}{E_o} \tag{6.3}$$

A convenient unit of field is that field, E_o, that will give one unit of energy, E_1^∞, of potential change from one side of the well to the other, i.e.,

$$\mathsf{E}_o = \frac{E_1^\infty}{eL_z} \tag{6.4}$$

and in those units, the (dimensionless) field will be

$$\mathsf{f} = \frac{\mathsf{E}}{\mathsf{E}_o} \tag{6.5}$$

A convenient unit of distance will be the thickness of the well, and so the dimensionless distance will be

$$\xi = z / L_z \tag{6.6}$$

Construction of Hamiltonian - 3

Dividing throughout by E_o, the Hamiltonian ($\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + e\mathsf{E}\left(z - L_z/2\right)$) within the well can now be written in these dimensionless units as

$$\hat{H} = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2} + \mathsf{f}\left(\xi - 1/2\right) \qquad (6.7)$$

with the corresponding time-independent Schrödinger equation

$$\hat{H}\phi\left(\xi\right) = \eta\phi\left(\xi\right) \qquad (6.8)$$

For the original "unperturbed" problem without field, we will write the "unperturbed" Hamiltonian within the well as

$$\hat{H}_o = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2} \qquad (6.9)$$

The normalized solutions of the corresponding Schrödinger equation

$$\hat{H}_o\psi_n = \varepsilon_n\psi_n \qquad (6.10)$$

are then

$$\psi_n\left(\xi\right) = \sqrt{2}\sin\left(n\pi\xi\right) \qquad (6.11)$$

We have now completed the setup of this problem in dimensionless units

Now we can use it to illustrate various approximation methods.

Use of finite matrices (finite basis subsets)

Though the use of finite basis subsets is quite common,

it is not normally discussed explicitly in quantum mechanics texts.

Quantum mechanical problems can often be reduced to linear algebra

with operators represented by matrices and functions by vectors.

The practical solution of some problem,

such as energy eigenvalues and eigenstates,

then reduces to a problem of finding the eigenvectors of a matrix.

Commonly, no exact analytic solution is known.

Then we may have to solve numerically for eigenvalues and eigenvectors,

which means we have to restrict the matrix to being a finite one.

We can also sometimes consider analytically a finite matrix

and solve that simpler problem exactly.

Then one can have an approximate analytic solution.

This approach is taken, for example, in the so-called $k \cdot p$ *("k dot p") method of calculating band structures in semiconductors,*

the principal band structure method used for calculating optical properties for, e.g., semiconductor lasers

Choice of basis function subset

In practice,

there is no substitute for intelligence in choosing the finite basis set

and this is something of an art.

If we choose the form of the basis set badly,

or make a poor choice as to what elements to include in our finite subset,

then we will end up with a poor approximation to the result,

or a matrix that is ill-conditioned.

A very frequent choice is to use

the energy eigenfunctions of the "unperturbed" problem,

or at least those of a simpler, though related, problem.

Finite matrix method for electron in a potential well with field - 1

We will need to construct the matrix of the Hamiltonian.

The matrix elements are

$$H_{ij} = -\frac{1}{\pi^2}\int_0^1 \psi_i^*(\xi)\frac{d^2}{d\xi^2}\psi_j(\xi)\,d\xi + \mathrm{f}\int_0^1 \psi_i^*(\xi)(\xi - 1/2)\psi_j(\xi)\,d\xi \qquad (6.12)$$

(In this particular case, because the wavefunctions happen to be real, the complex conjugation makes no difference in the integrals.)

For our explicit example here,

we will consider a field of 3 dimensionless units (i.e., $\mathrm{f} = 3$***),***

and we will take as our finite basis

the first three energy eigenfunctions of the "unperturbed" problem.

Then, performing the integrals in Eq. (6.12) numerically with the $\psi_n(\xi) = \sqrt{2}\sin(n\pi\xi)$**, we obtain the approximate Hamiltonian matrix**

$$\hat{H} = \begin{bmatrix} 1 & -0.54 & 0 \\ -0.54 & 4 & -0.584 \\ 0 & -0.584 & 9 \end{bmatrix} \qquad (6.13)$$

Note that this matrix is Hermitian, as expected.

Finite matrix method for electron in a potential well with field - 2

Now we can numerically find the eigenvalues of this matrix, which are

$$\eta_1 = 0.904,\ \ \eta_2 = 4.028,\ \ \eta_3 = 9.068 \tag{6.14}$$

Note that these are quite near to the "unperturbed" (zero field) values (which would be 1, 4, and 9, respectively).

We see also that the lowest energy eigenvalue has reduced from its unperturbed value.

These can be compared with the results from the exact, Airy function solutions, which are

$$\varepsilon_1 \simeq 0.90419,\ \varepsilon_2 \simeq 4.0275,\ \varepsilon_3 \simeq 9.0173 \tag{6.15}$$

The corresponding eigenvectors are solved numerically as

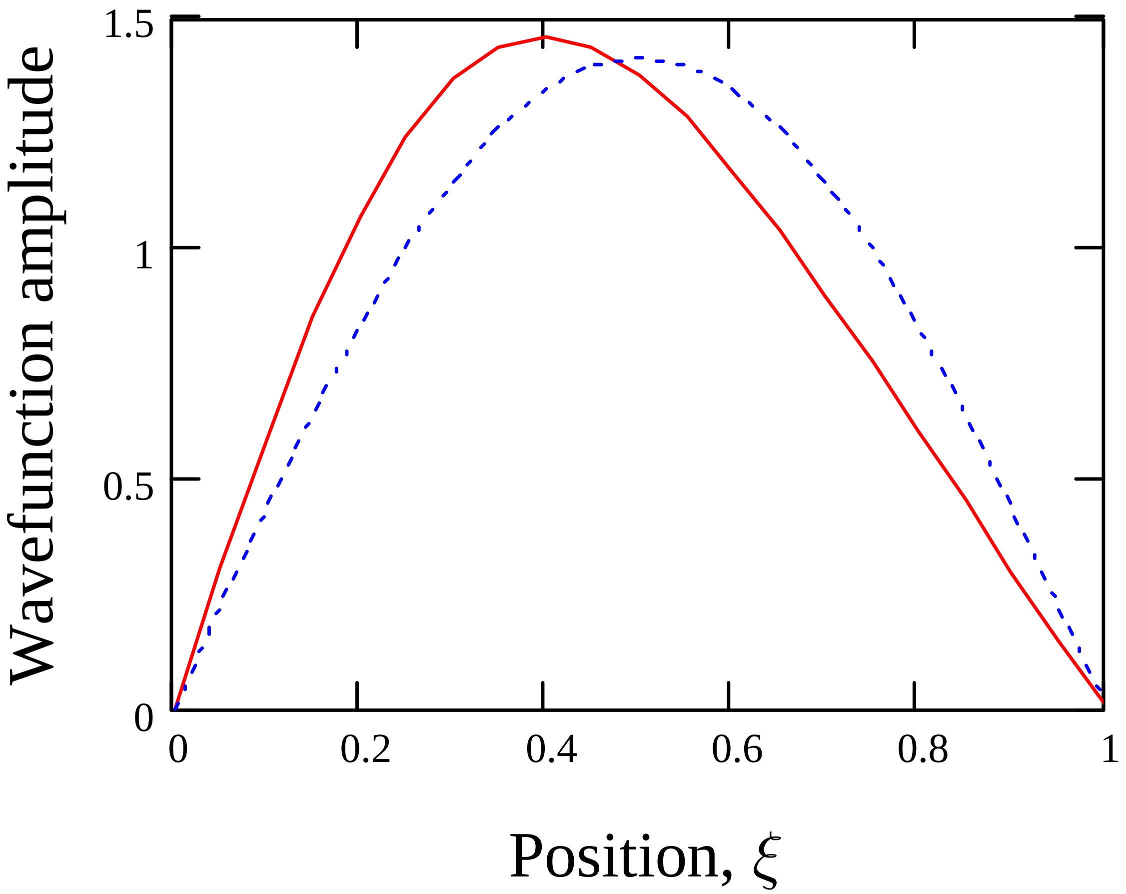
$$\left|\phi_1\right\rangle = \begin{bmatrix} 0.985 \\ 0.174 \\ 0.013 \end{bmatrix},\ \left|\phi_2\right\rangle = \begin{bmatrix} -0.175 \\ 0.978 \\ 0.115 \end{bmatrix},\ \left|\phi_2\right\rangle = \begin{bmatrix} -0.007 \\ -0.115 \\ 0.993 \end{bmatrix} \tag{6.16}$$

(These are normalized, with the sum of the squares of the elements of the vectors each adding to 1.)

Explicitly, this means that, for example, the first eigenfunction is

$$\phi_1(\xi) = 0.985\sqrt{2}\sin(\pi\xi) + 0.174\sqrt{2}\sin(2\pi\xi) + 0.013\sqrt{2}\sin(3\pi\xi) \tag{6.17}$$

Calculated wavefunction

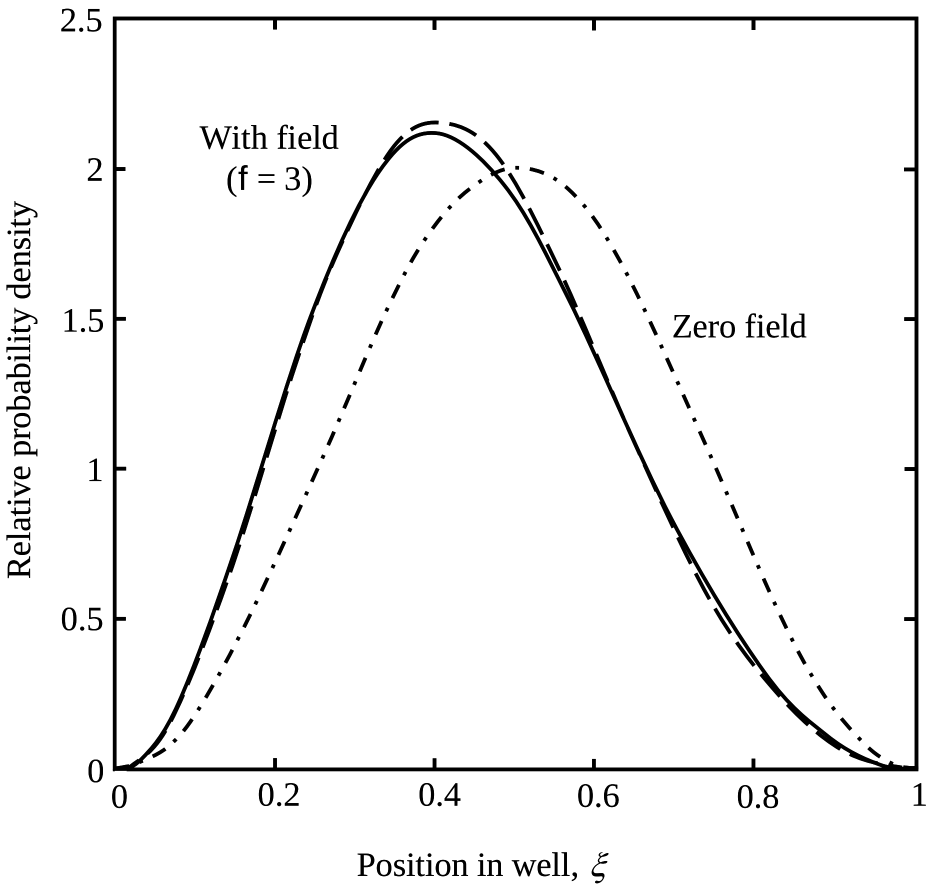


Unperturbed (zero field) wavefunction (broken line) and calculated wavefunction with 3 units of field for the first energy eigenstate in an infinitely deep quantum well

Note that the electron wavefunction with field has moved to the left.

Adding more elements to the finite basis set used makes negligible change in the calculated eigenvalue for the first state (i.e., < one part in a thousand).

Calculated probability densities



Relative probability density at zero field and with 3 units of field for the first energy eigenstate in an infinitely deep potential well, calculated

(1) using the finite basis subset method with a 3x3 matrix - solid line; and

(2) using first-order perturbation theory – dashed line.

Approximation methods in quantum mechanics – 2

Reading – Section 6.3 up to start of "Example of well with field"

Time-independent non-degenerate perturbation theory

- first-order perturbation theory
- second-order perturbation theory

Time-independent (stationary) non-degenerate perturbation theory

Presume some unperturbed Hamiltonian, $\hat{H}_o$, that has known normalized eigen solutions, i.e.,

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \tag{6.18}$$

We can imagine that the perturbation we are considering could be progressively mathematically "turned on", at least in a mathematical sense.

> ***For example, we could imagine that we are progressively increasing the applied field,*** E***, from zero.***

In perturbation theory we can successively look for the changes in the solutions that are

> ***proportional first to*** E ***(so-called "first-order corrections"),***
>
> ***proportional to*** E^2 ***("second-order corrections")***
>
> ***proportional to*** E^3***, and so on.***

Usually in this perturbation theory method, we stop at the first non-zero order.

Perturbation theory and a “house-keeping” parameter - 1

In general, we imagine that our perturbed system has some additional term in the Hamiltonian, the “perturbing Hamiltonian”, $\hat{H}_p$.

In our example case of an infinitely deep potential well with an applied field, that perturbing Hamiltonian would be $\hat{H}_p = e\text{E}\left(z - L_z/2\right)$.

We could construct the perturbation theory directly using the powers of E as discussed above.

More generally we introduce a mathematical “house-keeping” parameter γ.

In this way of writing the theory,

we say that the perturbing Hamiltonian is $\gamma\hat{H}_p$,

where $\hat{H}_p$ can be physically a fixed perturbation,

and we imagine we can smoothly increase γ,

looking instead for changes in the solutions that are proportional to

γ (for first-order corrections),

γ^2 (for second-order corrections), and so on.

Perturbation theory and a "house-keeping" parameter - 2

In the end,

- ***having used the powers of γ to help separate out the different orders of corrections,***

we can set $\gamma = 1$,

- ***or indeed to any other value we like as long as $\gamma \hat{H}_p$ corresponds to the actual physical perturbation of the system.***

If this concept is confusing at a first reading,

- ***just imagine that γ is the strength of the electric field in our example problem.***

Construction of the orders of the perturbation theory - 1

With this way of thinking about the problem mathematically, we can write for our Hamiltonian (e.g., Schrödinger) equation

$$\left(\hat{H}_o + \gamma \hat{H}_p\right)|\phi\rangle = E|\phi\rangle \tag{6.19}$$

We now presume that we can express the resulting perturbed eigenfunction and eigenvalue as power series in this parameter, i.e.,

$$|\phi\rangle = \left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \gamma^3\left|\phi^{(3)}\right\rangle + \cdots \tag{6.20}$$

$$E = E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \gamma^3 E^{(3)} + \cdots \tag{6.21}$$

Now we substitute these power series into the equation (6.19).

$$\begin{aligned}&\left(\hat{H}_0 + \gamma \hat{H}_p\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)\\ &= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)\end{aligned} \tag{6.22}$$

Construction of the orders of the perturbation theory - 2

If this power series description is to hold for any γ (at least within some convergence range),

it must be possible to equate terms in given powers of γ on the two sides of the equation.

Quite generally, if we had two power series that were equal, i.e.,

$$a_0 + a_1\gamma + a_2\gamma^2 + a_3\gamma^3 + \cdots = b_0 + b_1\gamma + b_2\gamma^2 + b_3\gamma^3 + \cdots = f(\gamma) \tag{6.23}$$

the only way this can be true for arbitrary γ is for the individual terms to be equal,

i.e., $a_i = b_i$.

This is the same as saying that the power series expansion of a function $f(\gamma)$ is unique.

Hence, equating powers of γ, we can obtain, from (6.22),

$$\left(\hat{H}_0 + \gamma \hat{H}_p\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

$$= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

a progressive set of equations.

Progressive set of perturbation theory equations - 1

$$\left(\hat{H}_0+\gamma\hat{H}_p\right)\left(\left|\phi^{(0)}\right\rangle+\gamma\left|\phi^{(1)}\right\rangle+\gamma^2\left|\phi^{(2)}\right\rangle+\cdots\right)$$

$$=\left(E^{(0)}+\gamma E^{(1)}+\gamma^2E^{(2)}+\cdots\right)\left(\left|\phi^{(0)}\right\rangle+\gamma\left|\phi^{(1)}\right\rangle+\gamma^2\left|\phi^{(2)}\right\rangle+\cdots\right)$$

Equating terms in γ^0(i.e., terms without γ) gives the "zeroth" order equation

$$\hat{H}_o\left|\phi^{(0)}\right\rangle=E^{(0)}\left|\phi^{(0)}\right\rangle \qquad (6.24)$$

i.e., the original unperturbed Hamiltonian equation,

with eigenfunctions $\left|\psi_n\right\rangle$ and eigenvalues E_n.

Consider now a particular state $\left|\psi_m\right\rangle$ and how it is perturbed.

We will therefore write $\left|\psi_m\right\rangle$ instead of $\left|\phi^{(0)}\right\rangle$ and E_m instead of $E^{(0)}$.

With this notation, our progressive set of equations, each equating a different power of γ, becomes

$$\hat{H}_o\left|\psi_m\right\rangle=E_m\left|\psi_m\right\rangle \qquad (6.25)$$

$$\hat{H}_o\left|\phi^{(1)}\right\rangle+\hat{H}_p\left|\psi_m\right\rangle=E_m\left|\phi^{(1)}\right\rangle+E^{(1)}\left|\psi_m\right\rangle \qquad (6.26)$$

$$\hat{H}_o\left|\phi^{(2)}\right\rangle+\hat{H}_p\left|\phi^{(1)}\right\rangle=E_m\left|\phi^{(2)}\right\rangle+E^{(1)}\left|\phi^{(1)}\right\rangle+E^{(2)}\left|\psi_m\right\rangle \qquad (6.27)$$

and so on.

Progressive set of perturbation theory equations - 2

We can choose to rewrite these equations, (6.25) - (6.27), as

$$\hat{H}_o |\psi_m\rangle = E_m |\psi_m\rangle \quad \rightarrow \quad \left(\hat{H}_o - E_m\right)|\psi_m\rangle = 0 \tag{6.28}$$

$$\hat{H}_o \left|\phi^{(1)}\right\rangle + \hat{H}_p |\psi_m\rangle = E_m \left|\phi^{(1)}\right\rangle + E^{(1)} |\psi_m\rangle \quad \rightarrow \quad \left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)|\psi_m\rangle \tag{6.29}$$

$$\hat{H}_o \left|\phi^{(2)}\right\rangle + \hat{H}_p \left|\phi^{(1)}\right\rangle = E_m \left|\phi^{(2)}\right\rangle + E^{(1)} \left|\phi^{(1)}\right\rangle + E^{(2)} |\psi_m\rangle \quad \rightarrow$$

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)} |\psi_m\rangle \tag{6.30}$$

and so on.

First order perturbation theory - 1

Now we proceed to show how to calculate the various perturbation terms.

It is straightforward to calculate $E^{(1)}$ from Eq. (6.29).

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_m\right\rangle$$

Premultiplying by $\left\langle\psi_m\right|$ gives

$$\begin{aligned}\left\langle\psi_m\right|\hat{H}_o - E_m\left|\phi^{(1)}\right\rangle &= \left(\left\langle\psi_m\right|\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left\langle\psi_m\right|\left(E_m - E_m\right)\left|\phi^{(1)}\right\rangle = 0 \\ &= \left\langle\psi_m\right|E^{(1)} - \hat{H}_p\left|\psi_m\right\rangle = E^{(1)} - \left\langle\psi_m\right|\hat{H}_p\left|\psi_m\right\rangle\end{aligned} \qquad (6.31)$$

i.e.,

$$E^{(1)} = \left\langle\psi_m\right|\hat{H}_p\left|\psi_m\right\rangle \qquad (6.32)$$

Hence we have quite a simple formula for the first-order correction, $E^{(1)}$, to the energy in the presence of our perturbation $\hat{H}_p$.

Note that it depends only on the zeroth order (i.e., the unperturbed) eigenfunction.

First order perturbation theory - 2

To calculate the first order correction, $\left|\phi^{(1)}\right\rangle$, to the wavefunction, we expand that correction in the basis set $\left|\psi_n\right\rangle$, i.e.,

$$\left|\phi^{(1)}\right\rangle = \sum_n a_n^{(1)} \left|\psi_n\right\rangle \tag{6.33}$$

Substituting this is in Eq. (6.29)

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_m\right\rangle$$

and premultiplying by $\left\langle\psi_i\right|$ ***gives***

$$\begin{aligned}\left\langle\psi_i\right|\hat{H}_o - E_m\left|\phi^{(1)}\right\rangle &= \left(E_i - E_m\right)\left\langle\psi_i\middle|\phi^{(1)}\right\rangle = \left(E_i - E_m\right)a_i^{(1)} \\ &= \left\langle\psi_i\right|E^{(1)} - \hat{H}_p\left|\psi_m\right\rangle = E^{(1)}\left\langle\psi_i\middle|\psi_m\right\rangle - \left\langle\psi_i\right|\hat{H}_p\left|\psi_m\right\rangle\end{aligned} \tag{6.34}$$

We presume that the energy eigenvalue E_m is not degenerate,

i.e., there is only one eigenfunction corresponding to this eigenvalue.

We are restricting to "non-degenerate" perturbation theory.

Degeneracy needs to be handled somewhat differently.

First order perturbation theory - 3

With no degeneracy, we still need to distinguish two cases in Eq. (6.34).

First, for $i \neq m$, we have from (6.34) $\left(E_i - E_m\right) a_i^{(1)} = -\langle \psi_i | \hat{H}_p | \psi_m \rangle$, i.e.,

$$a_i^{(1)} = \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_i} \tag{6.35}$$

For $i = m$, Eq. (6.34) gives us no additional information. Explicitly,

$$\begin{aligned} \left(E_m - E_m\right) a_m^{(1)} &= 0 a_m^{(1)} \\ &= E^{(1)} - \langle \psi_m | \hat{H}_p | \psi_m \rangle = E^{(1)} - E^{(1)} = 0 \end{aligned} \tag{6.36}$$

This means we are free to choose $a_m^{(1)}$.

The choice that makes the algebra simplest is to set $a_m^{(1)} = 0$,

which is the same as saying that we choose to make $\left|\phi^{(1)}\right\rangle$ orthogonal to $|\psi_m\rangle$.

The same happens for the higher order equations, such as (6.30).

Adding an arbitrary amount of $|\psi_m\rangle$ into $\left|\phi^{(j)}\right\rangle$ makes no difference to the left hand side of the equation.

Hence we make the convenient choice

$$\left\langle \psi_m \middle| \phi^{(j)} \right\rangle = 0 \tag{6.37}$$

First order perturbation theory - 4

Hence with (6.35) $a_i^{(1)} = \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_i}$ **and** $a_m^{(1)} = 0$

we obtain, for the first order correction to the wavefunction

$$\left| \phi^{(1)} \right\rangle = \sum_{n \neq m} \frac{\langle \psi_n | \hat{H}_p | \psi_m \rangle}{E_m - E_n} | \psi_n \rangle \qquad (6.38)$$

and we remember our result for the first order correction to the energy

$$E^{(1)} = \langle \psi_m | \hat{H}_p | \psi_m \rangle \qquad (6.32)$$

Second order perturbation theory - 1

We can continue similarly to find the higher order terms.

Premultiplying (6.30)

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)}\left|\psi_m\right\rangle$$

on both sides by $\left\langle\psi_m\right|$ ***gives***

$$\begin{aligned}\left\langle\psi_m\right|\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle &= \left\langle\psi_m\right|\left(E_m - E_m\right)\left|\phi^{(2)}\right\rangle = 0\\ &= \left\langle\psi_m\right|\left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + \left\langle\psi_m\right|E^{(2)}\left|\psi_m\right\rangle \qquad (6.39)\\ &= E^{(1)}\left\langle\psi_m|\phi^{(1)}\right\rangle - \left\langle\psi_m\right|\hat{H}_p\left|\phi^{(1)}\right\rangle + E^{(2)}\end{aligned}$$

Since we have chosen $\left|\psi_m\right\rangle$ ***orthogonal to*** $\left|\phi^{(j)}\right\rangle$ ***(Eq. (6.37)), we have***

$$E^{(2)} = \left\langle\psi_m\right|\hat{H}_p\left|\phi^{(1)}\right\rangle \qquad (6.40)$$

or, explicitly, using (6.38)

$$E^{(2)} = \left\langle\psi_m\right|\hat{H}_p\left(\sum_{n\neq m}\frac{\left\langle\psi_n\right|\hat{H}_p\left|\psi_m\right\rangle}{E_m - E_n}\left|\psi_n\right\rangle\right) \qquad (6.41)$$

i.e.,

$$E^{(2)} = \sum_{n\neq m}\frac{\left|\left\langle\psi_n\right|\hat{H}_p\left|\psi_m\right\rangle\right|^2}{E_m - E_n} \qquad (6.42)$$

Second order perturbation theory - 2

For the second order wavefunction correction,

We expand $\left|\phi^{(2)}\right\rangle$, noting now that $\left|\phi^{(2)}\right\rangle$ is orthogonal to $\left|\psi_m\right\rangle$, to obtain

$$\left|\phi^{(2)}\right\rangle = \sum_{n\neq m} a_n^{(2)}\left|\psi_n\right\rangle \tag{6.43}$$

We premultiply Eq. (6.30)

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)}\left|\psi_m\right\rangle$$

by $\left\langle\psi_i\right|$ to obtain

$$\begin{aligned}\left\langle\psi_i\right|\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle &= \left(E_i - E_m\right)a_i^{(2)} \\ &= \left\langle\psi_i\right|\left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + \left\langle\psi_i\right|E^{(2)}\left|\psi_m\right\rangle \\ &= E^{(1)}a_i^{(1)} - \sum_{n\neq m} a_n^{(1)}\left\langle\psi_i\right|\hat{H}_p\left|\psi_n\right\rangle\end{aligned} \tag{6.44}$$

Note that we can write the summation in (6.44) excluding the term $n = m$

because we chose $\left|\phi^{(1)}\right\rangle$ to be orthogonal to $\left|\psi_m\right\rangle$ (i.e., we have chosen $a_m^{(1)} = 0$).

Hence, for $i \neq m$ we have

$$a_i^{(2)} = \left(\sum_{n\neq m}\frac{a_n^{(1)}\left\langle\psi_i\right|\hat{H}_p\left|\psi_n\right\rangle}{E_m - E_i}\right) - \frac{E^{(1)}a_i^{(1)}}{E_m - E_i} \tag{6.45}$$

Second order perturbation theory - 3

Note that the second order wavefunction depends only on the first order energy and wavefunction.

We can write out (6.45) explicitly, using (6.32) to substitute for $E^{(1)}$ and (6.38) for $a_i^{(1)}$, to obtain

$$a_i^{(2)} = \left(\sum_{n \neq m} \frac{\langle \psi_i | \hat{H}_p | \psi_n \rangle \langle \psi_n | \hat{H}_p | \psi_m \rangle}{(E_m - E_i)(E_m - E_n)} \right) - \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle \langle \psi_m | \hat{H}_p | \psi_m \rangle}{(E_m - E_i)^2} \qquad (6.46)$$

We can now gather these results together, and write the perturbed energy and wavefunction up to second order as

$$E \cong E_m + \langle \psi_m | \hat{H}_p | \psi_m \rangle + \sum_{n \neq m} \frac{\left| \langle \psi_n | \hat{H}_p | \psi_m \rangle \right|^2}{E_m - E_n} \qquad (6.47)$$

$$\begin{aligned} |\phi\rangle \cong |\psi_m\rangle &+ \sum_{i \neq m} \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_n} |\psi_i\rangle \\ &+ \sum_{i \neq m} \left[\left(\sum_{n \neq m} \frac{\langle \psi_i | \hat{H}_p | \psi_n \rangle \langle \psi_n | \hat{H}_p | \psi_m \rangle}{(E_m - E_i)(E_m - E_n)} \right) - \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle \langle \psi_m | \hat{H}_p | \psi_m \rangle}{(E_m - E_i)^2} \right] |\psi_i\rangle \end{aligned} \qquad (6.48)$$

i.e.,

$$|\phi\rangle \cong |\psi_m\rangle + \sum_{i \neq m} \left[\frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_n} \left(1 - \frac{\langle \psi_m | \hat{H}_p | \psi_m \rangle}{E_m - E_i} \right) + \sum_{n \neq m} \frac{\langle \psi_i | \hat{H}_p | \psi_n \rangle \langle \psi_n | \hat{H}_p | \psi_m \rangle}{(E_m - E_i)(E_m - E_n)} \right] |\psi_i\rangle \qquad (6.49)$$

Approximation methods in quantum mechanics – 3

Reading – Section 6.3 starting from “Example of well with field" – Section 6.4

Time-independent non-degenerate perturbation theory

- **example of well with field**
- **remarks on perturbation theory**

Degenerate perturbation theory

Example of well with field

Now we consider the problem of the infinitely deep potential well with an applied field.

We write the Hamiltonian as the sum of the unperturbed Hamiltonian, which is, in the well, in the dimensionless units we chose,

$$\hat{H}_o = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2} \tag{6.50}$$

and the perturbing Hamiltonian

$$\hat{H}_p = \mathrm{f}\left(\xi - 1/2\right) \tag{6.51}$$

where again we will take $\mathrm{f} = 3$ for our explicit calculation.

Let us now calculate the various corrections.

First order energy correction - 1

In first order, the energy shift with applied field is

$$E^{(1)} = \langle \psi_m | \hat{H}_p | \psi_m \rangle = \mathrm{f} \int_0^1 \sqrt{2} \sin(m\pi\xi)(\xi - 1/2)\sqrt{2}\sin(m\pi\xi)\, d\xi$$

$$= 2\mathrm{f} \int_0^1 (\xi - 1/2)\sin^2(m\pi\xi)\, d\xi \qquad (6.52)$$

$$= 0$$

The integrals here are zero for all m

because the sine squared function is even with respect to the center of the well, whereas the $(\xi - 1/2)$ **is odd.**

Hence, for this particular problem there is no first order energy correction.

First order energy correction - 2

Why is there no first order energy correction?

- ***because of the symmetry of the problem.***
- ***Suppose that there was an energy correction proportional to the applied field*** f***.***
  - **Then, if we changed the direction of** f**, the energy correction would also have to change sign.**
    - *But, by the symmetry of this problem,*
      - the resulting change in energy cannot depend on the direction of the field;
        - the problem is symmetric in the + or - ξ directions,
      - so there cannot be any change in energy linearly proportional to the field, f.

Matrix elements for perturbation calculations

The general matrix elements that we will need for further perturbation calculations are

$$H_{puv} = f\int_0^1 \sqrt{2}\sin(u\pi\xi)(\xi - 1/2)\sqrt{2}\sin(v\pi\xi)\,d\xi \qquad (6.53)$$

In general we need u and v to have opposite parity

i.e., if one is odd, the other must be even

for these matrix elements to be non-zero,

since otherwise the overall integrand is odd about $\xi = 1/2$.

First order correction to the wavefunction - 1

Now we can calculate the first order correction to the wavefunction, for the first state

$$\phi^{(1)}(\xi) = \sum_{u=2}^{q} \frac{H_{pu1}}{\varepsilon_{o1} - \varepsilon_{ou}} \psi_u(\xi) \qquad (6.54)$$

where

$\varepsilon_{oi} = u^2$ **are the energies of the unperturbed states, and**

q **is a finite number that we must choose in practice.**

For these calculations here, we chose $q = 6$*, though a smaller number would likely be quite accurate*

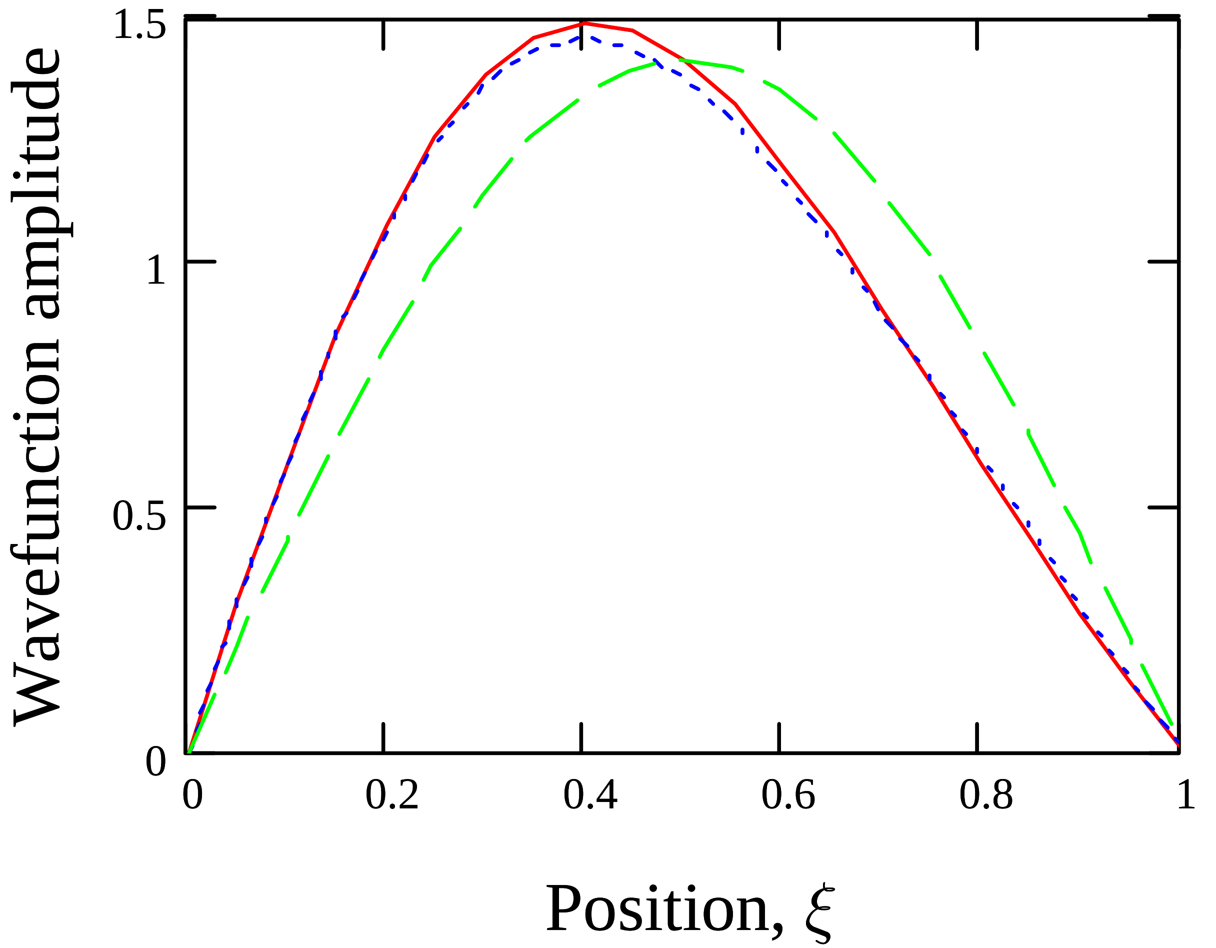
even $q = 2$ gives almost identical numerical answers, for reasons that will become apparent

Explicitly, for the expansion coefficients $a_u^{(1)} = H_{pu1} / (\varepsilon_1 - \varepsilon_u)$ **, we have numerically**

$$a_2^{(1)} \cong 0.180, \; a_3^{(1)} = 0, \; a_4^{(1)} = 0.003 \qquad (6.55)$$

Here the value of 0.180 for $a_2^{(1)}$ ***compares closely with the value of 0.174 for the second expansion coefficient in Eq. (6.16) obtained above in the finite basis subset method.***

First order correction to the wavefunction - 2



Comparison of the unperturbed (zero field) wavefunction (dashed line) and the wavefunction with 3 units of field for the first energy eigenstate in an infinitely deep quantum well, calculated using the finite basis subset method (dotted line) and the first order perturbation method (solid line).

Second order energy correction

Since the first order correction to the energy was zero,

we have to go to second order to get a perturbation correction to the energy.

Explicitly, we have

$$E^{(2)} \cong \sum_{u=2}^{q} \frac{\left|H_{pu1}\right|^2}{\varepsilon_1 - \varepsilon_u} \tag{6.56}$$

which numerically here gives

$$E^{(2)} = -0.0975 \tag{6.57}$$

or a final estimate of the total energy of

$$\eta_1 \cong \varepsilon_1 + E^{(1)} + E^{(2)} = 0.9025 \tag{6.58}$$

which compares with the result of $\eta_1 = 0.904$ ***from the finite basis subset method.***

Approximate analytic formulae - 1

Note that the second order energy correction, $E^{(2)}$ is analytically proportional to the square of the field, f^2.

Hence perturbation theory gives us an approximate analytic result for the energy,

which we can now use for any field without performing the perturbation theory calculation again.

Explicitly, we can write

$$\eta_1 \cong \varepsilon_1 - 0.0108\mathrm{f}^2 \tag{6.59}$$

This is a typical kind of a result from a perturbation calculation, allowing us to obtain an approximate analytic formula valid for small perturbations.

We similarly find that

the corrections to the wavefunction are approximately analytically proportional to the field,

and we have an approximate wavefunction of

$$\phi(\xi) \cong \sqrt{2}\sin(\pi\xi) + 0.06\mathrm{f}\sqrt{2}\sin(2\pi\xi) \tag{6.60}$$

Approximate analytic formulae - 2

We have dropped higher terms

because the next non-zero term (the term in $\sin(4\pi\xi)$*) is some 60 times smaller (see Eq. (6.55)).*

To a good degree of approximation,

the perturbed wavefunction at low fields simply involves an admixture of the second basis function.

Since it is the first order wavefunction that is used to calculate the second order energy,

we can now see why even including only one term in the sums (i.e., setting $q = 2$ *in the sums (6.54) and (6.56)) is quite accurate in this case.*

Remarks on perturbation theory

Perturbation theory

- ***is particularly useful for calculations involving small perturbations to the system***
- ***can give simple analytic formulae and values of coefficients for various effects involving weak interactions.***
- ***is also conceptually useful in understanding interactions in general***
  - **we can use perturbation theory to judge whether or not to include some level in, for example, a finite basis subset calculation.**
    - *If*
      - the level is far away in energy and/or
      - has a matrix element small compared to some closer level,
    - *we can safely neglect that farther level because of the energy separations that appear in the denominators in the perturbation terms.*

Higher order perturbation theory

Generally, perturbation calculations are most useful for the first non-zero order of correction.

- ***Specific effects sometimes require higher order calculations.***
  - **For example, nonlinear optical effects of different types are associated with particular orders of (time-dependent) perturbation theory calculations.**
    - *Linear optics is based on first order perturbation theory;*
    - *linear electro-optic effects, second-harmonic generation, and optical parametric generation use second order perturbation;*
    - *non-linear refraction and four-wave mixing (quite common effects in long-distance optical fiber systems) need third order perturbation calculations.*

Normalization

The perturbation wavefunction formulae are not quite normalized;

- ***we are merely adding the corrections to the original wavefunction in Eq. (6.20).***
  - **This is not a substantial issue for small corrections.**
    - *It is quite straightforward also to normalize the corrected wavefunctions if this is important.*

Energies and wavefunctions

It is quite generally true of approximation methods that

- ***energies can be calculated reasonably accurately even with relatively poor wavefunctions.***

In perturbation theory,

- ***the nth approximation to the energy only requires the $(n\text{–}1)$th approximation to the wavefunction.***

Convergence of perturbation series

The particular kind of perturbation method we have discussed here

known as Rayleigh-Schrödinger perturbation theory

tends to lead to a series that does not converges very rapidly.

Trying to get a more accurate calculation by adding more terms to the series is often not very productive.

This kind of perturbation approach is most often used up to only with the lowest non-zero terms in the perturbation expansion.

Such an approach often gives physical insight, and a first reasonable estimate of the effect of interest.

Other numerical techniques,

including other perturbation approaches (such as the Brillouin-Wigner theory)

can give more accurate numerical answers.

Degenerate perturbation theory - 1

Above we avoided above the “degenerate” case

Degeneracy is not uncommon in quantum mechanics,

especially in problems that are quite symmetric.

For example, the three different P orbitals of a hydrogen atom,

each corresponding to a different one of the directions x, y, *and* z,

all have the same energy.

Often perturbations, such as an electric field, will remove the degeneracy,

making each of the states have different energies,

and defining the distinct eigenfunctions uniquely.

We consider this case now, at least for first order perturbation theory.

Degenerate perturbation theory - 2

Suppose that there are

r ***degenerate orthonormal eigenfunctions,*** $\left|\psi_{ms}\right\rangle$ ***(where*** $s = 1, 2, \cdots r$ ***)***

associated with the eigenenergy E_m ***of the unperturbed problem.***

Then in general we can write a wavefunction corresponding to this eigenenergy as a linear combination of these, i.e.,

$$\left|\psi_{mtot}\right\rangle = \sum_{s=1}^{r} a_{ms}\left|\psi_{ms}\right\rangle \qquad (6.61)$$

Now let us consider the first order perturbation equation, Eq.(6.29),

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_m\right\rangle$$

in a fashion similar to before,

but now with the "unperturbed" or "zero order" wavefunction $\left|\psi_{mtot}\right\rangle$**, i.e.,**

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_{mtot}\right\rangle \qquad (6.62)$$

Degenerate perturbation theory - 3

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_{mtot}\right\rangle \tag{6.62}$$

Now let us premultiply by a specific one of the degenerate basis functions $\left|\psi_{mi}\right\rangle$ to obtain (analogously to Eq. (6.31))

$$\begin{aligned}\left\langle\psi_{mi}\right|\hat{H}_o - E_m\left|\phi^{(1)}\right\rangle &= \left(\left\langle\psi_{mi}\right|\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left\langle\psi_{mi}\right|\left(E_m - E_m\right)\left|\phi^{(1)}\right\rangle = 0 \\ &= \left\langle\psi_{mi}\right|E^{(1)} - \hat{H}_p\left|\psi_{mtot}\right\rangle = E^{(1)}\left\langle\psi_{mi}|\psi_{mtot}\right\rangle - \left\langle\psi_{mi}\right|\hat{H}_p\left|\psi_{mtot}\right\rangle\end{aligned} \tag{6.63}$$

i.e.,

$$\left\langle\psi_{mi}\right|\hat{H}_p\left|\psi_{mtot}\right\rangle = E^{(1)}\left\langle\psi_{mi}|\psi_{mtot}\right\rangle \tag{6.64}$$

or, explicitly in summation form

$$\sum_{s=1}^{r} H_{pmims}a_{ms} = E^{(1)}a_{mi} \tag{6.65}$$

where

$$H_{pmims} = \left\langle\psi_{mi}\right|\hat{H}_p\left|\psi_{ms}\right\rangle \tag{6.66}$$

Degenerate perturbation theory - 4

We can repeat Eq. (6.65)

$$\sum_{s=1}^{r} H_{pmims} a_{ms} = E^{(1)} a_{mi}$$

for every $i = 1, 2, \cdots r$**,**

and so obtain a set of r *equations of the form of Eq. (6.65).*

But this set of equations is simply identical to the matrix-vector equation

$$\begin{bmatrix} H_{pm1m1} & H_{pm1m2} & \cdots & H_{pm1mr} \\ H_{pm2m1} & H_{pm2m2} & \cdots & H_{pm2mr} \\ \vdots & \vdots & \ddots & \vdots \\ H_{pmrm1} & H_{pmrm2} & \cdots & H_{pmrmr} \end{bmatrix} \begin{bmatrix} a_{m1} \\ a_{m2} \\ \vdots \\ a_{mr} \end{bmatrix} = E^{(1)} \begin{bmatrix} a_{m1} \\ a_{m2} \\ \vdots \\ a_{mr} \end{bmatrix} \qquad (6.67)$$

This is just a matrix eigen equation,

a special case of the finite basis subset model

In this case, the finite basis we choose is the set of r **degenerate eigenfunctions corresponding to a particular unperturbed energy eigenvalue** E_m**.**

Degenerate perturbation theory - 5

The solution of the equation (6.67)

$$\begin{bmatrix} H_{pm1m1} & H_{pm1m2} & \cdots & H_{pm1mr} \\ H_{pm2m1} & H_{pm2m2} & \cdots & H_{pm2mr} \\ \vdots & \vdots & \ddots & \vdots \\ H_{pmrm1} & H_{pmrm2} & \cdots & H_{pmrmr} \end{bmatrix} \begin{bmatrix} a_{m1} \\ a_{m2} \\ \vdots \\ a_{mr} \end{bmatrix} = E^{(1)} \begin{bmatrix} a_{m1} \\ a_{m2} \\ \vdots \\ a_{mr} \end{bmatrix}$$

will give

a set of r first order corrections to the energy,

which we could call $E_i^{(1)}$,

each associated with a particular new eigenvector $|\phi_{mi}\rangle$ that is a linear combination of the degenerate basis functions $|\psi_{ms}\rangle$.

All of these new eigenvectors $|\phi_{mi}\rangle$ are orthogonal to one another.

To the extent that the energies $E_i^{(1)}$ are different from one another, the perturbation has "lifted the degeneracy".

Degenerate perturbation theory - 6

Note the eigenvectors $|\phi_{mi}\rangle$ are actually still zero-order wavefunctions,

not first-order wavefunctions;

each of them is an exact solution of the unperturbed problem with energy E_m.

Indeed, any linear combination of the $|\psi_{mi}\rangle$ or the $|\phi_{mi}\rangle$ is a solution of the unperturbed problem with energy E_m.

The perturbation theory has selected a particular set of linear combination of the unperturbed degenerate solutions.

This is consistent with the result for the non-degenerate perturbation theory,

in which the first-order energy correction depends only on the zero-order wavefunctions.

Approximation methods in quantum mechanics – 4

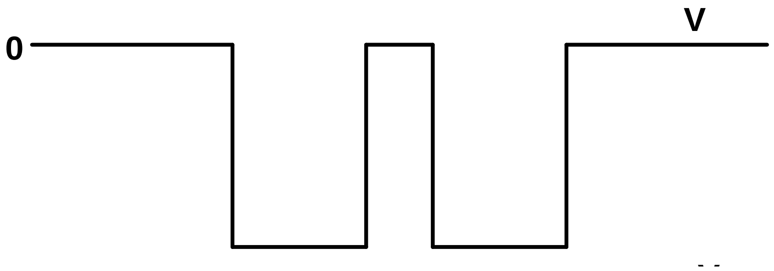
Reading – Sections 6.5 – 6.6

Tight binding model

Variational method

Coupled potential wells - 1

Consider two identical potential wells with a finite barrier thickness between them.



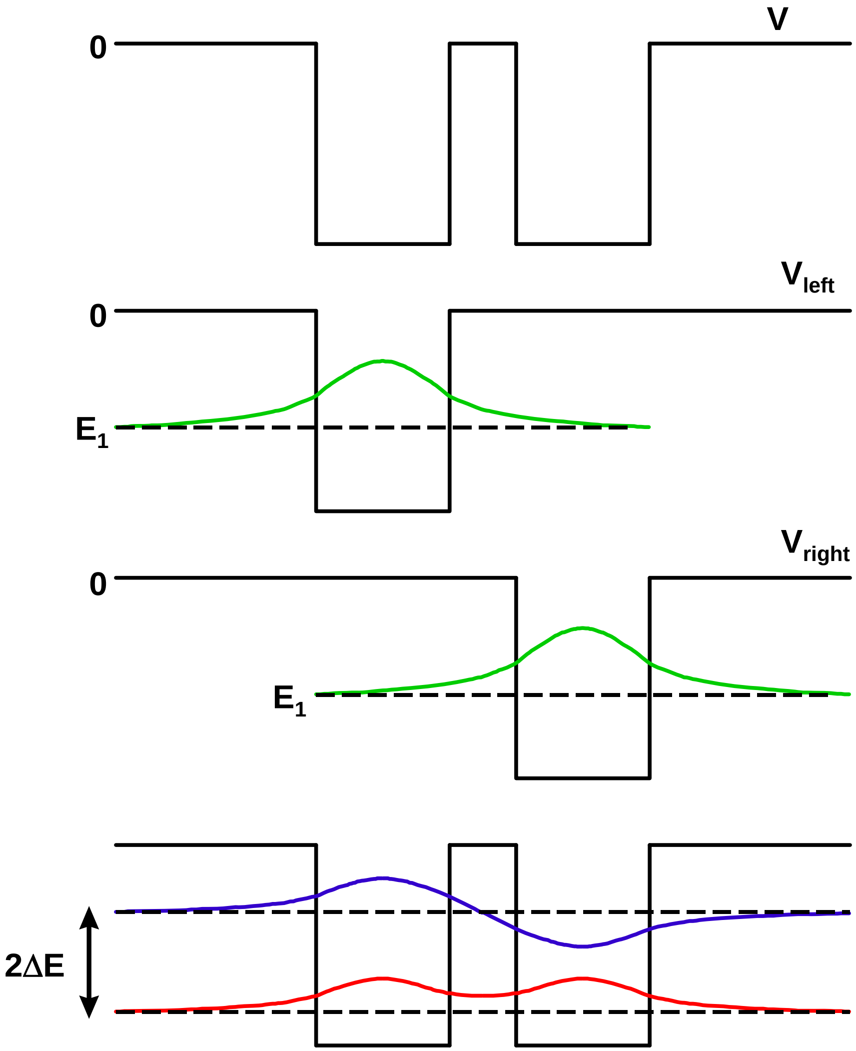
This is similar to a degenerate perturbation theory problem,

though it is slightly difficult mathematically to force it into a form where we are adding a simple perturbing potential.

We can certainly think of it as a finite basis set approach using approximate starting basis functions.

Solid state physicists would call this a “tight-binding” calculation.

Coupled potential wells - 2



Schematic illustration of a coupled potential well, showing the two coupled states formed from the lowest states of the isolated wells. The lower state is symmetric, and the upper state is antisymmetric.

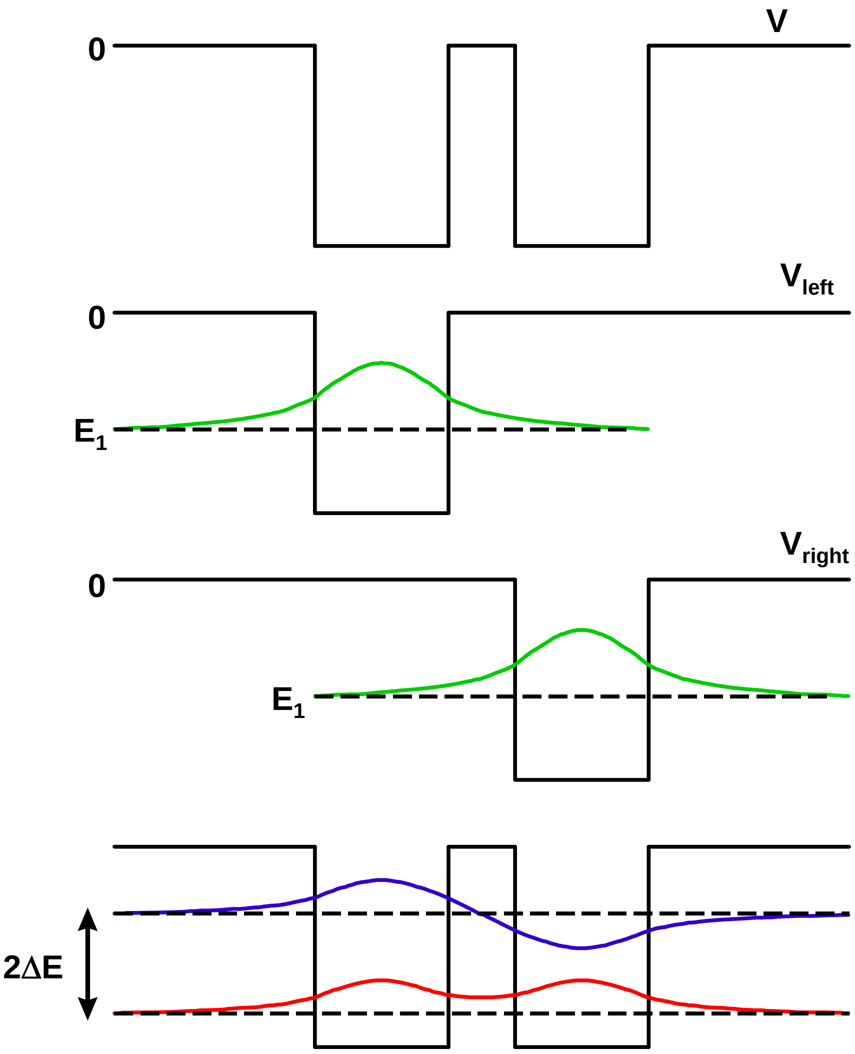
Coupled potential wells - 3

We imagine two separate "unperturbed" potential wells

- ***If we had the "left" potential well present on its own,***
  - **with corresponding potential $V_{left}(z)$,**
- ***we would have the wavefunction solution $\psi_{left}(z)$,***
  - **with associated energy E_1 for the first state,**
    - *a problem we already know how to solve exactly numerically.*

Similarly, if we considered the right potential well on its own,

- ***with potential $V_{right}(z)$,***
  - **we would have the wavefunction solution $\psi_{right}(z)$**
    - *which is the same as $\psi_{left}(z)$*
      - except that it is shifted over to the right,
  - **and would have the same energy E_1.**



Coupled potential wells - 4

The actual potential for which we wish to calculate the states is, however, the potential V,

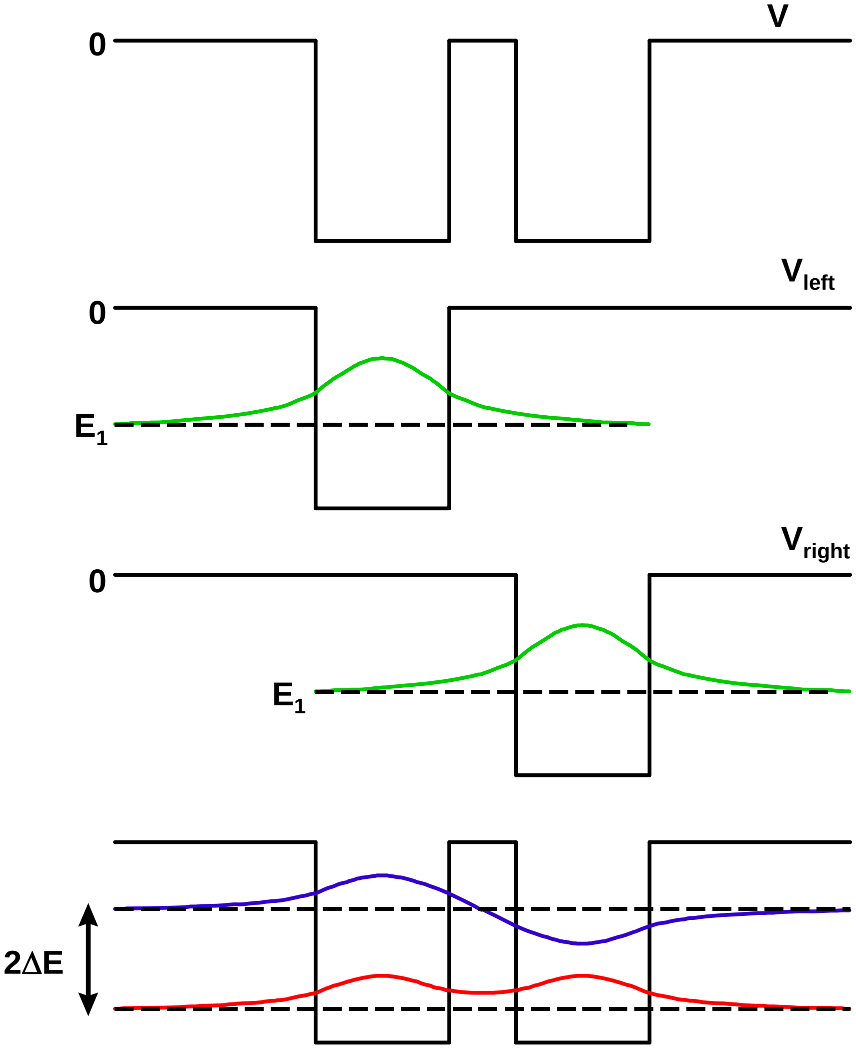
which we could call a coupled potential well.

Note here we have chosen the origin for the potential at the top of the well

so we can say $V(z)=V_{left}(z)+V_{right}(z)$ *simplifying the algebra.*

With our choice of energy origin, the Hamiltonian for this system is

$$\hat{H}=\frac{-\hbar^2}{2m}\frac{d^2}{dz^2}+V_{left}(z)+V_{right}(z) \qquad (6.68)$$



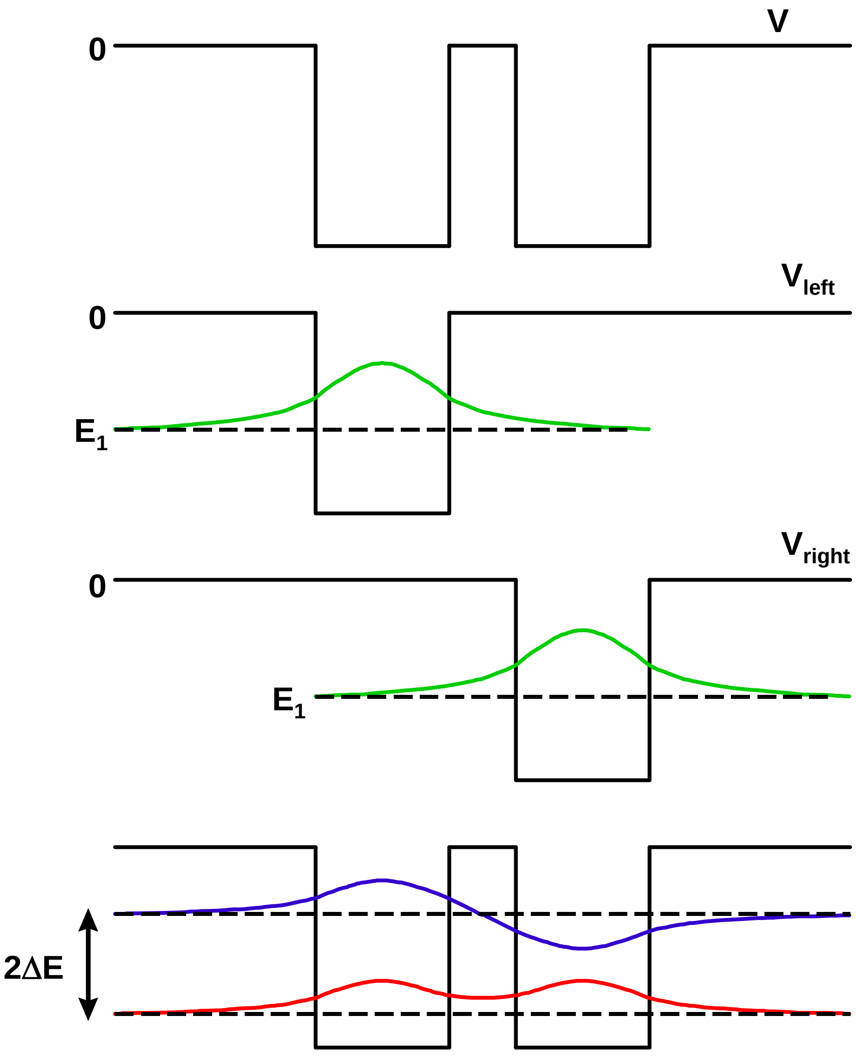
Coupled potential wells - 5

We now solve using the finite basis subset model,

choosing the wavefunctions in the isolated wells,

ψ_{left} and ψ_{right},

for our basis wavefunctions.



These two functions are approximately orthogonal as long as the barrier is reasonably thick

hence the term "tight-binding"

the basis wavefunctions are each assumed to be relatively tightly confined in one well,

with little wavefunction "leakage" into the adjacent well.

Hence the wavefunction can be written approximately in the form

$$\psi = a\psi_{left} + b\psi_{right} \quad (6.69)$$

Coupled potential wells - 6

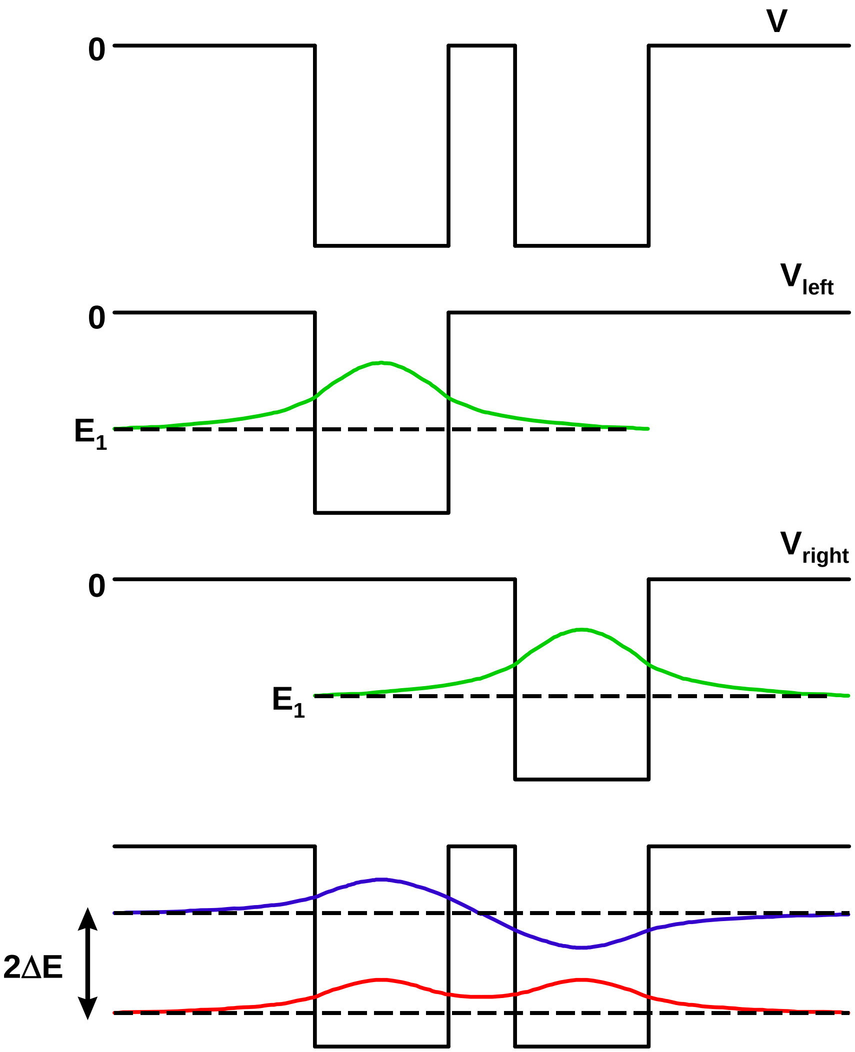
With the presumed form $\psi = a\psi_{left} + b\psi_{right}$, in matrix form,

our finite basis subset approximate version of Schrödinger's equation is

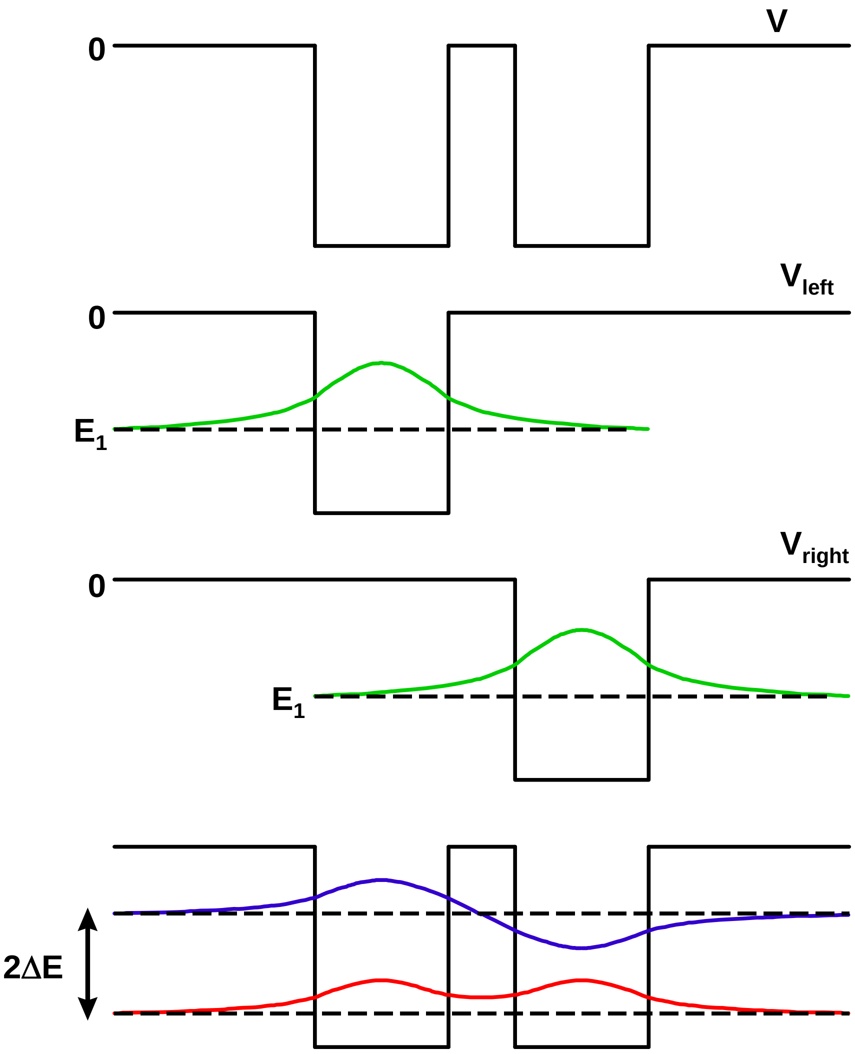
$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix} \tag{6.70}$$

where we should have, for example,

$$H_{11} = \int \psi_{left}^{*}(z) \left(\frac{-\hbar^2}{2m} \frac{d^2}{dz^2} + V_{left}(z) + V_{right}(z) \right) \psi_{left}(z)\, dz \tag{6.71}$$



Coupled potential wells - 7



Because we presume the barrier to be relatively thick,

the amplitude of the left wavefunction is essentially zero inside the right well,

so the integrand in

$$H_{11} = \int \psi_{left}^{*}(z)\left(\frac{-\hbar^2}{2m}\frac{d^2}{dz^2} + V_{left}(z) + V_{right}(z)\right)\psi_{left}(z)\,dz$$

is essentially zero for all z inside the right hand well,

and hence the term

$$\int \psi_{left}^{*}(z) V_{right}(z) \psi_{left}(z)\,dz$$

can be neglected.

We can argue similarly for H_{22}

Hence

$$H_{11} = H_{22} \cong E_1 \qquad (6.72)$$

Coupled potential wells - 8

For the same reason

(that $\psi_{left}(z) \cong 0$ *in the right hand well)*

or the complementary one

(that $\psi_{right}(z) \cong 0$ *in the left hand well),*

we neglect

$$\int \psi^*_{right}(z) V_{left} \psi_{right}(z)\, dz,$$

and

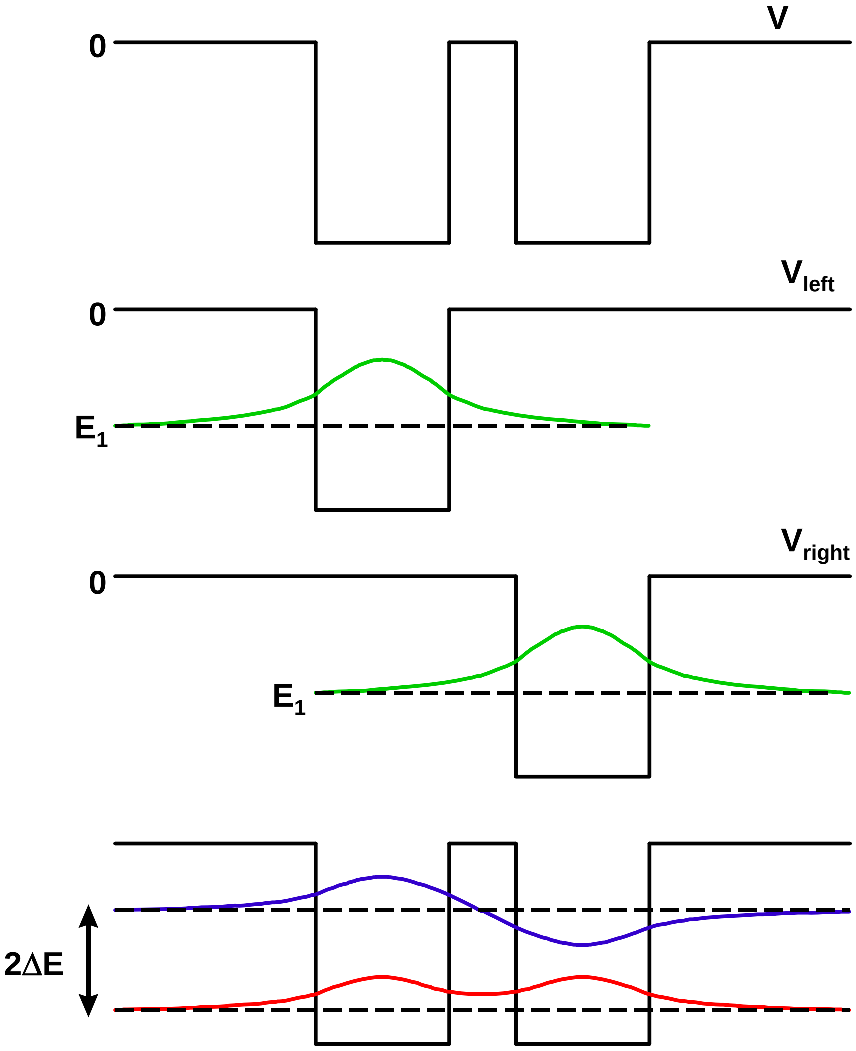
when we are integrating within either well

$$\int \psi^*_{left}(z) V_{right} \psi_{right}(z)\, dz$$

$$\int \psi^*_{left}(z) V_{left} \psi_{right}(z)\, dz,$$

$$\int \psi^*_{right}(z) V_{right} \psi_{left}(z)\, dz$$

$$\int \psi^*_{right}(z) V_{left} \psi_{left}(z)\, dz$$



Coupled potential wells - 9

We do, however, retain the interaction within the (middle) barrier

where the wavefunctions, though small, are presumed not negligible,

i.e., we retain a result

$$\Delta E =$$

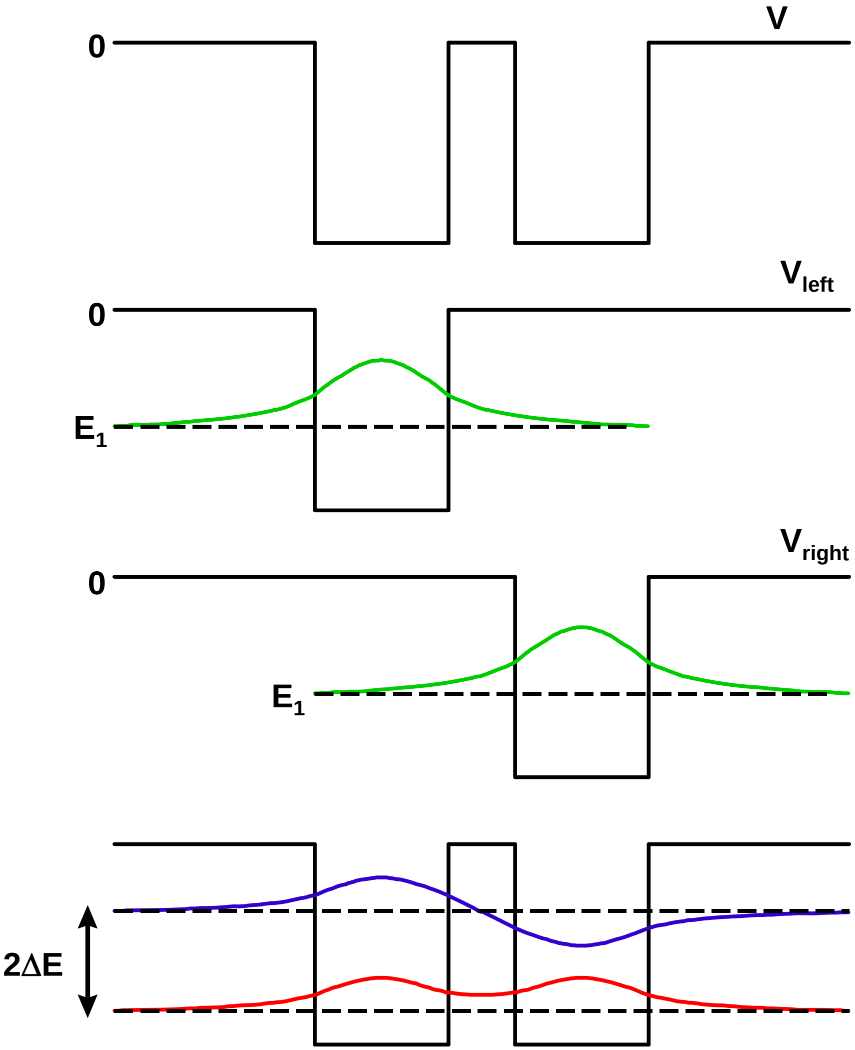
$$\int_{barrier} \psi_{left}^{*}(z)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V(z)(=0\text{ in barrier})\right)\psi_{right}(z)\,dz$$

(6.73)

neglecting contributions that would have come from regions outside the barrier

because again we presume one or other basis wavefunction to be zero there.

(Note: ΔE is a negative number here because the second derivative is > 0)



Coupled potential wells - 10

With these simplifications, we have

$$\begin{bmatrix} E_1 & \Delta E \\ \Delta E^* & E_1 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = E\begin{bmatrix} a \\ b \end{bmatrix} \qquad (6.74)$$

(ΔE here will in practice be real because the wavefunctions of this problem can be chosen to be real, but the complex conjugate is shown for completeness.)

We find the energy eigenvalues of Eq. (6.74) in the usual way by setting

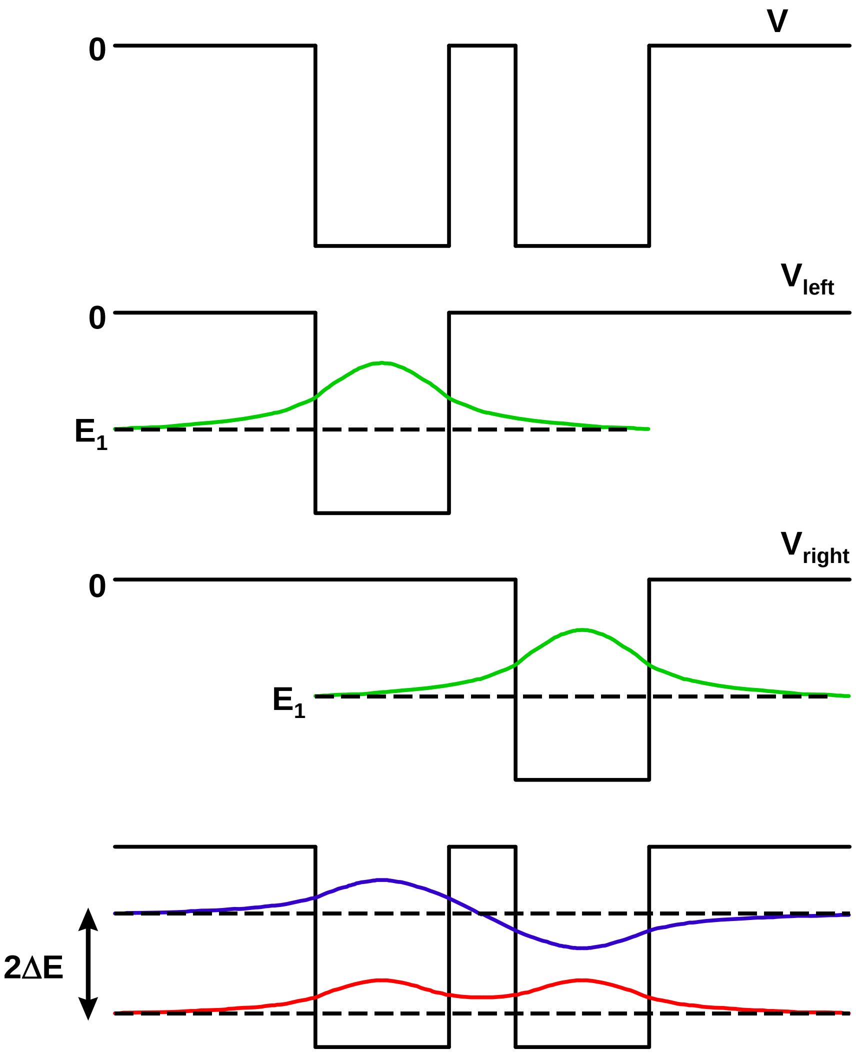
$$\det\begin{vmatrix} E_1 - E & \Delta E \\ \Delta E^* & E_1 - E \end{vmatrix} = 0 \qquad (6.75)$$

i.e.,

$$\left(E_1 - E\right)^2 - \left|\Delta E\right|^2 = E^2 - 2EE_1 + E_1^2 - \left|\Delta E\right|^2 = 0 \qquad (6.76)$$

obtaining eigenvalues

$$E = E_1 \pm \left|\Delta E\right| \qquad (6.77)$$



Coupled potential wells - 11

Note, at least within the approximations here, that

the energy levels are split by the coupling between the wells,

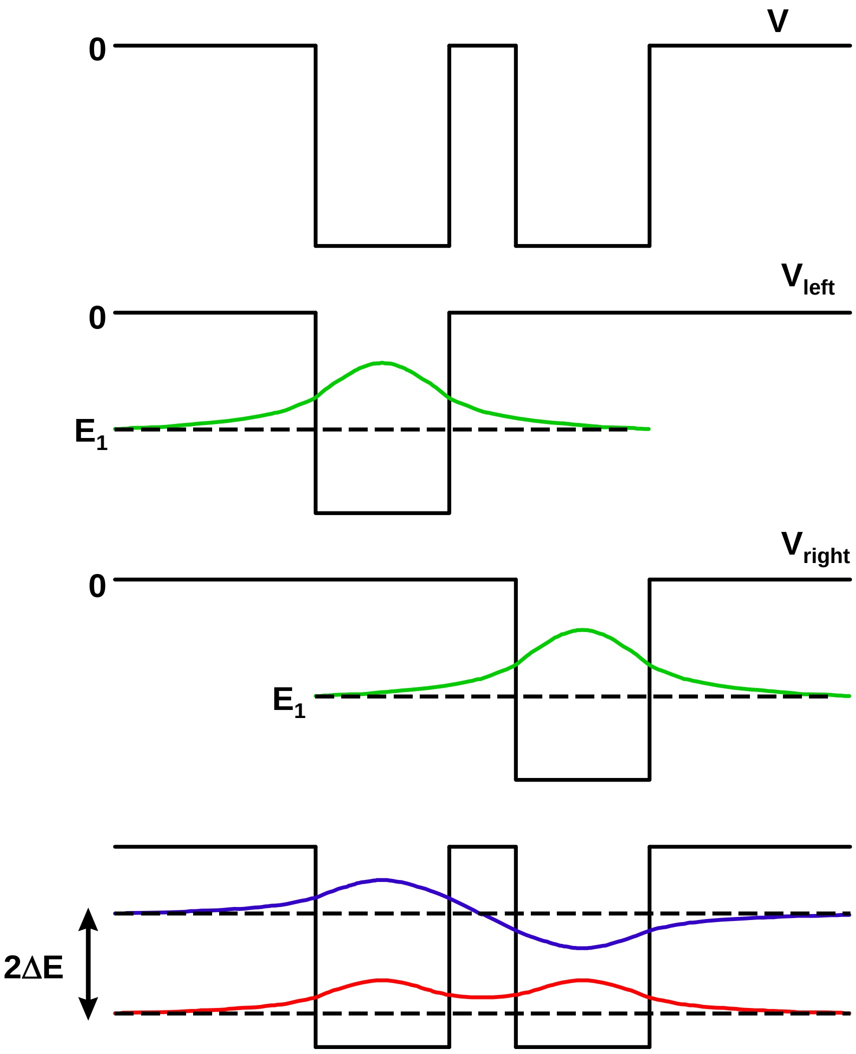
approximately symmetrically about the original "single-well" energy, E_1.

Substituting the eigenvalues back into Eq. (6.74)

$$\begin{bmatrix} E_1 & \Delta E \\ \Delta E^* & E_1 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix}$$

gives us

$$\psi_- = \frac{1}{\sqrt{2}}\left(\psi_{left} + \psi_{right}\right) \text{ and } \psi_+ = \frac{1}{\sqrt{2}}\left(\psi_{left} - \psi_{right}\right) \quad (6.78)$$



Coupled potential wells - 12

The lower energy state is associated with a

symmetric linear combination of the single-well eigenfunctions

(i.e., the wavefunction has the same sign in both wells),

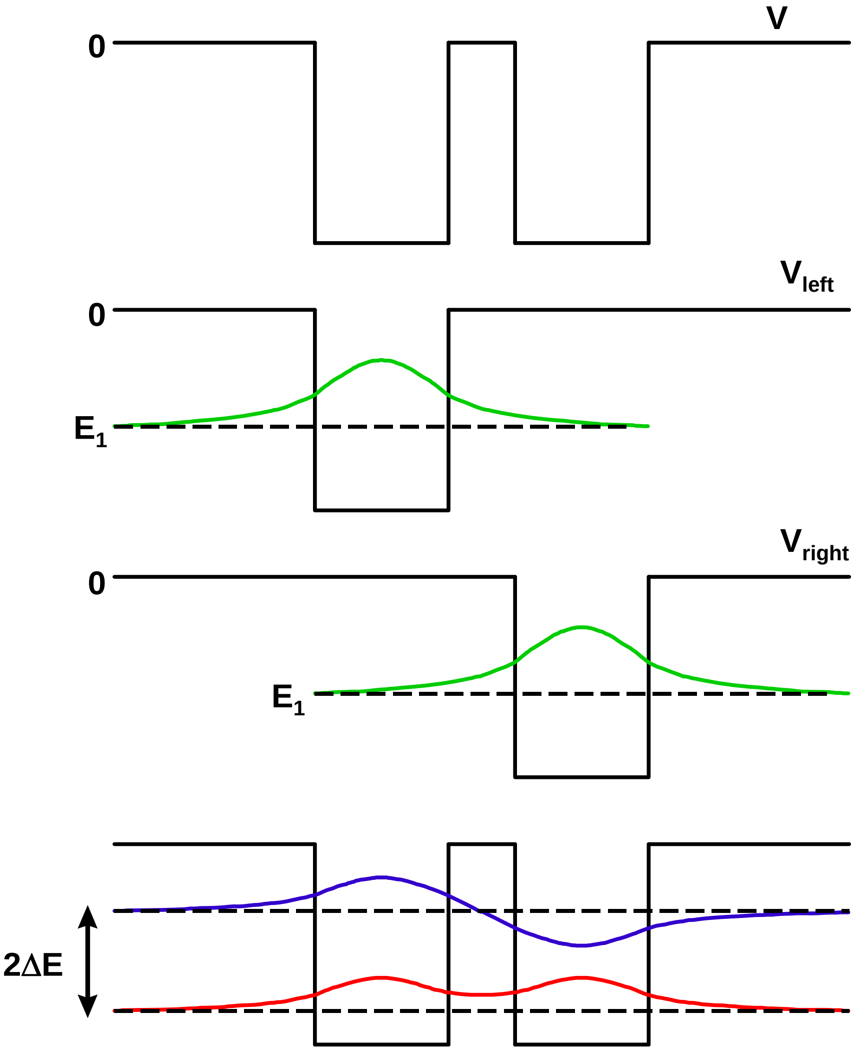
and the upper energy state is associated with

the anti-symmetric combination

(i.e., the wavefunction has the opposite sign in the two wells).

Note now that we can no longer view the states as corresponding to an electron in the "left" well or an electron in the "right" well;

in both states the electron is equally in both wells.



Coupled potential wells - 13

This general form of wavefunctions,

one symmetric, one antisymmetric,

is characteristic of such a symmetric problem,

and is retained even as we perform more accurate calculations.

Bringing two identical systems together leads to

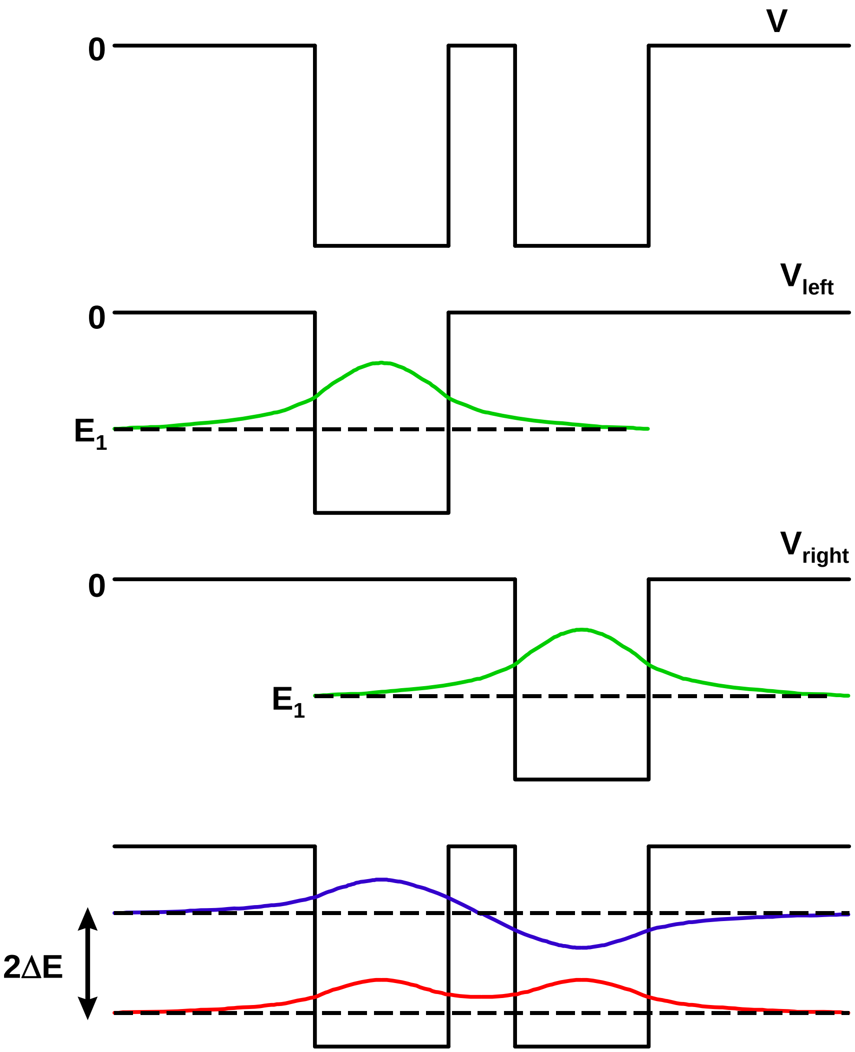
splitting of the degenerate eigenvalues

and

coupling of the states.

This is a very general phenomenon in quantum mechanics.

It occurs, for example, when we bring atoms together to form a crystalline solid,



and leads to the formation of energy bands of very closely spaced states rather than the discrete separated energy levels of the constituent atoms.

A relation to chemical bonding

Note that this calculation has features also found in molecular bonding.

If we have one electron to share between two potential wells,

as we bring these two potential wells together, two possible states emerge,

one of which has lower energy than any of the states the system previously had.

If we think of these potential wells as being analogous to atoms,

we get lower energy in this lowest state by bringing the “atoms” closer.

We would have to add energy to the electron if we were to try to pull the potential wells or “atoms” apart.

Hence this lowest state corresponds to a kind of chemically bonded state.

The actual theory of molecular bonding is more complex than this because it has to account for

multiple electrons in the system, and

potentials that are not simply square wells.

The symmetric and antisymmetric solutions are sometimes called

“bonding”

and

“anti-bonding”

states respectively.

Variational method - 1

Consider an arbitrary quantum mechanical state, $|\phi\rangle$, of some system.

The Hamiltonian of the system is $\hat{H}$,

and we want the expectation value of the energy, $\langle E\rangle$.

Since the Hamiltonian is presumably an appropriate Hermitian operator,

it has some complete set of eigenfunctions, $|\psi_n\rangle$, with associated eigenenergies E_n;

we may not know what they are –

they may be mathematically difficult to calculate –

but we do know that they exist.

(For simplicity here, we assume the eigenvalues are not degenerate.)

Consequently, we can certainly expand any arbitrary state in them,

and so we can write as usual, for some set of expansion coefficients a_i,

$$|\phi\rangle = \sum_i a_i |\psi_i\rangle \tag{6.79}$$

We presume this representation of the state is normalized, so

$$\sum_i |a_i|^2 = 1 \tag{6.80}$$

Variational method - 2

Hence, the expectation value of the energy becomes, as usual,

$$\langle E\rangle = \langle\phi|\hat{H}|\phi\rangle = \sum_i |a_i|^2 E_i \qquad (6.81)$$

We also presume for convenience here that

we have ordered all of the eigenfunctions in order of the eigenvalues, starting with the smallest, E_1.

What is the smallest possible expectation value of the energy that we can have for any state $|\phi\rangle$?

The answer is obvious from Eq. (6.81).

The smallest energy expectation value we can have is E_1,

with correspondingly $a_1 = 1$ and all the other expansion coefficients zero.

If we made one of the other expansion coefficients a_j finite,

then the energy expectation value would become,

using the normalization sum Eq. (6.80), $\sum_i |a_i|^2 = 1$,

$$\begin{aligned}\langle E\rangle &= |a_1|^2 E_1 + |a_j|^2 E_j = \left(1-|a_j|^2\right)E_1 + |a_j|^2 E_j = E_1 + |a_j|^2\left(E_j - E_1\right)\\ &> E_1\end{aligned} \qquad (6.82)$$

i.e., the energy would have to increase.

Variational method - 3

This property

> ***that the lowest possible expectation value of the energy is for the lowest energy eigenstate,***

allows us to construct an approximate method of solution of quantum mechanical problems for the ground state (the lowest energy state),

> ***and especially for its energy.***

The key idea is that we choose some mathematical form of state, called

> ***the trial wavefunction,***
>
> > **that is mathematically convenient for us**
> >
> > **and which we believe reasonably fits at least the expected qualitative features of the ground state,**
>
> ***and then vary some parameter in this mathematical form to minimize the resulting expectation value of the energy***

As a result of this minimization with respect to variation,

> ***this is known as the variational method.***

Variational method - 4

If we use this method, we do not formally know how accurate our result is for the energy,

but we do know that lower is better,

and we can if we wish keep refining our mathematical form so as to reduce the resulting calculated energy expectation value.

Why would we use such a method?

(i) it allows us to calculate an approximation for the ground state energy without having to solve for the exact eigenfunctions of any problem.

(ii) if we are careful in the choice of the form of the function to be varied,

so that the algebra of minimization gives simple analytic results,

we may get approximate analytic results for some perturbation.

Why does this method return even reasonable answers?

Go back to a point we discussed in relation to perturbation theory above;

we can get good answers for energies even with approximate wavefunctions;

remember that the first order energy correction uses the zero order wavefunction, for example.

Variational method for other levels

The variational approach can be progressively extended to higher levels of the system

> ***if we force the next trial wavefunction to be mathematically orthogonal to all the previous (lower energy) ones.***

As far as numerical calculations are concerned,

> ***the variational method is nearly always used only for ground states.***

Variational method and eigenfunctions

The variational method points out a basic, exact property of eigenfunctions and eigenvalues that is actually obvious from the equation (6.81)

$$\langle E\rangle = \langle\phi|\hat{H}|\phi\rangle = \sum_i |a_i|^2 E_i \ .$$

The eigenfunction corresponding to the lowest eigenvalue is that function that minimizes the expectation value.

The eigenfunction corresponding to the second eigenvalue is that function that minimizes the expectation value,

subject to the constraint that it is orthogonal to the first eigenfunction.

This property extends to higher eigenfunctions,

with successive eigenfunctions constrained orthogonal to the previous ones.

Indeed, this successive minimization property can be used mathematically to define eigenfunctions and eigenvalues.

Example of variational method - 1

We can calculate our example problem of an electron in an infinitely deep potential well with applied field.

We use as our trial function an unknown linear combination of the first two states of the infinitely deep quantum well,

though variational calculations more commonly choose some function unrelated to exact eigenfunctions of any problem.

Hence, our trial function is

$$\phi_{trial}\left(\xi, a_{\mathrm{var}}\right) = \frac{\sqrt{2}}{\sqrt{1+a_{\mathrm{var}}^2}}\left(\sin \pi\xi + a_{\mathrm{var}} \sin 2\pi\xi\right) \quad (6.83)$$

where a_{var} is the parameter we will vary to minimize the energy expectation value.

Note that we have normalized this wavefunction by dividing by $\sqrt{1+a_{\mathrm{var}}^2}$.

Example of variational method - 2

The expectation value of the energy then becomes, as a function of the parameter a_{var},

$$\left\langle E\left(a_{\text{var}}\right)\right\rangle = \frac{1}{1+a_{\text{var}}^{2}}\left[\int_{0}^{1}\left(\sqrt{2}\sin\pi\xi + a_{\text{var}}\sqrt{2}\sin 2\pi\xi\right)\right] \times\left(-\frac{1}{\pi^{2}}\frac{\partial^{2}}{\partial\xi^{2}} + \mathrm{f}\left(\xi - 1/2\right)\right)\left(\sqrt{2}\sin\pi\xi + a_{\text{var}}\sqrt{2}\sin 2\pi\xi\right)d\xi \qquad (6.84)$$

Using

the result

$$\int_{0}^{1}\sin\pi\xi\left(\xi - 1/2\right)\sin 2\pi\xi \, d\xi = -\frac{8}{9\pi^{2}}, \qquad (6.85)$$

the known eigenenergies of the unperturbed problem,

and the orthogonality of the sine functions,

Eq. (6.84) becomes

$$\left\langle E\left(a_{\text{var}}\right)\right\rangle = \frac{1}{1+a_{\text{var}}^{2}}\left[\varepsilon_{1}\left(1+4a_{\text{var}}^{2}\right) - \frac{32a_{\text{var}}\mathrm{f}}{9\pi^{2}}\right] \qquad (6.86)$$

Example of variational method - 3

Now to find the minimum in this expectation value,

we take the derivative, with respect to a_{var}***, of***

$$\langle E(a_{\text{var}})\rangle = \frac{1}{1+a_{\text{var}}^2}\left[\varepsilon_1\left(1+4a_{\text{var}}^2\right)-\frac{32a_{\text{var}}\mathrm{f}}{9\pi^2}\right]$$

to obtain

$$\frac{d\langle E(a_{\text{var}})\rangle}{da_{\text{var}}} = \frac{2}{9\pi^2}\,\frac{16\mathrm{f}a_{\text{var}}^2+27\pi^2a_{\text{var}}-16\mathrm{f}}{\left(1+a_{\text{var}}^2\right)^2} \tag{6.87}$$

This derivative is zero when the quadratic in the numerator is zero.

The root that gives the lowest value of $\langle E(a_{\text{var}})\rangle$ **is**

$$a_{\text{var min}} = \frac{-27\pi^2+\sqrt{\left(27\pi^2\right)^2+1024\mathrm{f}^2}}{32\mathrm{f}} \tag{6.88}$$

Example of variational method - 4

For $\mathrm{f} = 3$ in our example,

we find $a_{\text{var min}} \cong 0.175$,

which compares with

0.174 from the finite basis subset method and

0.180 from the perturbation calculation.

The corresponding energy expectation value,

which is the approximation to the ground state energy in the presence of the field, is,

substituting the value of $a_{\text{var min}}$ back into (6.86),

$$\left\langle E\left(0.175\right)\right\rangle \cong 0.906,$$

which compares with

0.904 from the finite basis subset method and

0.9025 from the perturbation calculation.

Variational method and finite basis method

Incidentally, it can be shown that

- ***a variational approach like this***
  - **using the same basis functions as a finite basis subset calculation**
- ***gives exactly the same results as that finite basis subset method;***

If we had calculated the finite basis subset method using only the first two basis functions,

- ***we would get exactly the same answer as our variational calculation here.***
  - **This is fundamentally because of the minimization property of eigenfunctions and eigenvalues discussed above.**

Time-dependent perturbation theory - 1

Reading – Sections 7.1 – Section 7.2 up to the end of the paragraph after Eq. (7.25)

Time-dependent perturbations

Simple oscillating perturbations

Time-dependent perturbation theory - 1

For time-dependent problems,

we consider some time-dependent perturbation,

$\hat{H}_p(t)$,

to an unperturbed Hamiltonian,

$\hat{H}_o$,

that is itself not dependent on time.

The total Hamiltonian is then

$$\hat{H} = \hat{H}_o + \hat{H}_p(t) \tag{7.1}$$

To deal with such a situation,

we return to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \tag{7.2}$$

where now the ket $|\Psi\rangle$ *is time-varying in general.*

Time-dependent perturbation theory - 2

With $|\psi_n\rangle$ and E_n as the energy eigenfunctions and eigenvalues of the time-independent equation

$$\hat{H}_o|\psi_n\rangle = E_n|\psi_n\rangle \tag{7.3}$$

we expand the solution of the time-dependent Schrödinger equation $|\Psi\rangle$ as

$$|\Psi\rangle = \sum_n a_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle \tag{7.4}$$

Note we chose to include the time-dependent factor $\exp(-iE_n t/\hbar)$ explicitly in the expansion.

We could have left that out, and merely included it in $a_n(t)$.

It is usually better to take out any major underlying time dependence

leaving the time dependence of $a_n(t)$ to deal only with the additional changes.

Time-dependent perturbation theory - 3

Now we can substitute the expansion (7.4)

$$|\Psi\rangle = \sum_n a_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle$$

into the time-dependent Schrödinger equation (7.2),

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$$

obtaining

$$\sum_n (i\hbar\dot{a}_n + a_n E_n)\exp(-iE_n t/\hbar)|\psi_n\rangle = \sum_n a_n\left(\hat{H}_o + \hat{H}_p(t)\right)\exp(-iE_n t/\hbar)|\psi_n\rangle \qquad (7.5)$$

where

$$\dot{a}_n \equiv \frac{\partial a_n}{\partial t} \qquad (7.6)$$

Using the time-independent Schrödinger equation (7.3) to replace $\hat{H}_o|\psi_n\rangle$ **with** $E_n|\psi_n\rangle$ **leads to the cancellation of terms in** $E_n|\psi_n\rangle$ **from the two sides.**

Now premultiplying by $\langle\psi_q|$ **on both sides of (7.5) leads to**

$$i\hbar\dot{a}_q(t)\exp(-iE_q t/\hbar) = \sum_n a_n(t)\exp(-iE_n t/\hbar)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle \qquad (7.7)$$

We have made no approximations in going from (7.2) $i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$ **to (7.7);**

these are entirely equivalent equations.

Time-dependent perturbation theory - 4

Now we consider a perturbation series.

We introduce the expansion parameter γ just as before,

now writing our perturbation as $\gamma \hat{H}_p$.

As before, we can set this parameter to a value of 1 at the end.

We presume that we can express the expansion coefficients a_n as a power series

$$a_n = a_n^{(0)} + \gamma a_n^{(1)} + \gamma^2 a_n^{(2)} + \cdots \tag{7.8}$$

and we substitute this expansion into Eq. (7.7).

$$i\hbar \dot{a}_q(t)\exp\left(-iE_q t/\hbar\right) = \sum_n a_n(t)\exp\left(-iE_n t/\hbar\right)\left\langle \psi_q \middle| \hat{H}_p(t) \middle| \psi_n \right\rangle$$

Equating powers of γ, we obtain for the zero order term

$$\dot{a}_q^{(0)}(t) = 0 \tag{7.9}$$

The zero order solution simply corresponds to the unperturbed solution,

and hence there is no change in the expansion coefficients in time.

Time-dependent perturbation theory - 5

Repeating the relevant equations

$$a_n = a_n^{(0)} + \gamma a_n^{(1)} + \gamma^2 a_n^{(2)} + \cdots$$

$$i\hbar \dot{a}_q(t)\exp\left(-iE_q t/\hbar\right) = \sum_n a_n(t)\exp\left(-iE_n t/\hbar\right)\left\langle \psi_q \middle| \hat{H}_p(t) \middle| \psi_n \right\rangle$$

For the first order term, we have

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)} \exp\left(i\omega_{qn} t\right)\left\langle \psi_q \middle| \hat{H}_p(t) \middle| \psi_n \right\rangle \qquad (7.10)$$

where we have introduced the notation

$$\omega_{qn} = \left(E_q - E_n\right)/\hbar \qquad (7.11)$$

Note here that the $a_n^{(0)}$ ***are all constants;***

we deduced in Eq. (7.9) that they do not change in time.

They represent the "starting" state of the system at time $t = 0$.

We note now that, if we know

the starting state, and

the perturbing potential and

the unperturbed eigenvalues and eigenfunctions,

we can integrate Eq. (7.10) to obtain the first order, time-dependent correction, $a_q^{(1)}(t)$**, to the expansion coefficients.**

Time-dependent perturbation theory - 6

If we know the new approximate expansion coefficients,

$$a_q \simeq a_q^{(0)} + a_q^{(1)}(t) \tag{7.12}$$

then we know the new wavefunction,

and can calculate the behavior of the system from this new wavefunction.

We can proceed to higher order in this time-dependent perturbation theory.

In general, equating powers of progressively higher order, we obtain

$$\dot{a}_q^{(p+1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(p)} \exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle \tag{7.13}$$

We see that this perturbation theory is also a method of successive approximations,

just like the time-independent perturbation theory.

We calculate each higher order correction from the preceding correction.

Time-dependent perturbation theory - 7

Just as for the time-independent perturbation theory,

- *the time-dependent theory is often most useful for calculating some process to the lowest non-zero order.*

Higher order time-dependent perturbation theory is very useful, for example, for understanding nonlinear optical processes.

- *First order time-dependent perturbation theory gives the ordinary, linear optical properties of materials.*
- *Higher order time-dependent perturbation theory is used to calculate processes such as*
  - second harmonic generation and
  - two photon absorption
- *in nonlinear optics,*
  - processes that are seen routinely with the high intensities of modern lasers.

Simple oscillating perturbations - 1

One of the most useful applications is the case of oscillating perturbations.

We will consider this problem here in first order time-dependent perturbation theory.

For example, the interaction of a monochromatic electromagnetic wave with a material

the perturbation, the electromagnetic field, is varying sinusoidally in time.

Such a sinusoidal perturbation is also called

a harmonic perturbation,

the same use of the term "harmonic" as in the harmonic oscillator.

One common form would be to have an electric field in, say, the z direction

$$\mathrm{E}(t)=\mathrm{E}_o\left[\exp(-i\omega t)+\exp(i\omega t)\right]=2\mathrm{E}_o\cos(\omega t) \tag{7.14}$$

where ω is a positive (angular) frequency.

Simple oscillating perturbations - 2

With

$$\mathrm{E}(t)=\mathrm{E}_o\left[\exp(-i\omega t)+\exp(i\omega t)\right]=2\mathrm{E}_o\cos(\omega t)$$

for an electron,

the resulting electrostatic energy in this field, relative to position $z=0$, gives a perturbing Hamiltonian

$$\hat{H}_p(t)=e\mathrm{E}(t)z=\hat{H}_{po}\left[\exp(-i\omega t)+\exp(i\omega t)\right] \tag{7.15}$$

where, in this case,

$$\hat{H}_{po}=e\mathrm{E}_o z \tag{7.16}$$

Note that this operator does not depend on time.

This particular form of the perturbing Hamiltonian is called

the electric dipole approximation.

In this particular case, this operator is just a scalar function of z,

though in other formulations of this problem it often has stronger operator character.

Simple oscillating perturbations - 3

We will presume that this perturbing Hamiltonian is only “on” for some finite time.

- ***For simplicity, we presume that***
  - **the perturbation starts at time** $t = 0$
  - **and ends at time** $t = t_o$**,**
- ***so formally we have***

$$\begin{aligned} \hat{H}_p(t) &= 0, t < 0 \\ &= \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right], 0 < t < t_p \qquad (7.17) \\ &= 0, t > t_o \end{aligned}$$

To be specific,

- ***we will be interested in a situation where, for times before*** $t = 0$***, the system is in some specific energy eigenstate,*** $|\psi_m\rangle$***.***
  - **We expect that the time-dependent perturbation theory will tell us**
    - *with what probability the system will make transitions into other states.*

Simple oscillating perturbations - 4

With this choice,

all of the $a_n^{(0)}$, the initial expansion coefficients, are zero

except $a_m^{(0)}$, which has the value 1.

With this simplification of the initial state to $|\psi_m\rangle$,

the first order perturbation solution, Eq. (7.10),

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar} \sum_n a_n^{(0)} \exp(i\omega_{qn} t) \langle \psi_q | \hat{H}_p(t) | \psi_n \rangle$$

becomes

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar} \exp(i\omega_{qm} t) \langle \psi_q | \hat{H}_p(t) | \psi_m \rangle \tag{7.18}$$

Simple oscillating perturbations - 5

Then we have, substituting the perturbing Hamiltonian, Eq. (7.17),

$$\begin{aligned}\hat{H}_p(t) &= 0,\, t<0\\ &= \hat{H}_{po}\left[\exp(-i\omega t)+\exp(i\omega t)\right],\, 0<t<t_p\\ &= 0,\, t>t_o\end{aligned}$$

into (7.18) $\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\exp(i\omega_{qm}t)\langle\psi_q|\hat{H}_p(t)|\psi_m\rangle$

and integrating over time

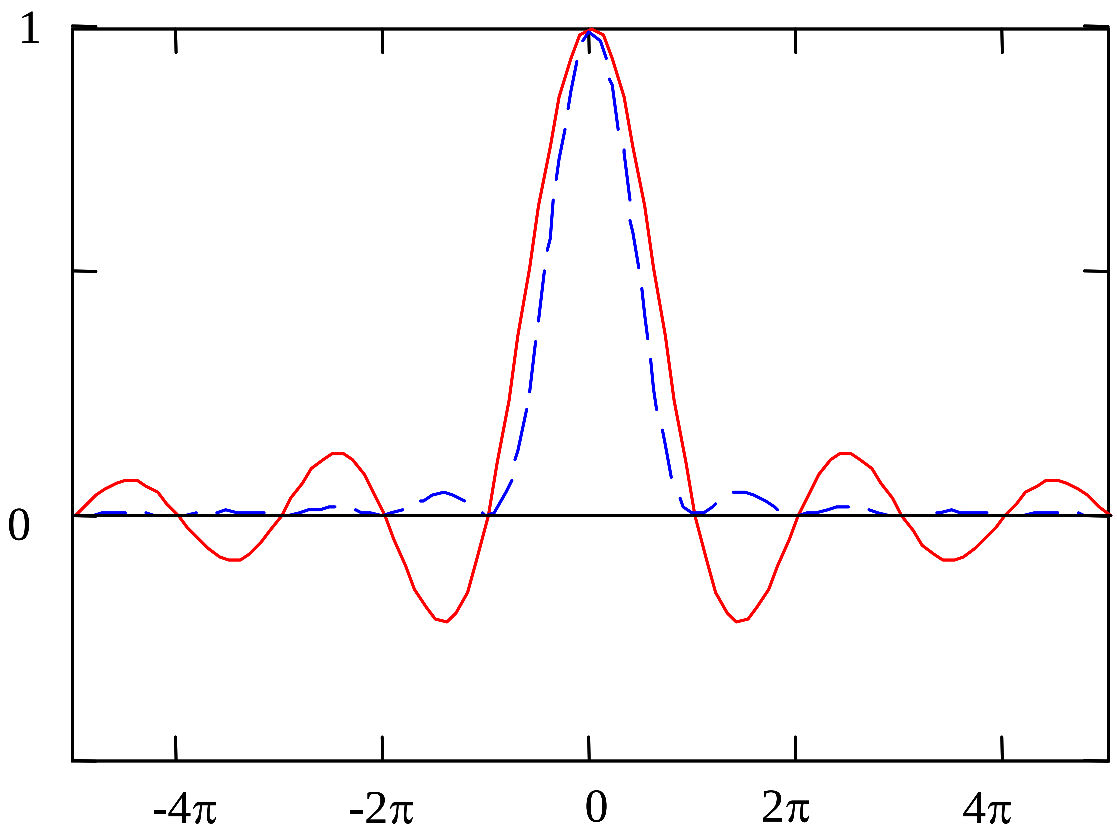
$$a_q^{(1)}(t>t_o) = \frac{1}{i\hbar}\int_0^{t_0}\langle\psi_q|\hat{H}_p(t_1)|\psi_m\rangle\exp(i\omega_{qm}t_1)\,dt_1$$

$$= \frac{1}{i\hbar}\langle\psi_q|\hat{H}_{po}|\psi_m\rangle\int_0^{t_o}\left\{\exp\left[i(\omega_{qm}-\omega)t_1\right]+\exp\left[i(\omega_{qm}+\omega)t_1\right]\right\}dt_1$$

$$= -\frac{1}{\hbar}\langle\psi_q|\hat{H}_{po}|\psi_m\rangle\left\{\frac{\exp\left(i(\omega_{qm}-\omega)t_o\right)-1}{\omega_{qm}-\omega}+\frac{\exp\left(i(\omega_{qm}+\omega)t_o\right)-1}{\omega_{qm}+\omega}\right\}$$

$$= \frac{t_o}{i\hbar}\langle\psi_q|\hat{H}_{po}|\psi_m\rangle\left\{\begin{aligned}&\exp\left[i(\omega_{qm}-\omega)t_o/2\right]\frac{\sin\left[(\omega_{qm}-\omega)t_o/2\right]}{(\omega_{qm}-\omega)t_o/2}\\ &+\exp\left[i(\omega_{qm}+\omega)t_o/2\right]\frac{\sin\left[(\omega_{qm}+\omega)t_o/2\right]}{(\omega_{qm}+\omega)t_o/2}\end{aligned}\right\} \qquad (7.19)$$

Simple oscillating perturbations - 6



Plot of the functions $\frac{\sin x}{x}$ (solid line) and $\left(\frac{\sin x}{x}\right)^2$ (dashed line)

The function $\mathrm{sinc}(x) \equiv (\sin x)/x$ **peaks at 1 for** $x = 0$

It is essentially only appreciably large for $x \cong 0$**,**

which tells us we have a strongly resonant behavior,

with relatively strong perturbations for the frequency ω *close to* $\pm\omega_{qm}$.

Simple oscillating perturbations - 7

What we have now calculated is the new quantum mechanical state for times $t > t_o$, which is, to first order,

$$\left|\Psi\right\rangle \simeq \exp\left(-iE_m t/\hbar\right)\left|\psi_m\right\rangle + \sum_q a_q^{(1)}(t>t_o)\exp\left(-iE_q t/\hbar\right)\left|\psi_q\right\rangle \tag{7.20}$$

with the $a_q^{(1)}(t>t_o)$ given by Eq. (7.19).

$$a_q^{(1)}(t>t_o) = \frac{t_o}{i\hbar}\left\langle\psi_q\right|\hat{H}_{po}\left|\psi_m\right\rangle \left\{ \begin{array}{l} \exp\left[i\left(\omega_{qm}-\omega\right)t_o/2\right]\dfrac{\sin\left[\left(\omega_{qm}-\omega\right)t_o/2\right]}{\left(\omega_{qm}-\omega\right)t_o/2} \\ +\exp\left[i\left(\omega_{qm}+\omega\right)t_o/2\right]\dfrac{\sin\left[\left(\omega_{qm}+\omega\right)t_o/2\right]}{\left(\omega_{qm}+\omega\right)t_o/2} \end{array} \right\}$$

Now that we have established our approximation to the new state,

we can start calculating the time dependence of measurable quantities.

Transition probabilities

In our example here, we chose the system initially to be in the energy eigenstate $|\psi_m\rangle$.

The application of the perturbation has changed the state of the system

We would like to know,

if we were to make a measurement of the energy after the perturbation is over (i.e., for $t > t_o$),

what is the probability that the system will be found in some other state, $|\psi_j\rangle$.

i.e., we want to know the transition probability from state $|\psi_m\rangle$ to $|\psi_j\rangle$.

Transition probability calculation - 1

Provided we are dealing with small perturbations

the probability, $P(j)$, of finding the system in state $|\psi_j\rangle$ is

$$P(j) = \left|a_j^{(1)}\right|^2 \tag{7.21}$$

i.e.,

$$P(j) \simeq \frac{t_o^2}{\hbar^2}\left|\left\langle\psi_j\left|\hat{H}_{po}\right|\psi_m\right\rangle\right|^2 \left\{ \begin{array}{l} \left[\dfrac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\right]^2 + \left[\dfrac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2}\right]^2 \\ +2\cos\left(\omega t_o\right)\dfrac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\dfrac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2} \end{array} \right\} \tag{7.22}$$

The sinc function and its square fall off rapidly for arguments >> 1.

Hence, for sufficiently long t_o,

either one or the other of the two sinc functions in the last term in Eq. (7.22) will be small.

Essentially, as the time t_o is increased, these two sinc line functions get sharper and sharper, and they will eventually not overlap for any value of ω.

Transition probability calculation - 2

Presuming we take t_o sufficiently large, we are left with

$$P(j) \simeq \frac{t_o^2}{\hbar^2}\left|\left\langle\psi_j\middle|\hat{H}_{po}\middle|\psi_m\right\rangle\right|^2 \left\{\left[\frac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\right]^2 + \left[\frac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2}\right]^2\right\} \tag{7.23}$$

We now have some finite probability that the system has changed state from its initial state, $|\psi_m\rangle$, to another "final" state, $|\psi_j\rangle$.

- ***This probability depends on***
  - **the strength of the perturbation squared, and**
  - **specifically on the modulus squared of the matrix element of the perturbation between the initial and final states.**

In the case where the perturbation is the oscillating electric field acting on an electron,

- ***this probability is proportional to the square of the electric field amplitude, E_o^2,***
  - **which in turn is proportional to the intensity I (power per unit area).**
    - *Hence, the probability of making a transition is proportional to the intensity, I.*
- ***This is the kind of behavior we expect for linear optical absorption.***

Absorption and emission terms

What is the meaning of the two different terms in Eq. (7.23)?

$$P(j) \simeq \frac{t_o^2}{\hbar^2}\left|\left\langle \psi_j \middle| \hat{H}_{po} \middle| \psi_m \right\rangle\right|^2 \left\{ \left[\frac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2} \right]^2 + \left[\frac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2} \right]^2 \right\}$$

The first term is significant if $\omega_{jm} \approx \omega$***, i.e., if***

$$\hbar\omega \approx E_j - E_m \qquad (7.24)$$

Since we chose ω **to be a positive quantity,**

this term is significant if we are absorbing energy into the system,

raising from a lower energy state, $\left|\psi_m\right\rangle$, to a higher energy state, $\left|\psi_j\right\rangle$.

We note that the amount of energy we are absorbing is $\approx \hbar\omega$*.*

This term behaves as we would require for absorption of a photon.

By contrast, the second term is significant if $\omega_{jm} \approx -\omega$***, i.e., if***

$$\hbar\omega \approx E_m - E_j \qquad (7.25)$$

This can only be the case if the system is moving

from a higher energy state $\left|\psi_m\right\rangle$*, to a lower energy state,* $\left|\psi_j\right\rangle$*.*

This term behaves as we would require for emission of a photon.

In fact, the process associated with this term is stimulated emission, the process used in lasers.

Time-dependent perturbation theory - 2

Reading – Section 7.2 from the paragraph before Eq. (7.26) – Section 7.3

Simple oscillating perturbations

Fermi's Golden Rule

Refractive index

Absorption - 1

Now let us consider only the case associated with absorption,

presuming we are starting in a lower energy state and transitioning to a higher energy one.

(The treatment of the stimulated emission case is essentially identical, with the energies of the states reversed.)

Then we have

$$P(j) \simeq \frac{t_o^2}{\hbar^2} \left| \left\langle \psi_j \middle| \hat{H}_{po} \middle| \psi_m \right\rangle \right|^2 \left[\frac{\sin\left[\left(\omega_{jm} - \omega \right) t_o / 2 \right]}{\left(\omega_{jm} - \omega \right) t_o / 2} \right]^2 \qquad (7.26)$$

Analyzing the case of a transition between one state and exactly one other state using this approach has some formal difficulties;

as we let the time t_o ***become arbitrarily large,***

the form of the sinc squared term becomes arbitrarily sharp in ω**, and unless we get the frequency exactly correct, we will get no absorption.**

This problem can be resolved for calculating, for example, transitions between states in atoms,

though it requires a more sophisticated analysis than we discuss here

specifically, the use of density matrices

Absorption - 2

Essentially,

we end up replacing the sinc squared function with a Lorentzian line whose width in angular frequency is $\sim 1/T_2$***,***

where T_2 **is the time between scattering events (e.g., collisions with other atoms) that disrupt at least the phase of the quantum mechanical oscillation of the wave function.**

We can rationalize such a change based on an energy-time uncertainty relation;

if the system only exists in its original form for some time T_2***,***

then we should expect that the energy of the transition is only defined

in energy to $\sim \pm\hbar/2T_2$*, or*

in angular frequency to $\sim \pm 1/2T_2$*.*

Absorption into dense sets of possible transitions - 1

Fortunately, however, a major class of problems can be analyzed using the present approach.

Suppose we have not one possible transition with energy difference $\hbar\omega_{jm}$,

but a whole dense set of such possible transitions in the vicinity of the photon energy $\hbar\omega$,

all with essentially identical matrix elements.

This kind of situation occurs routinely in solids.

We presume that this set is very dense,

with a density $g_J(\hbar\omega)$ per unit energy near the photon energy $\hbar\omega$.

($g_J(\hbar\omega)$ is sometimes known as a "joint density of states" since it refers to transitions between states, not the density of states of only the starting or ending states.)

Absorption into dense sets of possible transitions - 2

Then adding up all the probabilities for absorbing transitions, we obtain a total probability of absorption by this set of transitions of

$$P_{tot} \simeq \frac{t_o^2}{\hbar^2}\left|\langle\psi_j|\hat{H}_{po}|\psi_m\rangle\right|^2 \int\left[\frac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\right]^2 g_J\left(\hbar\omega_{jm}\right)d\hbar\omega_{jm} \qquad (7.27)$$

$g_J\left(\hbar\omega\right)$ ***is essentially constant over any small energy range,***

and the sinc squared term is essentially quite narrow in ω_{jm},

hence we can take $g_J\left(\hbar\omega_{jm}\right)$ out of the integral as, approximately, $g_J\left(\hbar\omega\right)$.

Formally changing the variable in the integral to $x=\left(\omega_{jm}-\omega\right)t_o/2$ gives

$$P_{tot} \simeq \frac{t_o^2}{\hbar^2}\left|\langle\psi_j|\hat{H}_{po}|\psi_m\rangle\right|^2 \frac{2\hbar}{t_o} g_J\left(\hbar\omega\right)\int\left[\frac{\sin x}{x}\right]^2 dx \qquad (7.28)$$

Using the mathematical result

$$\int_{-\infty}^{\infty}\left(\frac{\sin x}{x}\right)^2 dx = \pi \qquad (7.29)$$

we obtain

$$P_{tot} \simeq \frac{2\pi t_o}{\hbar}\left|\langle\psi_j|\hat{H}_{po}|\psi_m\rangle\right|^2 g_J\left(\hbar\omega\right) \qquad (7.30)$$

Fermi's Golden Rule

Now we see that we have a total probability of making some transition that is proportional to the time, t_o that the perturbation is turned on.

This allows us now to deduce a transition rate, or rate of absorption of photons,

$$W = \frac{2\pi}{\hbar}\left|\left\langle \psi_j \middle| \hat{H}_{po} \middle| \psi_m \right\rangle\right|^2 g_J\left(\hbar\omega\right) \qquad (7.31)$$

This result is sometimes known as "Fermi's Golden Rule" or, more completely, "Fermi's Golden Rule No. 2".

It is one of the most useful results of time-dependent perturbation theory,

and forms the basis for calculation of, for example, the optical absorption spectra of solids.

Though we have discussed it here in the context of optical absorption, it applies to any simple harmonic perturbation.

Alternative statement of Fermi's Golden Rule

This rule is sometimes also stated in the form

$$w_{jm} = \frac{2\pi}{\hbar}\left|\left\langle \psi_j \middle| \hat{H}_{po} \middle| \psi_m \right\rangle\right|^2 \delta\left(E_{jm} - \hbar\omega\right) \tag{7.32}$$

where w_{jm} is the transition rate between the specific states $\left|\psi_m\right\rangle$ and $\left|\psi_j\right\rangle$,

from which one calculates the total transition rate involving all the possible similar transitions in the neighborhood as

$$W = \int w_{jm} g_J\left(\hbar\omega_{jm}\right) d\hbar\omega_{jm} \tag{7.33}$$

which gives the expression (7.31).

Refractive index

We show how to calculate refractive index quantum mechanically using first-order time-dependent perturbation theory.

In classical electromagnetism, the relation between electric field and polarization for the linear case is

$$\mathsf{P} = \varepsilon_o \chi \mathsf{E} \qquad (7.34)$$

where

χ *is the susceptibility and*

ε_o *is the permittivity of free space.*

The refractive index, n_r***, can be deduced through the relation***

$$n_r = \sqrt{1+\chi} \qquad (7.35)$$

(at least if the material is transparent (non-absorbing) at the frequencies of interest).

Hence, if we can calculate the proportionality between P ***and*** E***, we can deduce the refractive index.***

Calculation of refractive index

Consider a system with a single electron,

or in which our interactions are only with a single electron.

Classically the dipole moment, μ_{dip} associated with moving a single electron through a distance z is, by definition,

$$\mu_{dip} = -ez \tag{7.36}$$

(the minus sign arises because the electron charge is negative).

The polarization P is the dipole moment per unit volume,

and so the quantum mechanical expectation value of the polarization is

$$\langle \mathrm{P} \rangle = \frac{-e\langle z \rangle}{V} \tag{7.37}$$

where V is the volume of the system.

Our quantum mechanical task of calculating refractive index reduces essentially to calculating $\langle \mathrm{P} \rangle$.

First-order perturbation calculation - 1

Since we are working in first-order perturbation theory, we can write the total state of the system as, approximately,

$$|\Psi\rangle = |\Phi^{(0)}\rangle + |\Phi^{(1)}\rangle \tag{7.38}$$

where we note now that we are dealing with the full time-dependent state vectors (kets).

Here

$|\Phi^{(0)}\rangle$ *is the unperturbed (time-dependent) state vector, and*

$|\Phi^{(1)}\rangle$ *is the first-order (time-dependent) correction*

$$|\Phi^{(1)}\rangle = \sum_n a_n^{(1)}(t)\exp(-i\omega_n t)|\psi_n\rangle \tag{7.39}$$

where

$$\omega_n = E_n / \hbar \tag{7.40}$$

and $|\psi_n\rangle$ are the time-independent energy eigenfunctions of the unperturbed system.

First-order perturbation calculation - 2

With such a state vector, $|\Psi\rangle = |\Phi^{(0)}\rangle + |\Phi^{(1)}\rangle$ (7.38), the expectation value of the polarization would be

$$\begin{aligned}\langle \mathsf{P}\rangle &= -\frac{e}{V}\langle\Psi|z|\Psi\rangle \\ &= -\frac{e}{V}\left[\langle\Phi^{(0)}|z|\Phi^{(0)}\rangle + \langle\Phi^{(1)}|z|\Phi^{(0)}\rangle + \langle\Phi^{(0)}|z|\Phi^{(1)}\rangle + \langle\Phi^{(1)}|z|\Phi^{(1)}\rangle\right]\end{aligned} \qquad (7.41)$$

The first term

$$-e\langle\Phi^{(0)}|z|\Phi^{(0)}\rangle$$

is just the static dipole moment of the material in its unperturbed state, so we will not consider it further.

The fourth term,

$$-e\langle\Phi^{(1)}|z|\Phi^{(1)}\rangle$$

is second order in the perturbation, and hence, in this first order calculation, we drop it also.

First-order perturbation calculation - 3

So,

noting that $\langle \Phi^{(1)} | z | \Phi^{(0)} \rangle = \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle^*$

(which follows from the Hermiticity of z as an operator),

we have

$$\langle \mathsf{P} \rangle = -\frac{2e}{V} \mathrm{Re}\left[\langle \Phi^{(0)} | z | \Phi^{(1)} \rangle \right] \tag{7.42}$$

For the sake of definiteness, we now presume that the system is initially in the eigenstate m, i.e.,

$$|\Phi^{(0)}\rangle = \exp(-i\omega_m t)|\psi_m\rangle \tag{7.43}$$

Hence, using the expansion (7.39) for $|\Phi^{(1)}\rangle$

$$|\Phi^{(1)}\rangle = \sum_n a_n^{(1)}(t)\exp(-i\omega_n t)|\psi_n\rangle$$

we have, from (7.42),

$$\langle \mathsf{P} \rangle = -\frac{2e}{V} \mathrm{Re}\left[\sum_n a_n^{(1)}(t)\exp(i\omega_{mn} t)\langle \psi_m | z | \psi_n \rangle \right] \tag{7.44}$$

First-order perturbation calculation - 4

We are interested here in the steady-state situation with a continuous oscillating field,

and we take the perturbing Hamiltonian (7.15)

$$\hat{H}_p(t) = e\mathrm{E}(t)z = \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right]$$ *as valid for all times.*

We can rewrite Eq. (7.18)

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\exp(i\omega_{qm}t)\langle\psi_q|\hat{H}_p(t)|\psi_m\rangle$$

as

$$\dot{a}_q^{(1)}(t) = \frac{e\mathrm{E}_o}{i\hbar}\langle\psi_q|z|\psi_m\rangle\exp(i\omega_{qm}t)\left[\exp(-i\omega t) + \exp(i\omega t)\right] \qquad (7.45)$$

to obtain

$$a_q^{(1)}(t) = -\frac{e\mathrm{E}}{\hbar}\langle\psi_q|z|\psi_m\rangle\left[\frac{\exp\left[i(\omega_{qm}-\omega)t\right]}{(\omega_{qm}-\omega)} + \frac{\exp\left[i(\omega_{qm}+\omega)t\right]}{(\omega_{qm}+\omega)}\right] \qquad (7.46)$$

First-order perturbation calculation - 5

Substituting (7.46)

$$a_q^{(1)}(t) = -\frac{e\mathsf{E}}{\hbar}\langle\psi_q|z|\psi_m\rangle\left[\frac{\exp\left[i(\omega_{qm}-\omega)t\right]}{(\omega_{qm}-\omega)}+\frac{\exp\left[i(\omega_{qm}+\omega)t\right]}{(\omega_{qm}+\omega)}\right]$$

into (7.44) $\langle\mathsf{P}\rangle = -\frac{2e}{V}\mathrm{Re}\left[\sum_n a_n^{(1)}(t)\exp(i\omega_{mn}t)\langle\psi_m|z|\psi_n\rangle\right]$ gives

$$\langle\mathsf{P}\rangle = \frac{2e^2\mathsf{E}_o}{\hbar V}\mathrm{Re}\sum_n|\langle\psi_m|z|\psi_n\rangle|^2\exp(i\omega_{mn}t)\left[\frac{\exp\left[i(\omega_{nm}-\omega)t\right]}{(\omega_{nm}-\omega)}+\frac{\exp\left[i(\omega_{nm}+\omega)t\right]}{(\omega_{nm}+\omega)}\right]$$

$$= \frac{2e^2\mathsf{E}_o}{\hbar V}\sum_n|\langle\psi_m|z|\psi_n\rangle|^2\left[\frac{\cos(-\omega t)}{(\omega_{nm}-\omega)}+\frac{\cos(\omega t)}{(\omega_{nm}+\omega)}\right] \tag{7.47}$$

$$= \frac{2e^2\mathsf{E}_o\cos(\omega t)}{\hbar V}\sum_n|\langle\psi_m|z|\psi_n\rangle|^2\left[\frac{1}{(\omega_{nm}-\omega)}+\frac{1}{(\omega_{nm}+\omega)}\right]$$

and so we have, from (7.34) $\mathsf{P} = \varepsilon_o\chi\mathsf{E}$,

$$\chi = \frac{e^2}{\varepsilon_o\hbar V}\sum_n|\langle\psi_m|z|\psi_n\rangle|^2\left[\frac{1}{(\omega_{nm}-\omega)}+\frac{1}{(\omega_{nm}+\omega)}\right] \tag{7.48}$$

from which we deduce the refractive index, n_r, from Eq. (7.35) $n_r = \sqrt{1+\chi}$, completing our calculation of refractive index.

Relation between absorption and refractive index - 1

Note a key difference

- *For absorption, the frequency ω must match the transition frequency ω_{nm} very closely for that particular transition to give rise to absorption of photons.*
- *For the refractive index, the contribution of a particular possible transition $|\psi_m\rangle \rightarrow |\psi_n\rangle$ to the susceptibility (and hence the refractive index) is finite*
  - **even when the frequencies do not match exactly or even closely;**
    - *that contribution to the susceptibility rises steadily as ω rises towards ω_{nm}.*

Note that

- *if we have an absorbing transition at some frequency ω_{nm},*
  - **it contributes to refractive index at all frequencies.**
- *refractive index (in a region where the material is transparent) arises entirely because of the absorption at other frequencies.*
- *if there is a refractive index different from unity then there must be absorption at some other frequency or frequencies.*

Relation between absorption and refractive index - 2

The fundamental relation between refractive index and absorption is known from classical physics,

and is expressed through the so-called Kramers-Kronig relations.

The derivation of those relations is entirely mathematical,

shedding no light on the physical mechanism whereby absorption and refractive index are related.

With our quantum mechanical expressions for these two processes,

we can understand any particular aspect in the relation between the two.

In the quantum mechanical picture, we find that,

even though we are in the transparent region of the material,

there are finite occupation probabilities for all of the states of the system.

such probabilities are essential if the material has a polarization

The polarization arises because the charges in the material change their physical wavefunctions in response to the field,

mixing in other states of the system in response to the perturbation.

If we examined the expectation value of the energy of the material,

we would also find quite real energy stored in the material as a result.

Time-dependent perturbation theory - 3

Reading – Section 7.4

Nonlinear optical coefficients

Nonlinear optical coefficients

We now extend the formalism of linear refractive index to calculate nonlinear optical effects

Nonlinear optical effects are important in, e.g.,

- ***engineering long-distance fiber optic communication***
- ***electric-field dependence of refractive index used in some optical modulators,***
- ***and a broad variety of effects that generate new optical frequencies by combining existing ones***
  - **such as second and third harmonic generations, difference frequency mixing, and optical parametric oscillators**

Perturbation classification of nonlinear optical effects

- **Nonlinear optical effects are also an excellent example of higher order time-dependent perturbation theory**
  - ***they show how the perturbation approach generates and classifies different processes.***
    - **Second order time-dependent perturbation theory leads, e.g., to**
      - *second harmonic generation*
      - *linear electro-optic effect*
      - *three-wave mixing.*
    - **Third order theory leads, e.g., to**
      - *intensity dependent refractive index*
      - *refractive index changes proportional to the square of the static electric field*
      - *third harmonic generation and four-wave mixing.*
- **Second and third order cover nearly all processes used practically**
  - ***the strongest effects are generally second-order ones***
    - **though the material needs to be asymmetric in a particular way.**
      - *Isotropic materials or those with a "center of symmetry",*
        - such as glass and non-polar materials such as silicon,
      - *do not show second-order phenomena,*
      - *and their lowest order nonlinear effects are therefore third order phenomena.*

Formalism for nonlinear optical coefficients

Nonlinear optical phenomena are usually weak effects,

We can expand the response of the material, the polarization $\mathsf{P}(t)$, as a power series in the electric field $\mathsf{E}(t)$, i.e.,

$$\frac{\mathsf{P}(t)}{\varepsilon_o} = \chi^{(1)}\mathsf{E}(t) + \chi^{(2)}\mathsf{E}^2(t) + \chi^{(3)}\mathsf{E}^3(t) + \dots \tag{7.49}$$

In general both the electric field E and the polarization P are vectors,

and the susceptibility coefficients $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$, etc., are tensors.

We will neglect such anisotropic effects here and treat the electric field and polarization as always being in the same direction, and hence scalars.

In Eq.(7.49),

$\chi^{(1)}$ ***is simply the linear susceptibility***

$\chi^{(2)}$ ***and*** $\chi^{(3)}$ ***are respectively the second and third order nonlinear susceptibilities.***

Formalism for multiple frequency components in the field

Many nonlinear optical effects involve multiple different frequencies

For two frequency components, at ω_1 and ω_2, the total field is

$$\begin{aligned}\mathsf{E}(t) &= 2\mathsf{E}_{o1}\cos(\omega_1 t+\delta_1)+2\mathsf{E}_{o2}\cos(\omega_2 t+\delta_2) \\ &= \mathsf{E}_{o1}\left\{\exp\left[-i(\omega_1 t+\delta_1)\right]+\exp\left[i(\omega_1 t+\delta_1)\right]\right\}+\mathsf{E}_{o2}\left\{\exp\left[-i(\omega_2 t+\delta_2)\right]+\exp\left[i(\omega_2 t+\delta_2)\right]\right\}\end{aligned} \quad (7.50)$$

where we formally allow the two fields to have different phase angles δ_1 and δ_2.

Another way of writing (7.50) is

$$\mathsf{E}(t)=\sum_s \mathsf{E}(\omega_s)\exp(-i\omega_s t) \quad (7.51)$$

where

$$\mathsf{E}(\omega_s)=\mathsf{E}_{os}\exp(-i\delta_s) \quad (7.52)$$

and the sum now also includes the "negative" frequencies, $-\omega_1$ and $-\omega_2$.

Hence there are four terms in the sum (7.51) for this two frequency case, corresponding to the four terms in the second line of Eq. (7.50).

Note also that

$$\mathsf{E}(-\omega_s)=\mathsf{E}^*(\omega_s) \quad (7.53)$$

as can be deduced from Eq. (7.52),

and is required for the actual electric field to be real.

We keep the form (7.51) as we extend to more different frequency components in the electric field.

Formal calculation of perturbative corrections - 1

We consider nonlinearities up to third order in electric field (i.e., up to $\chi^{(3)}$),

and hence consider up to third order time-dependent perturbation corrections.

Now we use expression (7.51) for the electric field,

and hence having a perturbing Hamiltonian

$$\hat{H}_p(t) = e\mathrm{E}(t)z = ez\sum_s \mathrm{E}(\omega_s)\exp(-i\omega_s t) \qquad (7.54)$$

Presuming the system starts in state m, as in Eq. (7.18)

$$\dot{a}_i^{(1)}(t) = \frac{1}{i\hbar}\exp(i\omega_{im}t)\langle\psi_i|\hat{H}_p(t)|\psi_m\rangle$$

or (7.45) $$\dot{a}_q^{(1)}(t) = \frac{e\mathrm{E}_o}{i\hbar}\langle\psi_q|z|\psi_m\rangle\exp(i\omega_{qm}t)\left[\exp(-i\omega t)+\exp(i\omega t)\right]$$

we have

$$\dot{a}_q^{(1)}(t) = \frac{-\mu_{qm}}{i\hbar}\sum_s \mathrm{E}(\omega_s)\exp\left[i(\omega_{qm}-\omega_s)t\right] \qquad (7.55)$$

where we define electric dipole moment between states

$$\mu_{qm} = -e\langle\psi_q|z|\psi_m\rangle \qquad (7.56)$$

Formal calculation of perturbative corrections - 2

Integrating Eq. (7.55)

$$\dot{a}_q^{(1)}(t)=\frac{-\mu_{qm}}{i\hbar}\sum_s \mathsf{E}(\omega_s)\exp\left[i(\omega_{qm}-\omega_s)t\right]$$

over time, we have

$$a_q^{(1)}(t)=\frac{1}{\hbar}\sum_s \frac{\mu_{qm}\mathsf{E}(\omega_s)}{(\omega_{qm}-\omega_s)}\exp\left[i(\omega_{qm}-\omega_s)t\right] \tag{7.57}$$

We may then use the relation (7.13)

$$\dot{a}_q^{(p+1)}(t)=\frac{1}{i\hbar}\sum_n a_n^{(p)}\exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle$$

to calculate subsequent levels of perturbative correction from the preceding one, to obtain

$$\begin{aligned}\dot{a}_j^{(2)}(t)&=\frac{-1}{i\hbar}\sum_q a_q^{(1)}\mu_{jq}\sum_u \mathsf{E}(\omega_u)\exp\left[i(\omega_{jq}-\omega_u)t\right]\\&=\frac{-1}{i\hbar^2}\sum_q\sum_{s,u}\frac{\mu_{jq}\mathsf{E}(\omega_u)\mu_{qm}\mathsf{E}(\omega_s)}{(\omega_{qm}-\omega_s)}\exp\left[i(\omega_{jm}-\omega_s-\omega_u)t\right]\end{aligned} \tag{7.58}$$

where we have noted that

$$\omega_{jq}+\omega_{qm}=\omega_{jm} \tag{7.59}$$

Formal calculation of perturbative corrections - 2

Hence

$$a_j^{(2)}(t)=\frac{1}{\hbar^2}\sum_q\sum_{s,u}\frac{\mu_{jq}\mathrm{E}(\omega_u)\mu_{qm}\mathrm{E}(\omega_s)}{(\omega_{jm}-\omega_s-\omega_u)(\omega_{qm}-\omega_s)}\exp\left[i(\omega_{jm}-\omega_s-\omega_u)t\right] \tag{7.60}$$

Similarly,

$$\begin{aligned}\dot{a}_k^{(3)}&=\frac{-1}{i\hbar}\sum_j a_j^{(2)}\mu_{kj}\sum_v\mathrm{E}(\omega_v)\exp\left[i(\omega_{kj}-\omega_v)t\right]\\&=\frac{-1}{i\hbar^3}\sum_{j,q}\sum_{s,u,v}\frac{\mu_{kj}\mathrm{E}(\omega_v)\mu_{jq}\mathrm{E}(\omega_u)\mu_{qm}\mathrm{E}(\omega_s)}{(\omega_{jm}-\omega_s-\omega_u)(\omega_{qm}-\omega_s)}\exp\left[i(\omega_{km}-\omega_s-\omega_u-\omega_v)t\right]\end{aligned} \tag{7.61}$$

and so

$$\begin{aligned}a_k^{(3)}(t)=\frac{1}{\hbar^3}\sum_{j,q}\sum_{s,u,v}&\frac{\mu_{kj}\mathrm{E}(\omega_v)\mu_{jq}\mathrm{E}(\omega_u)\mu_{qm}\mathrm{E}(\omega_s)}{(\omega_{km}-\omega_s-\omega_u-\omega_v)(\omega_{jm}-\omega_s-\omega_u)(\omega_{qm}-\omega_s)}\\&\times\exp\left[i(\omega_{km}-\omega_s-\omega_u-\omega_v)t\right]\end{aligned} \tag{7.62}$$

Note in these sums,

j ***and*** q ***are indices going over all possible states of the system, and***

s***,*** u***, and*** v ***are indices going over all the frequencies of electric fields,***

including both their positive and negative versions.

Formal calculation of linear and nonlinear susceptibilities - 1

In general, including all possible terms in the polarization up to third order in the perturbation, we have,

now formally write the expectation value of the polarization as being the observable quantity,

and with $\mu = -ez$ ***being formally the dipole moment (operator)***

$$\begin{aligned}\langle \mathrm{P}(t)\rangle &= \frac{1}{V}\langle \Psi|\mu|\Psi\rangle \cong \frac{1}{V}\left\langle \Phi^{(0)}+\Phi^{(1)}+\Phi^{(2)}+\Phi^{(3)}\middle|\mu\middle|\Phi^{(0)}+\Phi^{(1)}+\Phi^{(2)}+\Phi^{(3)}\right\rangle \\ &\cong \left\langle \mathrm{P}^{(0)}(t)\right\rangle + \left\langle \mathrm{P}^{(1)}(t)\right\rangle + \left\langle \mathrm{P}^{(2)}(t)\right\rangle + \left\langle \mathrm{P}^{(3)}(t)\right\rangle\end{aligned} \qquad (7.63)$$

Formal calculation of linear and nonlinear susceptibilities - 2

The polarization terms are

(i) $\left\langle \mathrm{P}^{(0)} \right\rangle = \frac{1}{V} \left\langle \Phi^{(0)} \middle| \mu \middle| \Phi^{(0)} \right\rangle$ (7.64)

is the static polarization of the material,

(ii) $\left\langle \mathrm{P}^{(1)}(t) \right\rangle = \frac{1}{V} \left(\left\langle \Phi^{(0)} \middle| \mu \middle| \Phi^{(1)} \right\rangle + \left\langle \Phi^{(1)} \middle| \mu \middle| \Phi^{(0)} \right\rangle \right)$ (7.65)

is the linear polarization giving linear refractive index

(iii) $\left\langle \mathrm{P}^{(2)}(t) \right\rangle = \frac{1}{V} \left(\left\langle \Phi^{(0)} \middle| \mu \middle| \Phi^{(2)} \right\rangle + \left\langle \Phi^{(2)} \middle| \mu \middle| \Phi^{(0)} \right\rangle + \left\langle \Phi^{(1)} \middle| \mu \middle| \Phi^{(1)} \right\rangle \right)$ (7.66)

is the second order polarization, giving rise to phenomena such as second harmonic generation, and sum and difference frequency mixing,

(iv) $\left\langle \mathrm{P}^{(3)}(t) \right\rangle = \frac{1}{V} \left(\left\langle \Phi^{(0)} \middle| \mu \middle| \Phi^{(3)} \right\rangle + \left\langle \Phi^{(3)} \middle| \mu \middle| \Phi^{(0)} \right\rangle + \left\langle \Phi^{(1)} \middle| \mu \middle| \Phi^{(2)} \right\rangle + \left\langle \Phi^{(2)} \middle| \mu \middle| \Phi^{(1)} \right\rangle \right)$ (7.67)

is the third order polarization, giving rise to phenomena such as third harmonic generation, nonlinear refractive index, and four-wave mixing.

Linear susceptibility

We have already calculated this, but we briefly repeat the result in the present notation as used in nonlinear optics.

Since by choice $\left|\Phi^{(0)}\right\rangle = \exp\left(-i\omega_m t\right)\left|\psi_m\right\rangle$***, and using the standard expansion notation (7.39)***

$$\left|\Phi^{(1)}\right\rangle = \sum_n a_n^{(1)}\left(t\right)\exp\left(-i\omega_n t\right)\left|\psi_n\right\rangle$$

for $\left|\Phi^{(1)}\right\rangle$***, we have,***

from the definition (7.65) $\left\langle \mathsf{P}^{(1)}\left(t\right)\right\rangle = \dfrac{1}{V}\left(\left\langle \Phi^{(0)}\middle|\mu\middle|\Phi^{(1)}\right\rangle + \left\langle \Phi^{(1)}\middle|\mu\middle|\Phi^{(0)}\right\rangle\right)$ **above**

$$\left\langle \mathsf{P}^{(1)}\left(t\right)\right\rangle = \frac{1}{V}\frac{1}{\hbar}\sum_q\sum_s \left\{ \begin{aligned} &\frac{\mu_{mq}\mu_{qm}}{\omega_{qm}-\omega_s}\mathsf{E}\left(\omega_s\right)\exp\left(i\omega_{mq}t\right)\exp\left[i\left(\omega_{qm}-\omega_s\right)t\right] \\ &+\frac{\mu_{qm}\mu_{mq}}{\omega_{qm}-\omega_s}\mathsf{E}^*\left(\omega_s\right)\exp\left(i\omega_{qm}t\right)\exp\left[-i\left(\omega_{qm}-\omega_s\right)t\right] \end{aligned} \right\} \tag{7.68}$$

$$= \frac{1}{V}\frac{1}{\hbar}\sum_q\sum_s \mu_{mq}\mu_{qm}\left\{ \frac{\mathsf{E}\left(\omega_s\right)}{\omega_{qm}-\omega_s}\exp\left(-i\omega_s t\right) + \frac{\mathsf{E}\left(-\omega_s\right)}{\omega_{qm}-\omega_s}\exp\left(i\omega_s t\right) \right\}$$

Formal algebraic rearrangement trick

Since we are summing over positive and negative values of ω_s

we can change ω_s to $-\omega_s$ in any terms we wish without changing the final result for the sum.

Hence we can write

$$\left\langle \mathrm{P}^{(1)}(t)\right\rangle = \frac{1}{V}\frac{1}{\hbar}\sum_q\sum_s \mu_{mq}\mu_{qm}\left\{\frac{1}{\omega_{qm}-\omega_s}+\frac{1}{\omega_{qm}+\omega_s}\right\}\mathrm{E}(\omega_s)\exp(-i\omega_s t) \qquad (7.69)$$

We can if we wish now write

$$\frac{\left\langle \mathrm{P}^{(1)}(t)\right\rangle}{\varepsilon_o} = \sum_s \chi^{(1)}(\omega_s;\omega_s)\mathrm{E}(\omega_s)\exp(-i\omega_s t) \qquad (7.70)$$

where by $\chi^{(1)}(\omega_s;\omega_s)$ we mean the (linear) susceptibility that gives rise to a polarization at frequency ω_s in response to a field at frequency ω_s, and

$$\chi^{(1)}(\omega_s;\omega_s) = \frac{1}{\varepsilon_o \hbar V}\sum_q \mu_{mq}\mu_{qm}\left[\frac{1}{\omega_{mq}-\omega_s}+\frac{1}{\omega_{mq}+\omega_s}\right] \qquad (7.71)$$

We can see directly from this, incidentally, that

$$\chi^{(1)}(\omega_s;\omega_s) = \chi^{(1)}(-\omega_s;-\omega_s) \qquad (7.72)$$

Second order susceptibility - 1

In the second order case, we use (7.66)

$$\left\langle \mathsf{P}^{(2)}(t)\right\rangle = \frac{1}{V}\left(\left\langle \Phi^{(0)}\middle|\mu\middle|\Phi^{(2)}\right\rangle + \left\langle \Phi^{(2)}\middle|\mu\middle|\Phi^{(0)}\right\rangle + \left\langle \Phi^{(1)}\middle|\mu\middle|\Phi^{(1)}\right\rangle\right)$$

For the first pair of terms, we have

$$\frac{1}{V}\left(\left\langle \Phi^{(0)}\middle|\mu\middle|\Phi^{(2)}\right\rangle + \left\langle \Phi^{(2)}\middle|\mu\middle|\Phi^{(0)}\right\rangle\right) = \frac{1}{V}\frac{1}{\hbar^2}\sum_{j,q}\sum_{s,u}\mu_{mj}\mu_{jq}\mu_{qm}$$
$$\times\left[\frac{\mathsf{E}(\omega_u)\mathsf{E}(\omega_s)\exp\left[-i(\omega_u+\omega_s)t\right]}{(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)} + \frac{\mathsf{E}^*(\omega_u)\mathsf{E}^*(\omega_s)\exp\left[i(\omega_u+\omega_s)t\right]}{(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)}\right] \qquad (7.73)$$

Making the formal substitution of $-\omega_s$ for ω_s and $-\omega_u$ for ω_u, we obtain.

$$\frac{1}{V}\left(\left\langle \Phi^{(0)}\middle|\mu\middle|\Phi^{(2)}\right\rangle + \left\langle \Phi^{(2)}\middle|\mu\middle|\Phi^{(0)}\right\rangle\right) = \frac{1}{V}\frac{1}{\hbar^2}\sum_{j,q}\sum_{s,u}\mu_{mj}\mu_{jq}\mu_{qm}\mathsf{E}(\omega_u)\mathsf{E}(\omega_s)$$
$$\times\left[\frac{1}{(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)} + \frac{1}{(\omega_{jm}+\omega_u+\omega_s)(\omega_{qm}+\omega_s)}\right]\exp\left[-i(\omega_u+\omega_s)t\right] \qquad (7.74)$$

Second order susceptibility - 2

Now examining the third term above in (7.66)

$$\left\langle \mathsf{P}^{(2)}(t)\right\rangle = \frac{1}{V}\left(\left\langle \Phi^{(0)}\middle|\mu\middle|\Phi^{(2)}\right\rangle + \left\langle \Phi^{(2)}\middle|\mu\middle|\Phi^{(0)}\right\rangle + \left\langle \Phi^{(1)}\middle|\mu\middle|\Phi^{(1)}\right\rangle\right)$$

we similarly have

$$\begin{aligned}\frac{1}{V}\left\langle \Phi^{(1)}\middle|\mu\middle|\Phi^{(1)}\right\rangle &= \frac{1}{V}\frac{1}{\hbar^2}\sum_{j,q}\sum_{s,u}\mu_{mj}\mu_{jq}\mu_{qm}\frac{\mathsf{E}^*(\omega_u)\mathsf{E}(\omega_s)}{(\omega_{jm}-\omega_u)(\omega_{qm}-\omega_s)}\exp\left[i(\omega_u-\omega_s)t\right] \\ &= \frac{1}{V}\frac{1}{\hbar^2}\sum_{j,q}\sum_{s,u}\mu_{mj}\mu_{jq}\mu_{qm}\frac{\mathsf{E}(\omega_u)\mathsf{E}(\omega_s)}{(\omega_{jm}+\omega_u)(\omega_{qm}-\omega_s)}\exp\left[-i(\omega_u+\omega_s)t\right]\end{aligned} \tag{7.75}$$

where we made the formal substitution of $-\omega_u$ for ω_u.

Hence, now having all terms arranged with the same formal time dependence of $\exp\left[-i(\omega_u+\omega_s)t\right]$, we can write

$$\frac{\left\langle \mathsf{P}^{(2)}(t)\right\rangle}{\varepsilon_o} = \sum_{s,u}\chi^{(2)}(\omega_u+\omega_s;\omega_u,\omega_s)\mathsf{E}(\omega_u)\mathsf{E}(\omega_s)\exp\left[-i(\omega_u+\omega_s)t\right] \tag{7.76}$$

where $\chi^{(2)}(\omega_u+\omega_s;\omega_u,\omega_s) = \frac{1}{\varepsilon_o V}\frac{1}{\hbar^2}\sum_{j,q}\mu_{mj}\mu_{jq}\mu_{qm}$

$$\times\left\{\frac{1}{(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)} + \frac{1}{(\omega_{jm}+\omega_u)(\omega_{qm}-\omega_s)} + \frac{1}{(\omega_{jm}+\omega_u+\omega_s)(\omega_{qm}+\omega_s)}\right\} \tag{7.77}$$

Second order nonlinear optical phenomena

For example, if we consider $\omega_u = \omega_s$,

we see that this $\chi^{(2)}(2\omega_s;\omega_s,\omega_s)$ gives the strength of the second harmonic generation process with input frequency ω_s.

We can see, incidentally, that this effect would be relatively quite strong if

we had an energy level j such that ω_{jm} was close to $2\omega_s$, and if

there was another energy level q such that ω_{qm} was close to ω_s,

because then we would have two strong resonant denominators.

If the electric field has two frequency components, ω_u and ω_s,

$\chi^{(2)}(\omega_u+\omega_s;\omega_u,\omega_s)$ *gives the strength of the sum frequency generation.*

The negative of the actual frequency should be considered as well since it is included in the sums over frequencies, and so

we have a process whose strength is given by $\chi^{(2)}(\omega_u-\omega_s;\omega_u,-\omega_s)$,

which is one of the difference frequency generation terms.

We can proceed with any combination of input frequencies to calculate the strengths of the processes giving rise to all of the new generated frequencies given by this second order perturbation correction.

Symmetry and second order effects

If all the states in a system have definite parity (in the single direction we are considering),

there will be exactly no second order nonlinear optical effects.

If the states have definite parity, then

for μ_{qm} to be finite,

states q and m must have opposite parity,

for μ_{jq} to be finite, states j and q must have opposite parity,

which then means that states j and m must have the same parity,

and hence μ_{mj} must be zero.

Hence the product of these three matrix elements is always zero if all the states have definite parity.

Hence a certain asymmetry is required in the material if the second order effects are to be finite.

Third order susceptibility

Using

$$\frac{\langle \mathrm{P}^{(3)}(t)\rangle}{\varepsilon_o}=\sum_{s,u,v}\chi^{(3)}(\omega_v+\omega_u+\omega_s;\omega_v,\omega_u,\omega_s)\mathrm{E}(\omega_v)\mathrm{E}(\omega_u)\mathrm{E}(\omega_s)\times\exp\left[-i(\omega_v+\omega_u+\omega_s)t\right] \tag{7.78}$$

gives

$$\chi^{(3)}(\omega_v+\omega_u+\omega_s;\omega_v,\omega_u,\omega_s)=\frac{1}{\varepsilon_o V}\frac{1}{\hbar^3}\sum_{k,j,q}\mu_{mk}\mu_{kj}\mu_{jq}\mu_{qm}$$

$$\times\left[\begin{array}{l}\dfrac{1}{(\omega_{km}-\omega_v-\omega_u-\omega_s)(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)}\\+\dfrac{1}{(\omega_{km}+\omega_v)(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)}\\+\dfrac{1}{(\omega_{km}+\omega_v)(\omega_{jm}+\omega_v+\omega_u)(\omega_{qm}-\omega_s)}\\+\dfrac{1}{(\omega_{km}+\omega_v)(\omega_{jm}+\omega_v+\omega_u)(\omega_{qm}+\omega_v+\omega_u+\omega_s)}\end{array}\right] \tag{7.79}$$

For example, setting $\omega_v=\omega_u=\omega_s$**,**

as would be particularly relevant if there was only one input frequency,

would give the strength of the process for third harmonic generation.

Quantum mechanics in crystalline materials – 1

Reading – Sections 8.1 – 8.4

This is of major importance for engineering applications in

- **Electronics**
- **Optoelectronics**

Here we summarize some key quantum mechanical approaches for crystalline materials

- **Crystals**
- **One electron approximation**
- **Bloch theorem**
- **Density of states in k-space**

Crystals - 1

Crystal

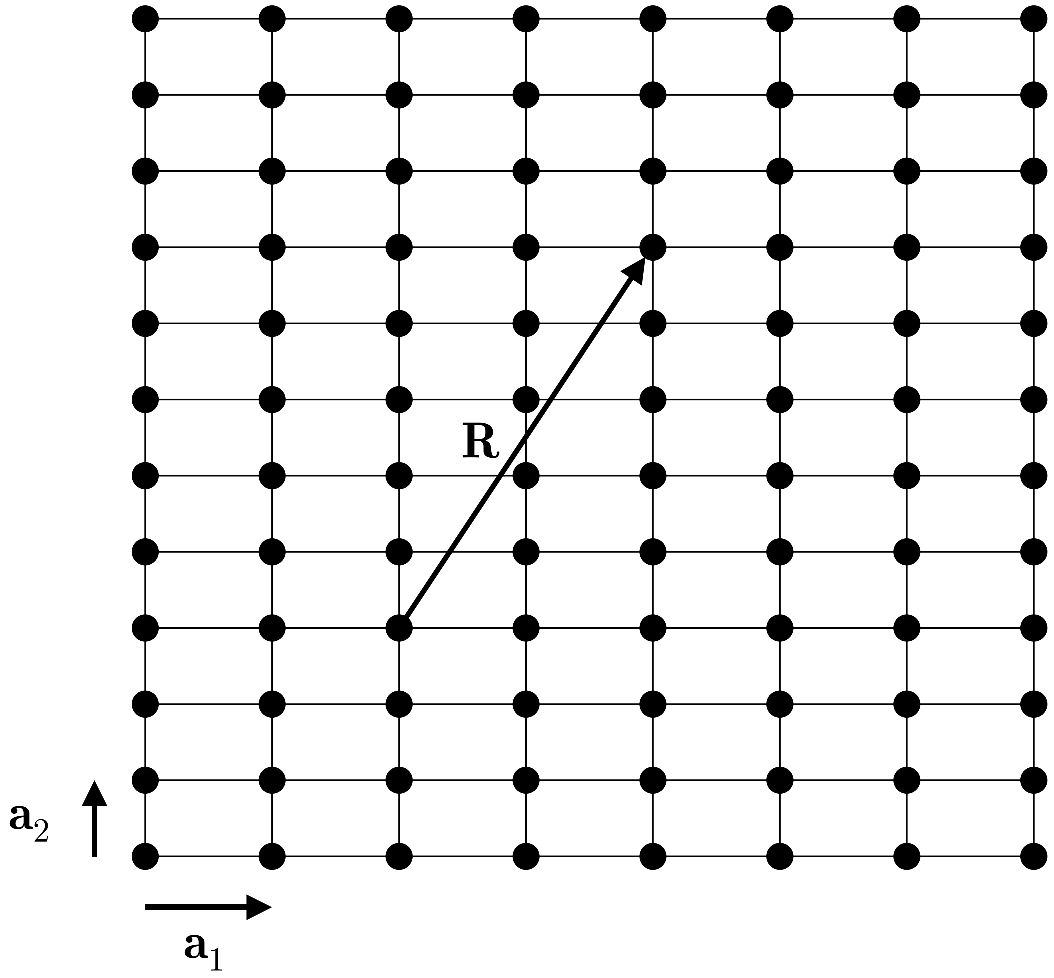
material whose measurable properties are periodic in space.

Crystal structure

is one that can fill all space by the regular stacking of identical blocks or unit cells.

Crystal lattice

If we put a mark on the same spot of the surface of each block, these spots would form a crystal lattice.



Crystals - 2

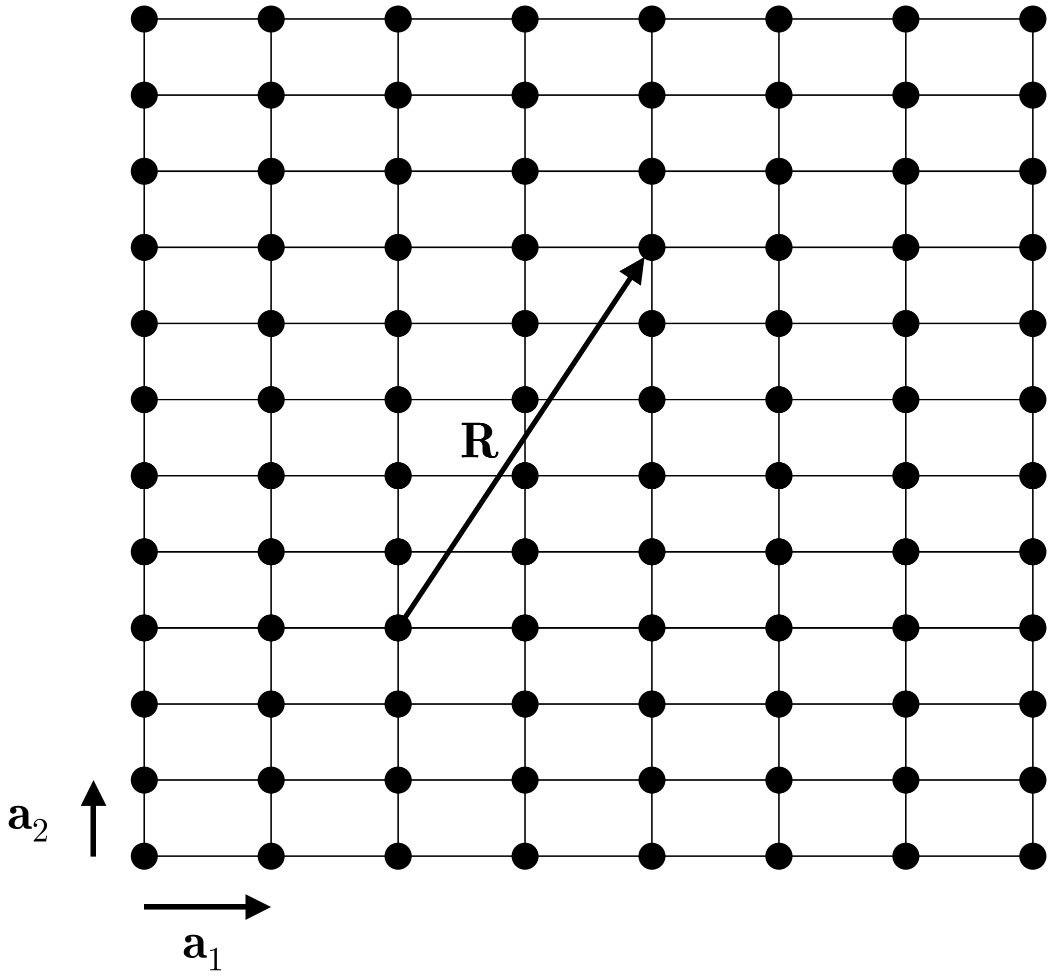
Lattice vectors

The set of lattice vectors consists of all of the vectors that link points on this lattice, i.e.,

$$\mathbf{R}_L = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \qquad (8.1)$$

$\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the three linearly independent vectors that take us from a given point in one unit cell to the equivalent point in the adjacent unit cell.

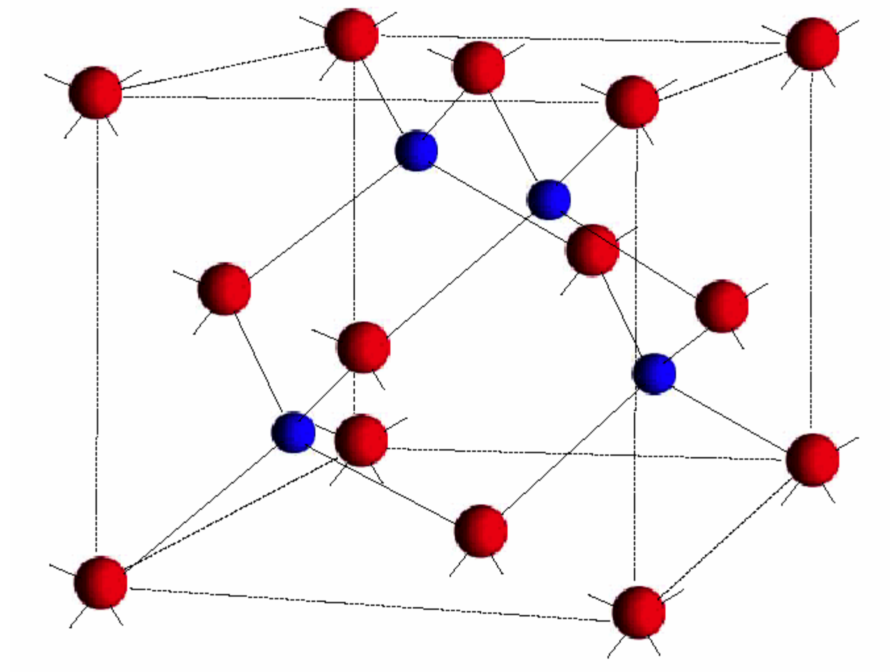
In a simple cubic lattice, these vectors lie along the x, y, and z directions.



The numbers n_1, n_2, and n_3 range through all (positive and negative) integer values.

Bravais lattices

In three dimensions, there are only 14 distinct kinds of crystal lattice (Bravais lattices) that can be made that will fill all space by the stacking of identical blocks.



A large fraction of the semiconductor materials of practical interest,

such as silicon, germanium, and most of the III-V (e.g., GaAs) and II-VI (e.g., ZnSe) materials

have a specific form of cubic lattice.

This lattice is based on two interlocking face-centered cubic lattices.

Zinc-blende – (most III-V and II-VI materials)

the group III (or II) atoms lie on one such face-centered cubic lattice, and the group V (or VI) lie on the interlocking face-centered cubic lattice.

Diamond – (some group IV materials (e.g., silicon, germanium))

both interlocking lattices of course have the same atoms on them

One electron approximation - 1

How can we start to deal with 10^{23} atoms and/or electrons?

Key first approximation

presume that any given electron sees a periodic potential, $V_P(\mathbf{r})$, periodic with the same periodicity as the crystal lattice.

Because it is periodic with the crystal lattice periodicity, we have

$$V_P\left(\mathbf{r}+\mathbf{R}_L\right)=V_P(\mathbf{r}) \tag{8.2}$$

This represents the effective periodic potential

from the charged nuclei, which are presumed to be fixed,

from all the other electrons, whose charge distribution is also presumed to be effectively fixed.

Note this is only an approximation

Any given electron state will tend to distort the crystal lattice by pulling on the nuclei.

Any given electron state will also in reality interact with other electrons

There are also many other interactions that we can consider

These interactions are very often handled as perturbations, starting with the one-electron model results as the “unperturbed” solutions.

One electron approximation - 2

In this approximation,

we therefore presume that we can write an effective, approximate Schrödinger equation for the one electron in which we are interested

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r})+V_P(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{8.3}$$

and this will constitute our one-electron approximation.

Bloch theorem

The Bloch theorem is a very important simplification for crystalline structures

enables us to separate the problem into two parts,

one that is the same in every unit cell, and

one that describes global behavior.

For simplicity, we will prove this in one direction and then generalize to three dimensions.

We know that the crystal is periodic, having the same potential at $x + sa$ as it has at x (where s is an integer).

Any observable quantity must also have the same periodicity because the crystal must look the same in every unit cell.

For example charge density $\rho \propto |\psi|^2$ must be periodic in the same way. Hence

$$|\psi(x)|^2 = |\psi(x+a)|^2 \tag{8.4}$$

which means

$$\psi(x) = C\psi(x+a) \tag{8.5}$$

where C is a complex number of unit amplitude.

Note that there is no requirement that the wavefunction itself be periodic with the crystal periodicity since it is not apparently an observable or measurable quantity.

Periodic boundary conditions - 1

As is often the case, the boundary conditions lead to the quantization of the problem.

What boundary conditions represent a crystal?

How can we introduce the concept of the finiteness of the crystal,

and corresponding finite countings of states,

without having to abandon our simple description in terms of infinite periodicity?

In one dimension, we could argue as follows.

Suppose that we had a very long chain of N equally spaced atoms,

and that we joined the two ends of the chain together.

With x as the distance along this loop; then on this loop,

$$V_P(x+ma) = V_P(x),$$

where m is any integer

even much larger than N.

just like our definition for the infinite crystal

If this chain is very long,

we do not expect that its internal properties will be substantially different from an infinitely long chain,

and so this finite system will be a good model.

Periodic boundary conditions - 2

Such a loop introduces a boundary condition, however.

We do expect that the wavefunction is a single-valued function

(otherwise how could we differentiate it, evaluate its squared modulus, etc.)

so when we go round the loop we must get back to where we started, i.e., explicitly

$$\psi(x) = \psi(x + Na) \quad (8.6)$$

This is known as a periodic boundary condition

also known as a Born-von Karman boundary condition.

Combining this with our condition (8.5), we have

$$\psi(x) = \psi(x + Na) = C^N \psi(x) \quad (8.7)$$

so

$$C^N = 1 \quad (8.8)$$

and so C ***is one of the*** N ***roots of unity, i.e.,***

$$C = \exp(2\pi i s / N);\ s = 0, 1, 2, \ldots N-1 \quad (8.9)$$

(We could also choose

$$C = \exp\left(2\pi i\left(\frac{s}{N} + m\right)\right);\ s = 0, 1, 2, \ldots N-1,\ m \text{ any integer} \quad (8.10)$$

so there is some arbitrariness here.)

Periodic boundary conditions - 3

Substituting C from (8.9)

$$C = \exp\left(2\pi is / N\right);\ s = 0, 1, 2, \ldots N-1$$

in (8.7),

$$\psi(x+a) = \exp\left(ika\right)\psi(x) \tag{8.11}$$

where we could choose

$$k = \frac{2\pi s}{Na};\ s = 0, 1, 2, \ldots N-1 \tag{8.12}$$

Note we could also choose

$$k = \frac{2\pi s}{Na} + \frac{2m\pi}{a};\ s = 0, 1, 2, \ldots N-1 \tag{8.13}$$

Conventionally, we choose

$$k = \frac{2\pi n}{Na} \quad \ldots n = 0, \pm 1, \pm 2, \ldots \pm N/2 \tag{8.14}$$

which still gives essentially N states, but now symmetrically disposed about $k = 0$.

Note the allowed k values are evenly spaced by $2\pi / L$ where $L = Na$ is the length of the crystal (loop) in this dimension,

regardless of the detailed form of the periodic potential.

Bloch theorem – one statement

The wavefunction in a (one-dimensional) crystal can be written in the form

$$\psi(x+a) = \exp(ika)\,\psi(x) \tag{8.11}$$

subject to the condition

$$k = \frac{2\pi n}{Na} \quad \ldots n = 0, \pm 1, \pm 2, \ldots \pm N/2 \tag{8.14}$$

Bloch theorem – alternative (equivalent) statement

Multiply Eq. (8.11) by $\exp(-ik(x+a))$ to obtain

$$\psi(x+a)\exp(-ik(x+a)) = \psi(x)\exp(-ikx) \tag{8.15}$$

Hence if we define a function

$$u(x) = \psi(x)\exp(-ikx) \tag{8.16}$$

we can restate Eq. (8.15) as

$$u(x+a) = u(x) \tag{8.17}$$

and hence $u(x)$ is periodic with the lattice periodicity.

Hence, we can rewrite the Bloch theorem equation (8.11) in the alternative form

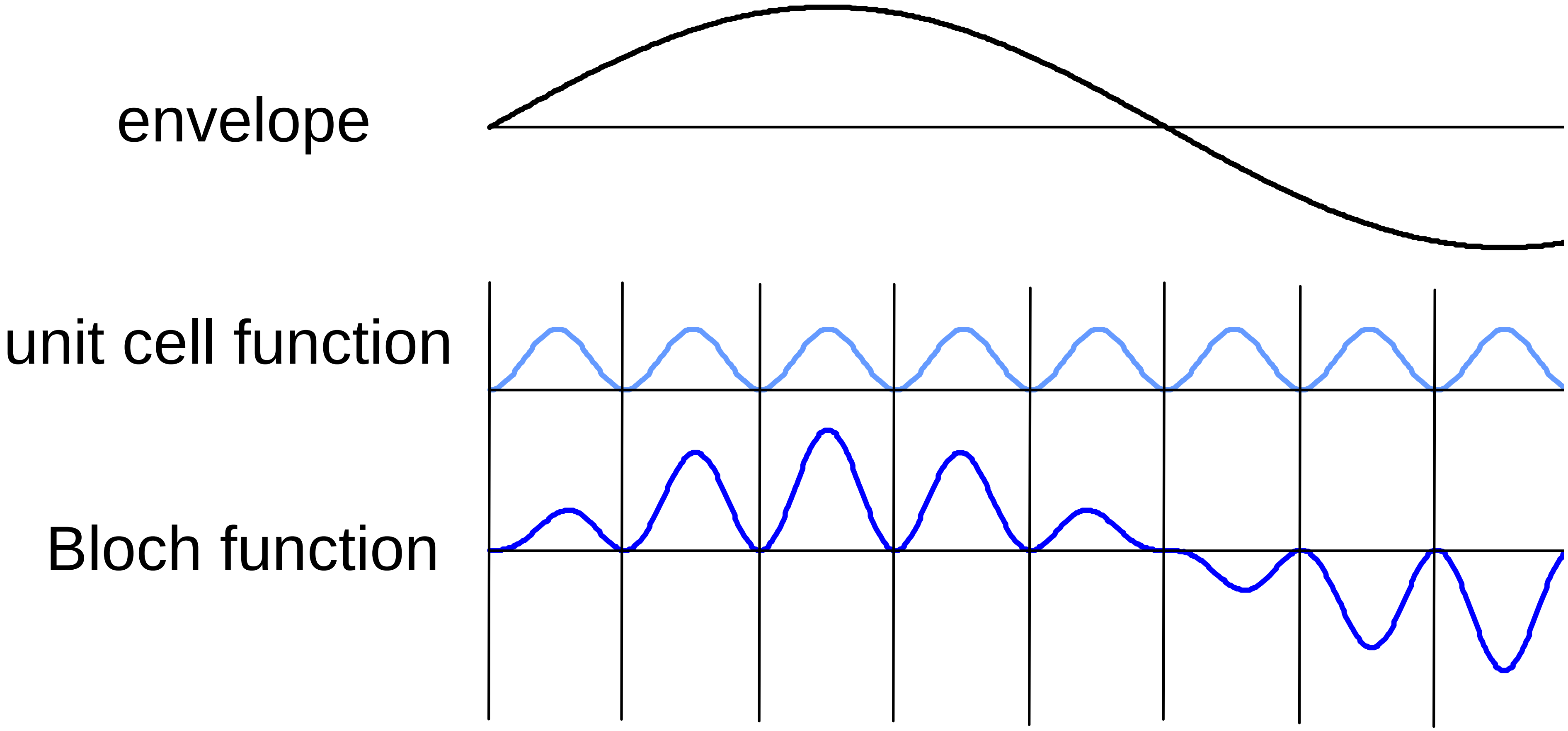
$$\psi(x) = u(x)\exp(ikx) \tag{8.18}$$

where $u(x)$ is periodic with the lattice periodicity.

Note that the two forms (8.11) and (8.18) are entirely equivalent –

we have just proved that (8.11) implies (8.18), and it is trivial to show by mere substitution that (8.18) implies (8.11).

Bloch theorem – wavefunction visualization



Concept of the Bloch functions in the form of Eq. (8.18). We can think of the $\exp(ikx)$ as being an example of an "envelope" function that multiplies the unit cell function $u(x)$.

Bloch theorem in three dimensions - 1

In three dimensions, we can follow similar arguments.

- ***Periodic boundary conditions are absurd if we treat them too literally***
  - **we would then need to imagine a crystal where each face is joined to the opposite one in a long loop, something we cannot do in three dimensions.**
- ***Periodic boundary conditions in three dimensions***
  - **allow our simple definition of periodicity**
    - *and yet correctly count the available states.*

The Bloch theorem in three dimensions is otherwise a straightforward extension of the 1-D version. We have

$$\psi(\mathbf{r}+\mathbf{a}) = \exp(i\mathbf{k}.\mathbf{a})\psi(\mathbf{r}) \tag{8.19}$$

or equivalently

$$\psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k}.\mathbf{r}) \tag{8.20}$$

where $\mathbf{a}$ ***is any crystal lattice vector.***

Bloch theorem in three dimensions - 2

Considering the three crystal basis vector directions,

1, 2, and 3,

with lattice constants (repeat distances) a_1, a_2, and a_3, and

numbers of atoms N_1, N_2, and N_3

$$k_1 = \frac{2\pi n_1}{N_1 a_1} \quad ...n_1 = 0, \pm 1, \pm 2, ... \pm N_1 / 2 \tag{8.21}$$

and similarly for the other two components of $\mathbf{k}$ in the other two crystal basis vector directions.

Note that the number of possible values of $\mathbf{k}$ is the same as the number of unit cells in the crystal.

Density of states in k-space - 1

We see that the allowed values of k_1, k_2, and k_3 are each equally spaced, with separations

$$\delta k_1 = \frac{2\pi}{N_1 a_1} = \frac{2\pi}{L_1},\ \delta k_2 = \frac{2\pi}{N_2 a_2} = \frac{2\pi}{L_2},\ \text{and}\ \delta k_3 = \frac{2\pi}{N_3 a_3} = \frac{2\pi}{L_3} \qquad (8.22)$$

respectively along the three axes.

Note that the lengths of the crystal along the three axes are respectively

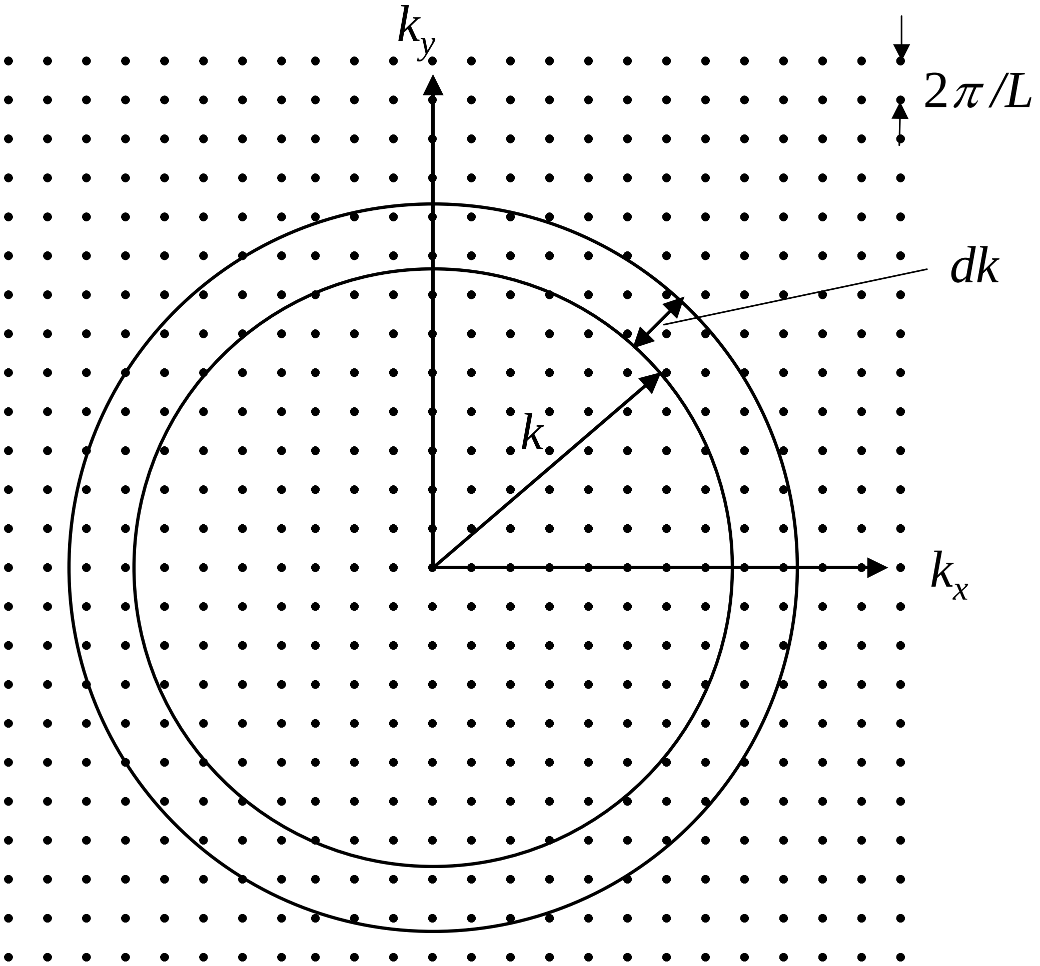
$$L_1 = N_1 a_1,\ L_2 = N_2 a_2,\ L_3 = N_3 a_3 .$$

Reciprocal lattice

We could draw a three-dimensional diagram, with axes k_1, k_2, and k_3, and mark the allowed values of $\mathbf{k}$.

This set of dots themselves constitute a mathematical lattice.

This kind of lattice is known as a reciprocal lattice.



Density of states in k-space - 2

We then imagine each point has a volume surrounding it, with these volumes touching one another to completely fill all the space.

For our cubic lattices, these volumes in k-space will be of size $\delta V_k = \delta k_1 \delta k_2 \delta k_3$ (assuming for simplicity that the crystal axes are all perpendicular, as they would be in a cubic crystal), i.e.,

$$\delta V_k = \frac{(2\pi)^3}{V} \tag{8.23}$$

where

$$V = L_1 L_2 L_3$$

is the volume of our crystal.

Hence the density of states in k-space is $1/\delta V_k$.

Note that this density grows as we make the crystal larger.

Commonly we use the density of states per unit volume of the crystal.

Hence we have the density of states in *k*-space per unit volume of the crystal

$$g(\mathbf{k}) = \frac{1}{(2\pi)^3} \tag{8.24}$$

The density of states is a very useful quantity for quantum mechanical calculations in crystalline materials.

Quantum mechanics in crystalline materials – 2

Reading – Sections 8.5 – 8.7

Band structure

Effective mass theory

Density of states in energy

Band structure - 1

If we knew the potential $V_P(\mathbf{r})$,

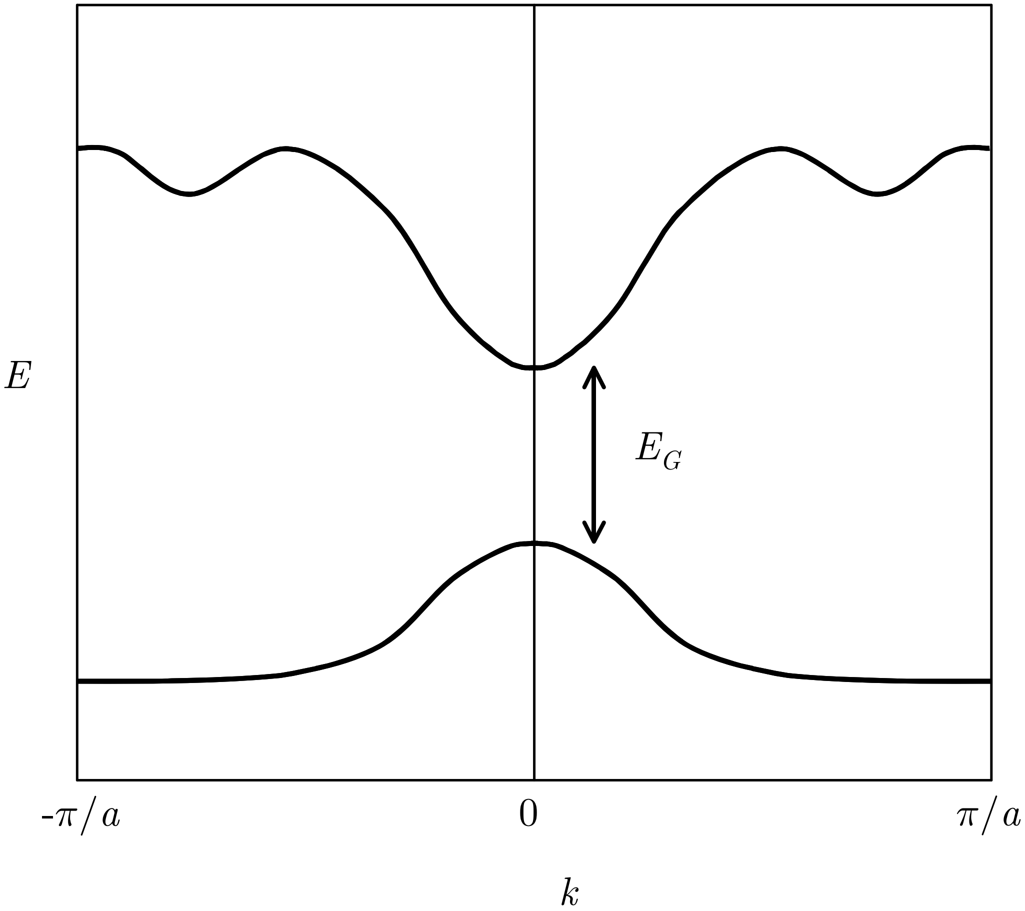
and could solve the one-electron Schrödinger equation (8.3),

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) + V_P(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

using the Bloch function form (8.20)

$$\psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k}.\mathbf{r})$$

we would calculate the energies E of all of the various possible states.



There are various ways of approaching such calculations from first principles, and we will not go into those here.

The results of such calculations give what is known as a band structure.

Band structure - 2

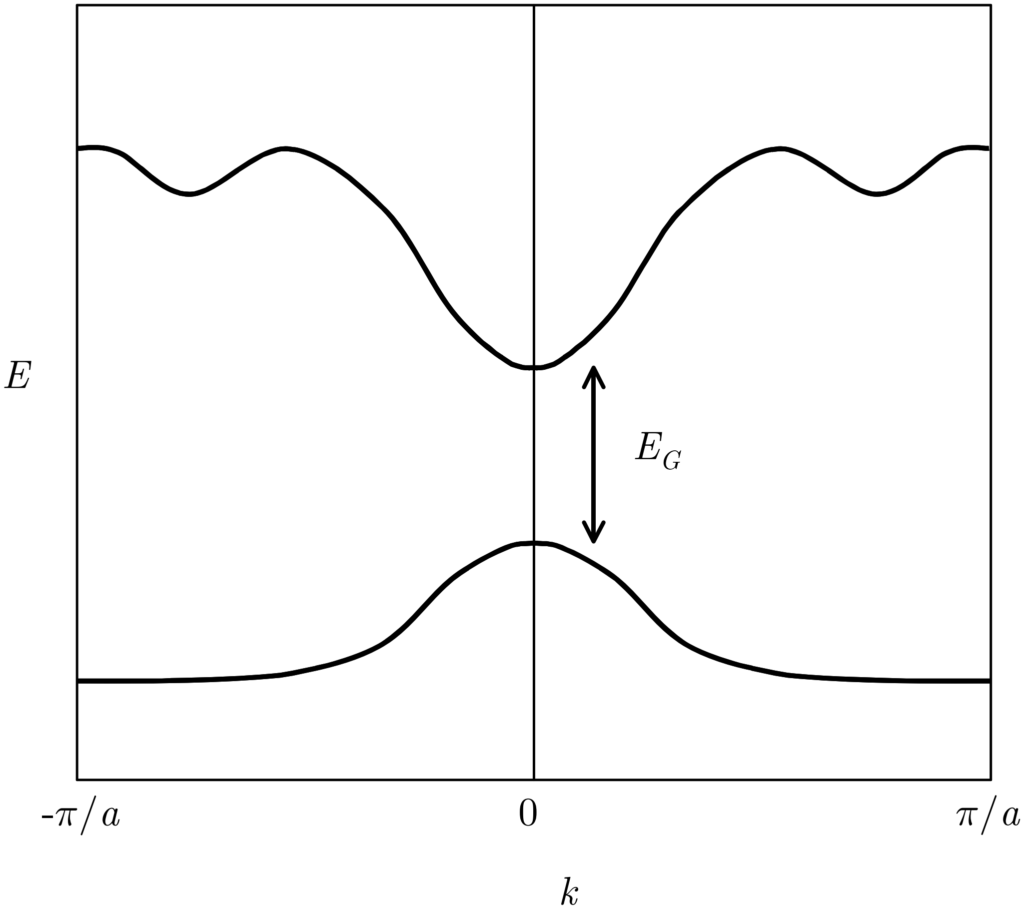
There are multiple bands in a band structure (in fact an infinite number),

but usually only a few are important for the properties of a material.

Each band has a total number of allowed k-states equal to the number of unit cells in the crystal.

These states are evenly spaced in k-space, as discussed above.

Each band loosely corresponds to a different atomic state in the constituent atoms



the bands can be viewed as being formed from the atomic states as the atoms are pushed together into the crystal.

Band structure - 3

In each band, we only have to plot k-values from $-\pi/a$ to π/a.

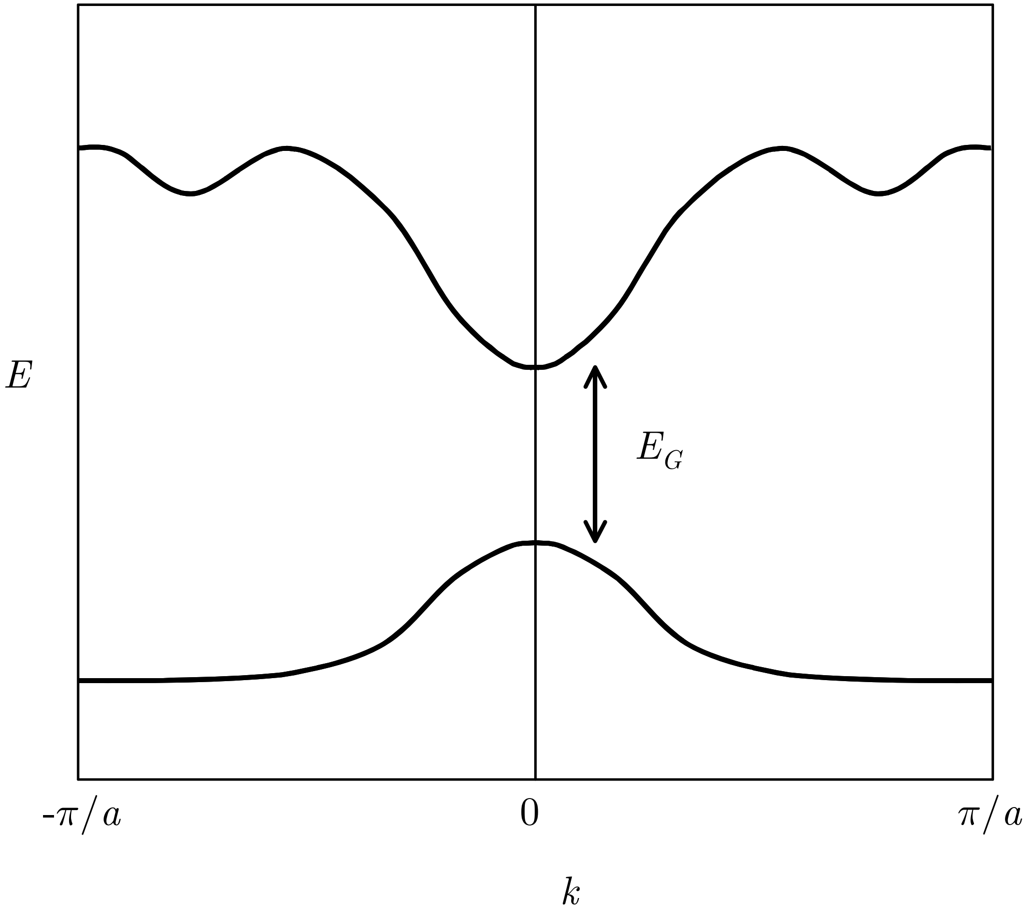
This range is sometimes known as the (first) Brillouin zone.

The bands are usually plotted as if they were continuous,

but in fact k can only take on discrete (though evenly spaced) values.

The lower band is like the highest valence band in a semiconductor

it is typically full of electrons.



The upper band is like the lowest conduction band in some semiconductors

it is typically empty of electrons.

E_G is the band gap energy that separates the lowest point in the conduction band from the highest point in the valence band.

Direct and indirect band gaps

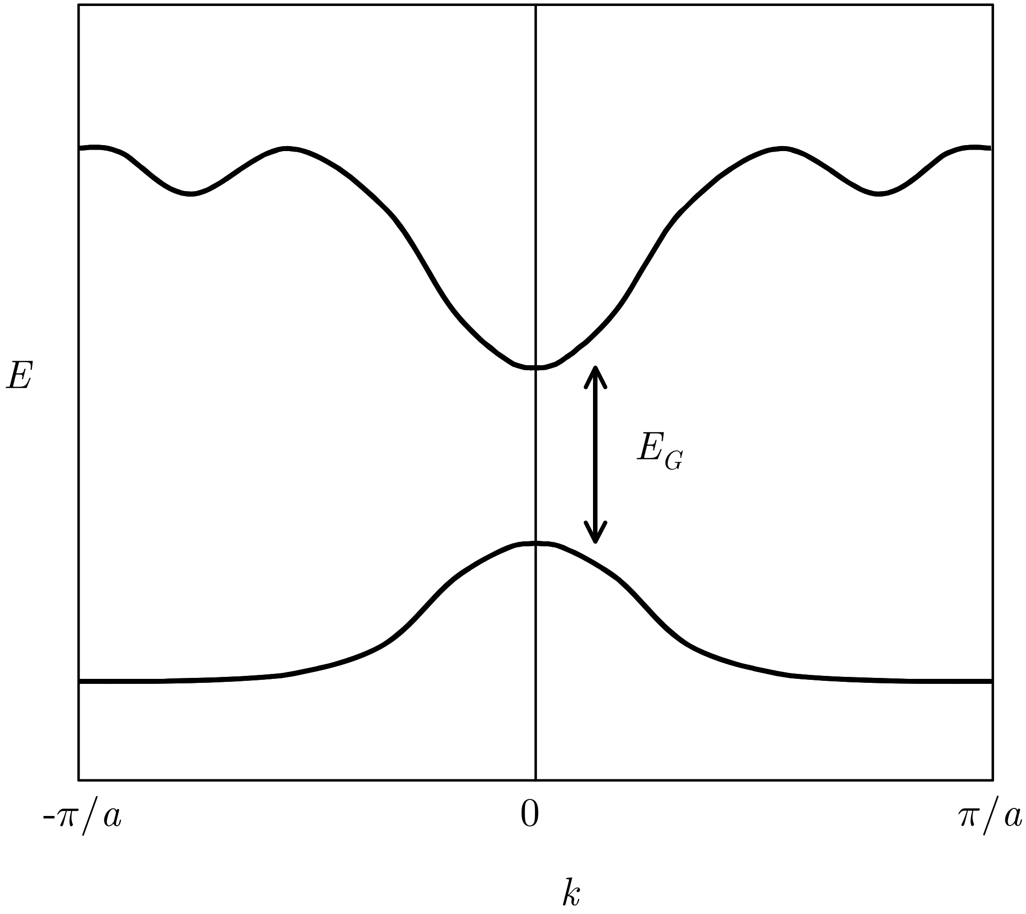
The particular band structure above corresponds to what is called a direct gap semiconductor;

the lowest point in the conduction band is directly above the highest point in the valence band.

Many III-V and II-VI semiconductors are of this type.

It is also very common for there to be minima or maxima in the bands at $k = 0$.

Also shown in the conduction band are subsidiary minima away from $k = 0$*.*



It is possible that these minima, rather than any minimum at $k = 0$, are the lowest points in a semiconductor conduction band structure,

in which case we have an indirect gap semiconductor.

Silicon and germanium are both indirect gap semiconductors.

Symmetry around k = 0 and Kramers degeneracy - 1

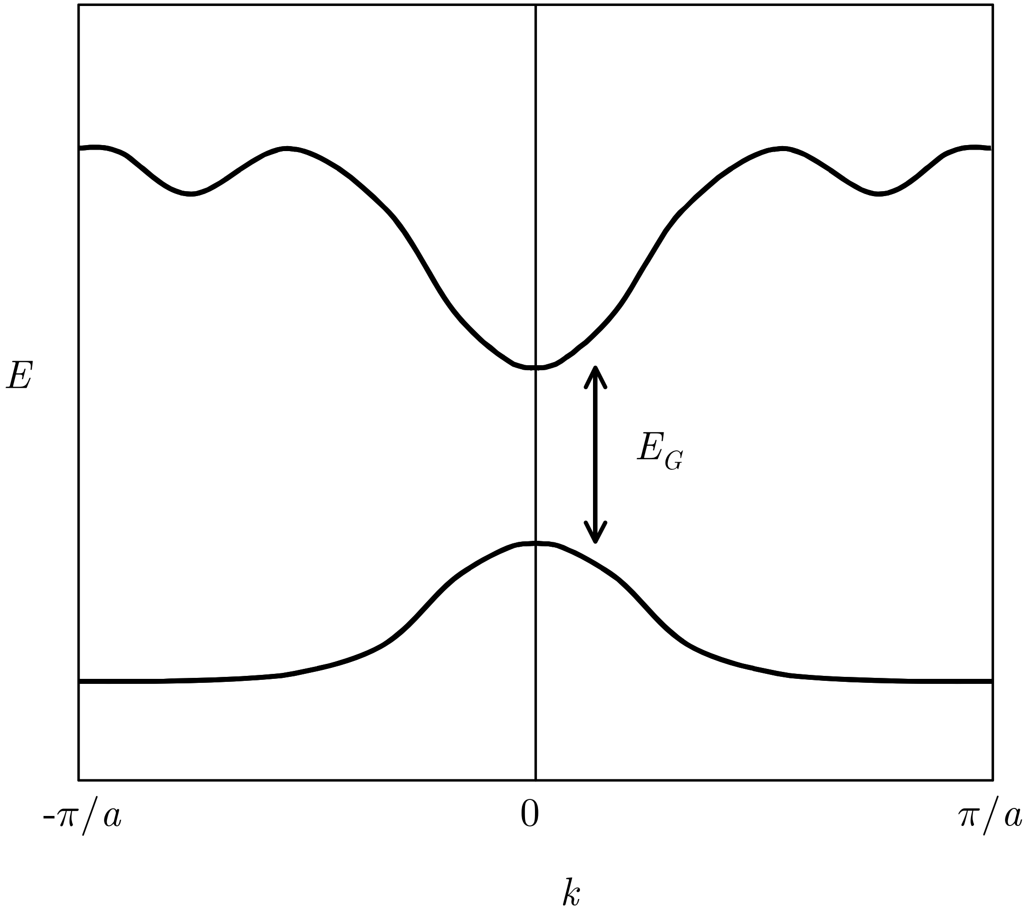
The band structure is drawn to be symmetric about $k = 0$.

In our simple one-electron model this common symmetry is easily proved.

Suppose that $\psi(\mathbf{k},\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}.\mathbf{r})$ is the Bloch function that satisfies the Schrödinger equation for a specific $\mathbf{k}$.

Note $\mathbf{k}$ as an explicit notation in our Bloch function parts.

Note, incidentally, that the unit cell part of the wavefunction, $u_{\mathbf{k}}(\mathbf{r})$, is in general different for every different $\mathbf{k}$.



Hence we have

$$H\psi(\mathbf{k},\mathbf{r}) = E_{\mathbf{k}}\psi(\mathbf{k},\mathbf{r}) \tag{8.25}$$

where $E_{\mathbf{k}}$ is the eigenenergy associated with this specific $\mathbf{k}$

and $H = -\left(\hbar^2/2m_e\right)\nabla^2 + V_P(\mathbf{r})$.

Symmetry around k = 0 and Kramers degeneracy - 2

Now take the complex conjugate of both sides of Eq. (8.25) ($H\psi(\mathbf{k},\mathbf{r}) = E_{\mathbf{k}}\psi(\mathbf{k},\mathbf{r})$*).*

We note that $H = H^*$,

and we also know that $E_{\mathbf{k}}$ is real since it is an eigenvalue associated with a Hermitian operator.

Hence we have

$$H\psi^*(\mathbf{k},\mathbf{r}) = E_{\mathbf{k}}\psi^*(\mathbf{k},\mathbf{r}) \tag{8.26}$$

But $\psi^*(\mathbf{k},\mathbf{r}) = u_{\mathbf{k}}^*(\mathbf{r})\exp(-i\mathbf{k}.\mathbf{r})$*,*

which is also a wavefunction in Bloch form,

but for wavevector $-\mathbf{k}$*.*

Hence we are saying that for every Bloch function solution with wavevector $\mathbf{k}$ and energy $E_{\mathbf{k}}$,

there is one with wavevector $-\mathbf{k}$ *with the same energy.*

Hence the band structure is symmetric about $k = 0$*.*

We can if we wish choose to write

$$\psi^*(\mathbf{k},\mathbf{r}) = u_{\mathbf{k}}^*(\mathbf{r})\exp(-i\mathbf{k}.\mathbf{r}) \equiv u_{-\mathbf{k}}(\mathbf{r})\exp(-i\mathbf{k}.\mathbf{r}) = \psi(-\mathbf{k},\mathbf{r}) \tag{8.27}$$

This equivalence of the energies for $\mathbf{k}$ and $-\mathbf{k}$ is known as Kramers degeneracy.

Effective mass theory - 1

It is very common to have minima or maxima in the bands at $\mathrm{k} = 0$.

- *In fact the Kramers degeneracy essentially ensures band minima or maxima at $\mathrm{k} = 0$,*
  - since otherwise the bands cannot be symmetric about $\mathrm{k} = 0$.

It is also common to have other minima or maxima in the band structure

The minima in the conduction band and the maxima in the valence band are very important in the operation of both electronic and optoelectronic semiconductor devices.

- *Any extra electrons in the conduction band will tend to fall into the lowest minimum.*
- *Any absences of electrons in the valence band will tend to "bubble up" to the highest maximum in the valence band.*
  - Such absences of electrons are often described as positively charged "holes".

Effective mass theory - 2

The properties of

most electronic devices and

many optoelectronic devices

especially light emitting devices,

which involve recombination of electrons in the conduction band with holes in the valence band

are dominated by what happens in these minima and maxima.

It is also the case in optoelectronics that many other devices,

such as some optical modulators,

work for photon energies very near to the band gap energy, E_G**,**

and their properties are also determined by the behavior of electrons and holes in these minima and maxima.

It is therefore very useful to have approximate models that give simplified descriptions of what happens in these regions.

Fortunately there are such models, and they are very useful in practice.

One of these is the effective mass approximation.

Effective mass approximation - 1

Near a minimum or maximum, the energy $E_{\mathbf{k}}$ should vary ~ quadratically as $\mathbf{k}$ is varied along some direction in *k*-space.

For simplicity here, we will presume

the variation is isotropic,

the minimum or maximum of interest is located at $k = 0$.

(Neither of these simplifications is necessary for this effective mass approach.)

This isotropic $k = 0$ minimum or maximum is an appropriate first approximation for

the lowest conduction band, and

the highest valence bands,

in the direct gap semiconductors that are important in optoelectronics (e.g., GaAs, InGaAs).

Neither approximation is appropriate for

the lowest conduction bands in silicon or germanium or other indirect gap semiconductors such as AlAs,

though the theory is easily extended to cover those cases.

Effective mass approximation - 2

If the energy at the minimum or maximum itself is some amount V ,

then, by assumption, we have

$$E_{\mathbf{k}} - V \propto k^2 .$$

For reasons that will become obvious, we choose to write this as

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_{eff}} + V \tag{8.28}$$

where the quantity m_{eff} is a parameter that sets the appropriate proportionality.

A relation such as Eq. (8.28) between energy and *k*-value is called a dispersion relation.

This particular approximation for the behavior of the energies in a band is called an isotropic parabolic band.

Consideration of behavior of a wavepacket - 1

Consider a wave packet –

a linear superposition of different Bloch states.

Since we are going to consider the time evolution,

we will also include the time-varying factor

$$\exp\left(-iE_{\mathbf{k}}t/\hbar\right)$$

for each component in the superposition.

Hence we consider a wavefunction

$$\Psi(\mathbf{r},t)=\sum_{\mathbf{k}} c_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}.\mathbf{r})\exp\left(-iE_{\mathbf{k}}t/\hbar\right) \quad (8.29)$$

where $c_{\mathbf{k}}$ ***are the coefficients of the different Bloch states in this superposition.***

We have restricted this superposition to states within only one band.

We will make the further assumption that this superposition is only from a small range of k-states (near $k=0$***).***

This is what can be called a slowly varying envelope approximation since it means that the resulting wavepacket does not vary rapidly in space.

Consideration of behavior of a wavepacket - 2

Because of this slowly varying envelope approximation,

we can presume that, for all the $\mathbf{k}$ ***of interest to us,***

all of the unit cell functions $u_{\mathbf{k}}(\mathbf{r})$ **are approximately the same.**

Hence we presume $u_{\mathbf{k}}(\mathbf{r}) \cong u_0(\mathbf{r})$ *for the range of interest to us*

Hence we can factor out this unit cell part, writing

$$\Psi(\mathbf{r},t) = u_0(\mathbf{r})\Psi_{env}(\mathbf{r},t) \tag{8.30}$$

where the envelope function $\Psi_{env}(\mathbf{r},t)$ can be written

$$\Psi_{env}(\mathbf{r},t) = \sum_{\mathbf{k}} c_{\mathbf{k}} \exp(i\mathbf{k}.\mathbf{r})\exp\left(-iE_{\mathbf{k}}t/\hbar\right) \tag{8.31}$$

Now we construct a Schrödinger equation for this envelope function Differentiating with respect to time gives

$$\begin{aligned} i\hbar\frac{\partial\Psi_{env}}{\partial t} &= \sum_{\mathbf{k}} c_{\mathbf{k}} E_{\mathbf{k}} \exp(i\mathbf{k}.\mathbf{r})\exp\left(-iE_{\mathbf{k}}t/\hbar\right) \\ &= \frac{\hbar^2}{2m_{eff}}\sum_{\mathbf{k}} c_{\mathbf{k}} k^2 \exp(i\mathbf{k}.\mathbf{r})\exp\left(-iE_{\mathbf{k}}t/\hbar\right) + V\sum_{\mathbf{k}} c_{\mathbf{k}} \exp(i\mathbf{k}.\mathbf{r})\exp\left(-iE_{\mathbf{k}}t/\hbar\right) \qquad (8.32) \\ &= \frac{\hbar^2}{2m_{eff}}\sum_{\mathbf{k}} \left[-c_{\mathbf{k}}\nabla^2 \exp(i\mathbf{k}.\mathbf{r})\right]\exp\left(-iE_{\mathbf{k}}t/\hbar\right) + V\Psi_{env} \end{aligned}$$

since $\nabla^2 \exp(i\mathbf{k}.\mathbf{r}) = -k^2 \exp(i\mathbf{k}.\mathbf{r})$**.**

Consideration of behavior of a wavepacket - 3

Hence finally we have

$$-\frac{\hbar^2}{2m_{eff}}\nabla^2\Psi_{env}(\mathbf{r},t)+V(\mathbf{r})\Psi_{env}(\mathbf{r},t)=i\hbar\frac{\partial}{\partial t}\Psi_{env}(\mathbf{r},t) \qquad (8.33)$$

We have managed to construct a Schrödinger equation for this envelope function.

All of the details of the periodic potential and the unit cell wavefunction have been suppressed in this equation

their consequences are all contained in the single parameter, the effective mass m_{eff}.

This effective mass model is a very powerful simplification, and is at the root of a large number of models of processes in semiconductors.

Use of V(r)

Note that we have allowed the potential $V(\mathbf{r})$

i.e., the energy of the band at $k = 0$

to vary with position $\mathbf{r}$ in Eq. (8.33).

This is justifiable if the changes in that potential are very small compared to $\hbar^2 k^2 / 2m_{eff}$ over the scale of a unit cell and over the wavelength $2\pi / k$.

Technically, if that potential changes with position,

then we no longer have a truly periodic structure,

and we might presume that we cannot use our crystalline theory to model it,

but in practice we presume the material is to a good enough approximation still locally crystalline as long as that potential is slowly varying.

In fact, comparisons with experiment show that this kind of approach remains valid even for some very rapid changes in potential;

it does not apparently take many periods of the crystal structure to define the basic properties of the crystalline behavior.

We can also handle abrupt changes in $V(\mathbf{r})$ in practice through the use of appropriate boundary conditions.

Changes in $V(\mathbf{r})$ with position can result, for example, from applying electric fields, or from changes in material composition.

Semiconductor heterostructures

Structures involving more than one kind of material are called heterostructures.

e.g., changing x in the alloy semiconductor $Al_xGa_{1-x}As$.

Such changes are made routinely in modern semiconductor structures,

especially abrupt changes in material concentration

e.g., the interface between GaAs and $Al_{0.3}Ga_{0.7}As$ in laser diodes,

quantum well structures involving very thin layers (e.g., 10 nm).

Analyzing heterostructures with effective mass theory

Note that the effective mass is in general different in different materials.

It is then better to write Eq. (8.33) as

$$-\frac{\hbar^2}{2}\nabla\cdot\left[\frac{1}{m_{eff}}\nabla\Psi_{env}(\mathbf{r},t)\right]+V(\mathbf{r})\Psi_{env}(\mathbf{r},t)=i\hbar\frac{\partial}{\partial t}\Psi_{env}(\mathbf{r},t) \tag{8.34}$$

and to use boundary conditions such as

$$\Psi_{env}\ \text{continuous} \tag{8.35}$$

and

$$\frac{1}{m_{eff}}\nabla\Psi_{env}\ \text{continuous} \tag{8.36}$$

to handle abrupt changes in material and/or potential.

The choice of Eq. (8.34) and of the boundary conditions (8.35) and (8.36) is to some extent arbitrary.

These new choices do conserve probability density if the mass changes with position,

see Problem 3.14.2

They do work well in modeling many experimental situations.

Density of states in energy - 1

We deduced above the form of the density of states in ***k***-space,

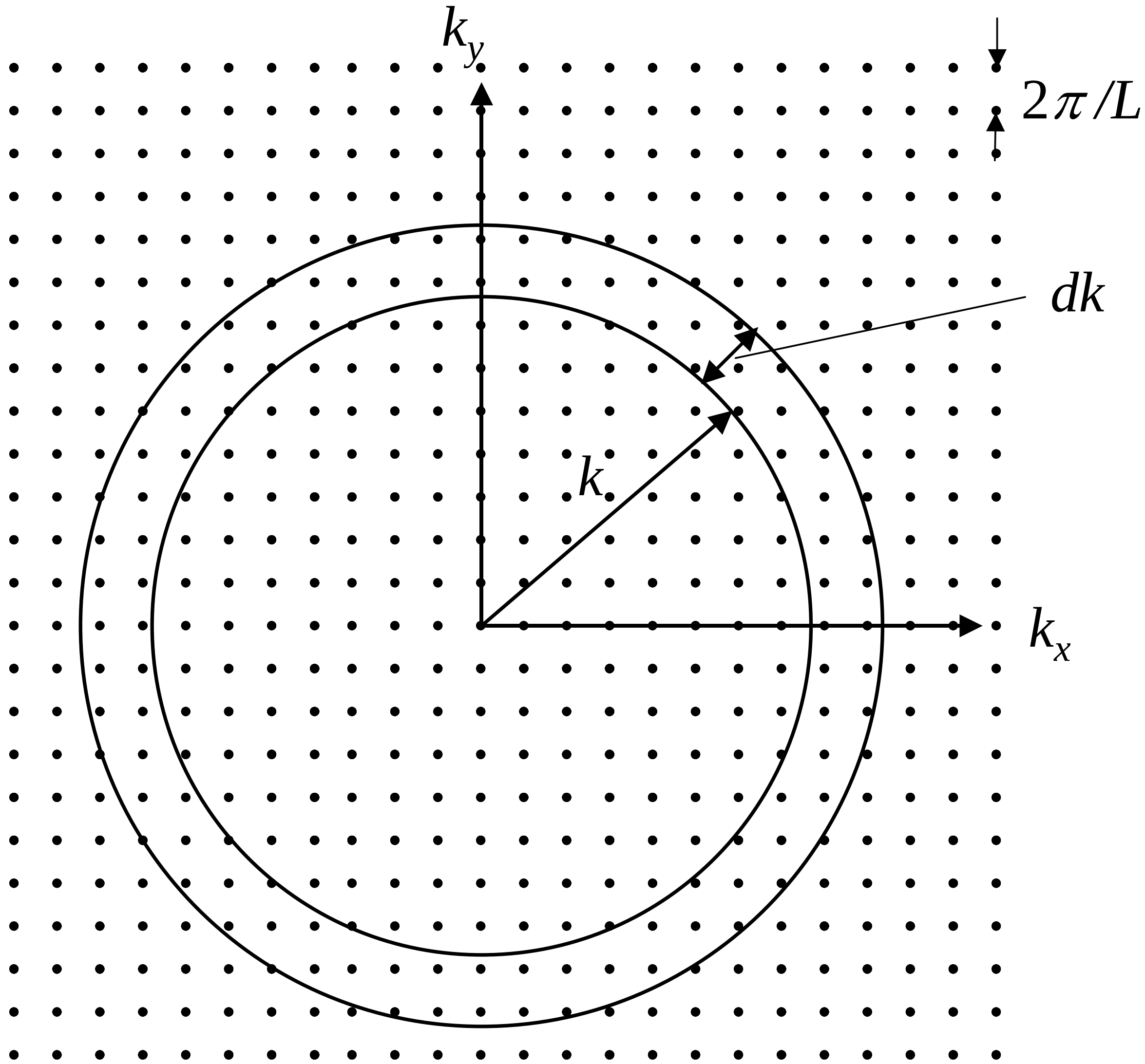
> *which is constant (Eq. (8.24)) and*
>
> *independent of the form of the band structure.*

For many calculations, however, we need the density of states in energy,

> *which does depend on the band structure*

To deduce the density of states in energy per unit (real) volume,

$$g(E)$$



we need to know the relation between the electron energy, E, and $\mathbf{k}$.

Here we will work out that density of states for an isotropic parabolic band.

Density of states in energy - 2

The number of states between energies E and $E+dE$,

i.e., $g(E)dE$,

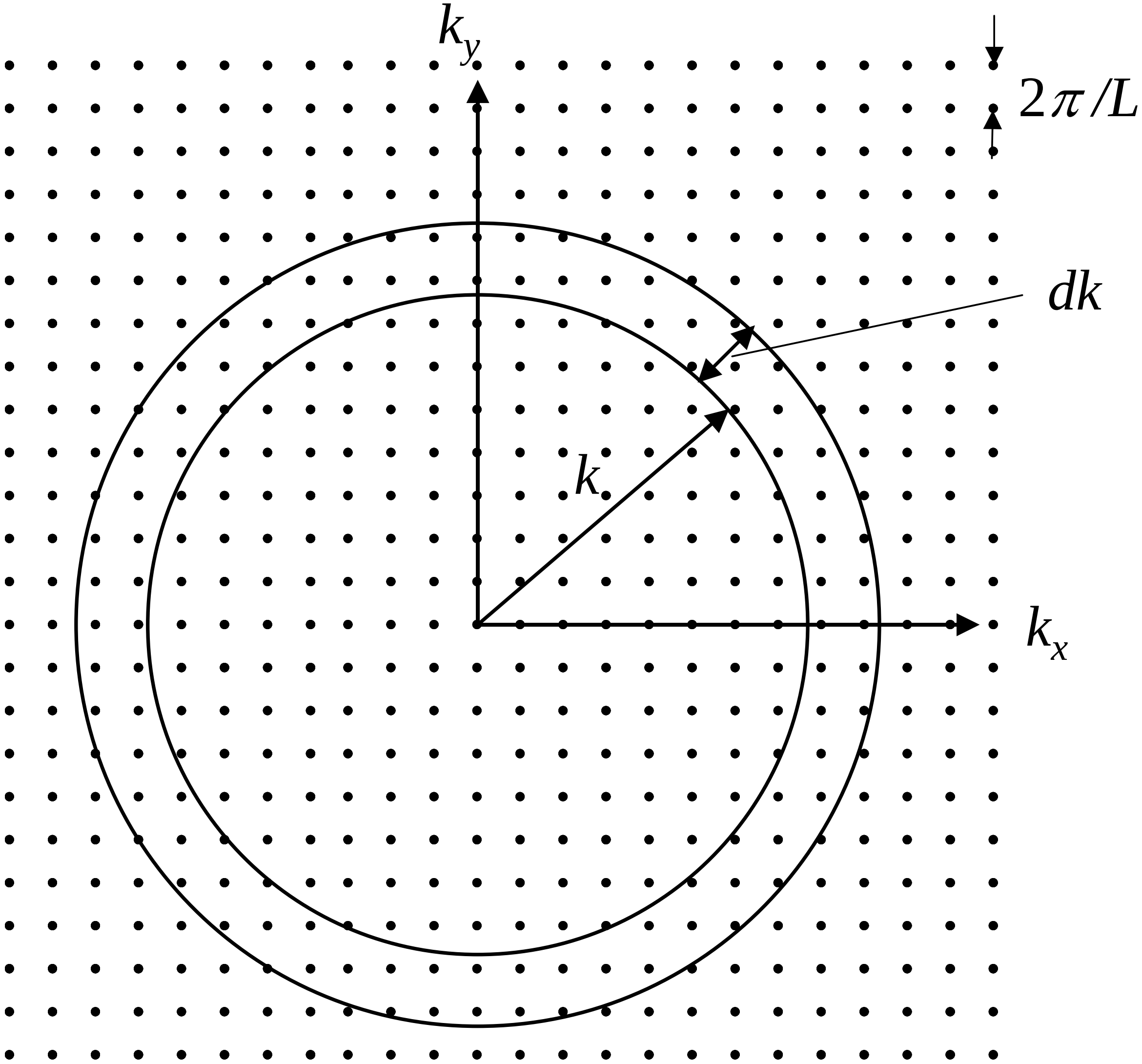
is then the number of states in *k*-space in a spherical shell between k and $k+dk$, where

$$dk = \left(\frac{dk}{dE}\right)dE \,. \qquad (8.37)$$

Using the parabolic band dispersion relation Eq. (8.28), we have

$$\frac{dk}{dE} = \frac{1}{2}\sqrt{\frac{2m_{eff}}{\hbar^2}}\frac{1}{\sqrt{E-V}} \qquad (8.38)$$

We now introduce the idea that electrons can have two possible spin states



For now it means we must multiply our density of states by a factor of 2,

hence the factor of 2 in front of $g(\mathbf{k})$ below.

Density of states in energy - 3

Putting all of this together gives

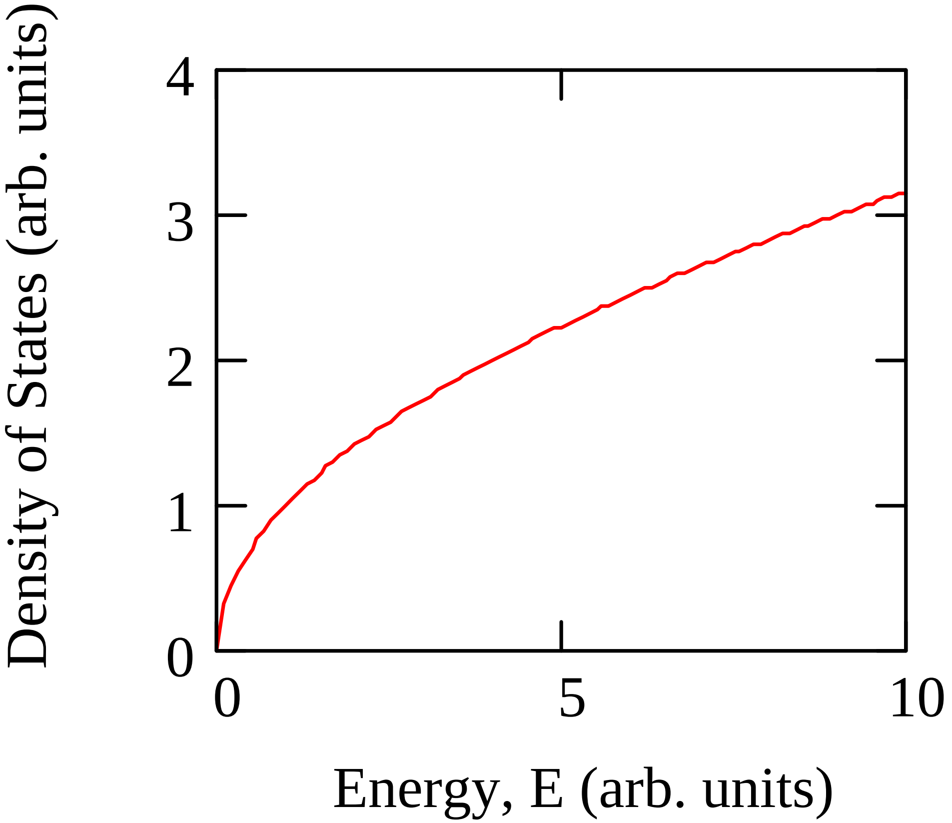
$$g(E)\,dE = 2g(\mathbf{k})\,d^3\mathbf{k} = \frac{2}{(2\pi)^3}4\pi k^2 dk = \frac{2}{(2\pi)^3}4\pi k^2 \frac{1}{2}\sqrt{\frac{2m_{eff}}{\hbar^2}}\frac{1}{\sqrt{E-V}}\,dE\,, \tag{8.39}$$

i.e.

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m_{eff}}{\hbar^2}\right)^{3/2}(E-V)^{1/2}. \tag{8.40}$$

This gives the classic " $E^{1/2}$ " density of states.

As the energy E rises above the energy of the bottom of the "parabola", the density of states rises as the square root of the extra energy.



Density of states as a function of energy above the bottom of the band for the case of a parabolic band ($V = 0$ for simplicity).

Quantum mechanics in crystalline materials – 3

Reading – Sections 8.8 – 8.9

Density of states in quantum wells

k·p method

Densities of states in quantum wells

Semiconductor quantum well –

a thin layer of a narrow band gap material,

such as GaAs,

between two wider band gap (e.g., AlGaAs) layers

It is a good example of a quantum confined structure

Quantum confinement changes the form of the density of states

useful for engineering improved optoelectronic devices,

such as lasers and optical modulators.

Our discussion now extends

one-dimensional "particle in a box" quantum mechanical behavior to

the full density of states including motion in the x and y directions.

Formal separation of the quantum well problem

Simple picture

- ***eigenstates of a particle (electron or hole)***
  - **particle in one of the states of the one-dimensional potential,**
    - *with envelope wavefunction, $\psi_n(z)$, in the z direction,*
  - **and unconstrained "free" plane-wave motion in the two directions in the plane of the quantum well layer, with wavevector k$_{xy}$.**

Formally, the Schrödinger equation for the envelope function is

$$-\frac{\hbar^2}{2m_{eff}}\nabla^2\psi(\mathbf{r})+V(z)\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{8.41}$$

- ***where $V(z)$ is only a function of z.***
  - **For quantum-confined structures such as quantum wires or quantum boxes or “dots”,**
    - *we formally would have a potential that was a function of two directions or three directions, respectively.*

Formal separation of the quantum well problem - 1

To solve (8.41), we formally separate the equation. We have

$$-\frac{\hbar^2}{2m_{eff}}\nabla_{xy}^2\psi(\mathbf{r})-\frac{\hbar^2}{2m_{eff}}\frac{\partial^2}{\partial z^2}\psi(\mathbf{r})+V(z)\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{8.42}$$

where

$$\nabla_{xy}^2 \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2} \tag{8.43}$$

We postulate a separation

$$\psi(\mathbf{r})=\psi_n(z)\psi_{xy}\left(\mathbf{r}_{xy}\right) \tag{8.44}$$

where $\mathbf{r}_{xy}\equiv x\mathbf{i}+y\mathbf{j}$ *is the electron position in the quantum well plane.*

Substituting this form, and dividing by it throughout, leads to

$$-\frac{\hbar^2}{2m_{eff}}\frac{1}{\psi_{xy}(\mathbf{r})}\nabla_{xy}^2\psi_{xy}(\mathbf{r})-\frac{\hbar^2}{2m_{eff}}\frac{1}{\psi_n(z)}\frac{\partial^2}{\partial z^2}\psi_n(z)+V(z)=E \tag{8.45}$$

We can formally separate the equation as

$$-\frac{\hbar^2}{2m_{eff}}\frac{1}{\psi_{xy}\left(\mathbf{r}_{xy}\right)}\nabla_{xy}^2\psi_{xy}\left(\mathbf{r}_{xy}\right)=E+\frac{\hbar^2}{2m_{eff}}\frac{1}{\psi_n(z)}\frac{\partial^2}{\partial z^2}\psi_n(z)-V(z) \tag{8.46}$$

Formal separation of the quantum well problem - 2

These must also equal a separation constant, here chosen to be E_{xy}, giving

$$-\frac{\hbar^2}{2m_{eff}}\nabla_{xy}^2\psi_{xy}\left(\mathbf{r}_{xy}\right)=E_{xy}\psi_{xy}\left(\mathbf{r}_{xy}\right) \tag{8.47}$$

and, with the formal choice

$$E=E_{xy}+E_n \tag{8.48}$$

we have also

$$-\frac{\hbar^2}{2m_{eff}}\frac{d^2}{dz^2}\psi_n\left(z\right)+V\left(z\right)\psi_n\left(z\right)=E_n\psi_n\left(z\right) \tag{8.49}$$

Eq. (8.47) is easily solved to give

$$\psi_{xy}\left(\mathbf{r}_{xy}\right)\propto\exp\left(i\mathbf{k}_{xy}.\mathbf{r}\right) \tag{8.50}$$

with

$$E_{xy}=\frac{\hbar^2k_{xy}^2}{2m_{eff}} \tag{8.51}$$

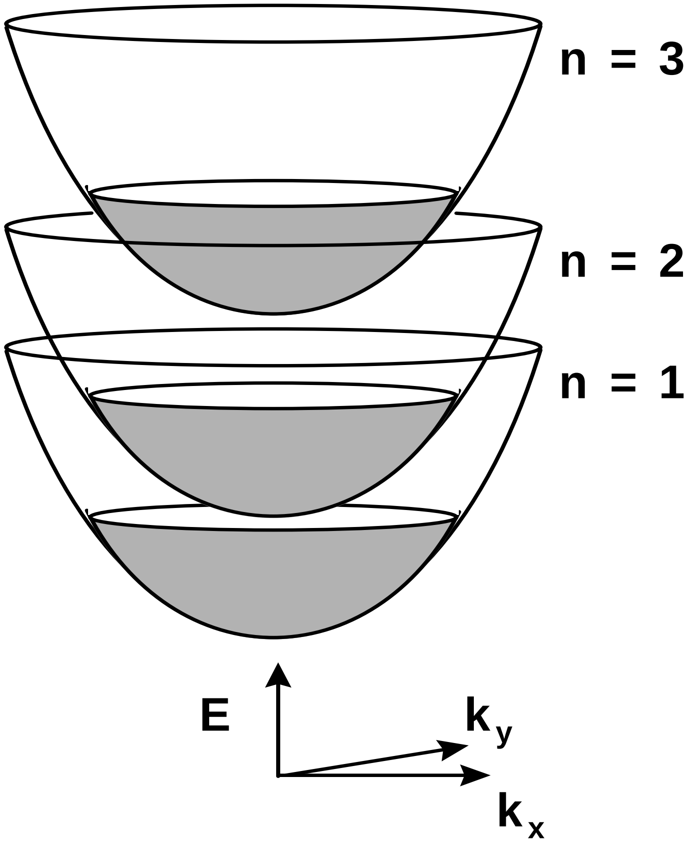
and Eq. (8.49) is the simple one-dimensional quantum well equation already solved for simple "square" potentials for the quantum well energy levels and wavefunctions in the z direction.

Subbands

The total allowed energies are

the energies E_n for the quantum well energies associated with state n,

plus the additional energy $\hbar^2 k_{xy}^2 / 2m_{eff}$ associated with the in-plane motion.



As a result,

instead of discrete energy levels,

we have so-called "subbands,".

Note that the bottom of each subband has the energy E_n of the one-dimensional quantum well problem.

Quantum well density of states - 1

Just as for the bulk case, we formally impose periodic boundary conditions in the *x* and *y* directions.

This gives us allowed values of the wavevector

in the x direction, k_x, spaced by $2\pi/L_x$

in the y direction, k_y, spaced by $2\pi/L_y$.

Each k_{xy} state occupies a k_{xy}-space "area" of $(2\pi)^2/A_{qw}$, where $A_{qw} = L_xL_y$,

and there is altogether one allowed value of k_{xy} for each unit cell in the x-y plane of the quantum well.

Therefore, the number of states in a small area d^2k_{xy} of k_{xy}-space is $(A_{qw}/(2\pi)^2)\mathbf{d}^2\mathrm{k}$.

Hence we can usefully define a (k_{xy}-space) density of states per unit (real) area, $g_{2D}(k_{\mathrm{xy}})$, given by

$$g_{2D}\left(\mathbf{k}_{xy}\right)=\frac{1}{\left(2\pi\right)^2} \quad (8.52)$$

Quantum well density of states - 2

The number of k states between energies E_{xy} and $E_{xy} + dE_{xy}$, i.e., $g_{2D}(E_{xy})dE_{xy}$,

is then the number of states in k_{xy}-space in the annular ring, of area $2\pi k_{xy} dk_{xy}$, between $\mathbf{k}_{xy}$ and $k_{xy} + dk_{xy}$, where

$$dk_{xy} = \left(\frac{dk_{xy}}{dE_{xy}}\right) dE_{xy} \tag{8.53}$$

Using the assumed parabolic relation between E_{xy} and k_{xy}, we have therefore, now multiplying by 2 to include the different spins

$$\begin{aligned} g_{2D}\left(E_{xy}\right) dE_{xy} &= 2 g_{2D}\left(\mathbf{k}_{xy}\right) 2\pi k_{xy} \frac{dk_{xy}}{dE_{xy}} dE_{xy} \\ &= \frac{2}{(2\pi)^2} 2\pi \sqrt{\frac{2m_{eff}}{\hbar^2}} \sqrt{E_{xy}} \frac{1}{2} \sqrt{\frac{2m_{eff}}{\hbar^2}} \frac{1}{\sqrt{E_{xy}}} dE_{xy} \end{aligned} \tag{8.54}$$

i.e.,

$$g_{2D}\left(E_{xy}\right) = \frac{m_{eff}}{\pi \hbar^2} \tag{8.55}$$

This density of states therefore has the very simple form that it is constant for all $E_{xy} > 0$.

It is therefore a "step" density of states, starting at $E_{xy} = 0$, i.e., starting at $E = E_n$. Hence, the total density of states as a function of the energy E rises as a series of steps, with a new step starting as we reach each E_n.

Special case of "infinite" quantum well density of states - 1

The "3D" density of states is

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m_{eff}}{\hbar^2}\right)^{3/2} E^{1/2} \tag{8.56}$$

The density of states in a bulk semiconductor at the energy E_1 that corresponds to the first confined state of a quantum well of thickness L_z is

$$g(E_1) = \frac{m_{eff}}{\pi\hbar^2}\frac{1}{L_z} \tag{8.57}$$

which is the same as the density of states per unit volume (rather than per unit area) of an "infinite" quantum well, i.e., dividing g_{2D} by L_z

$$g(E_1) = \frac{g_{2D}}{L_z} \tag{8.58}$$

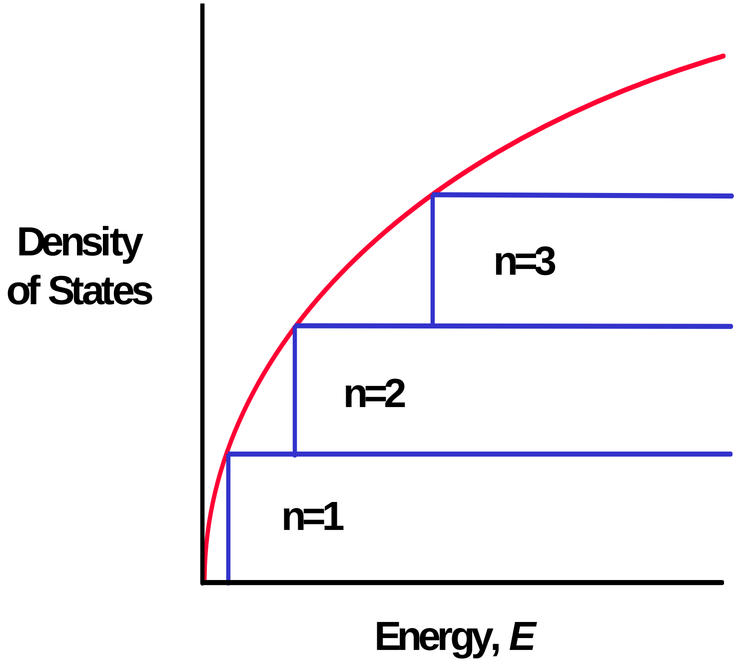
Special case of "infinite" quantum well density of states - 2

If we plot the "infinite" quantum well density of states (per unit volume),

it "touches" the bulk density of states (per unit volume) at the edge of the first step.

Furthermore, since the steps are space quadratically in energy,

and the bulk density of states is a "parabola on its side",



the quantum well (volume) density of states touches the bulk (volume) density of states at the corner of *each* step.

If we started to increase the thickness of the quantum well,

the steps would get closer and closer together,

but their corners would still touch the bulk density of states,

so that, as the quantum well became very thick

we would eventually not be able to distinguish its density of states from that of the bulk material.

k·p method - 1

We are particularly interested in the behavior of semiconductors near to maxima and minima.

- ***It is possible to construct simple, semi-empirical models useful near band minima and maxima.***
  - **The k.p method allows us to calculate how properties change near to those maxima and minima,**
    - *and allows us to relate various different phenomena,*
    - *such as optical absorption strengths and band gap energies.*
  - **Only a few measurable parameters are required to define the most useful properties of the band structure.**

k·p method - 2

We start by substituting the Bloch form, Eq. (8.20), into the Schrödinger equation, Eq. (8.3).

Now we explicitly label the band n of a given unit cell function.

Noting that

$$\nabla\left[u_{n\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})\right]=\left\{\left[\nabla u_{n\mathbf{k}}(\mathbf{r})\right]+i\mathbf{k}u_{n\mathbf{k}}(\mathbf{r})\right\}\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad (8.59)$$

and

$$\nabla^2\left[u_{n\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})\right]=\left\{\nabla^2 u_{n\mathbf{k}}(\mathbf{r})+2i\mathbf{k}\cdot\nabla u_{n\mathbf{k}}(\mathbf{r})-k^2u_{n\mathbf{k}}(\mathbf{r})\right\}\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad (8.60)$$

we have

$$\left[\hat{H}_o+\frac{\hbar}{m_o}\mathbf{k}\cdot\hat{\mathbf{p}}\right]u_{n\mathbf{k}}(\mathbf{r})=\left[E_n(\mathbf{k})-\frac{\hbar^2k^2}{2m_o}\right]u_{n\mathbf{k}}(\mathbf{r}) \qquad (8.61)$$

where $\hat{\mathbf{p}}=-i\hbar\nabla$*,*

$E_n(\mathbf{k})$ *is the energy eigenvalue for the state* $\mathbf{k}$ *in band n*

Note also we can write

$$\hat{H}_o=\frac{-\hbar^2}{2m_o}\nabla^2+V_L(\mathbf{r}) \qquad (8.62)$$

$$\hat{H}_o u_{n0}(\mathbf{r})=E_n(0)u_{n0}(\mathbf{r}) \qquad (8.63)$$

Note we are now using the notation m_o for the electron mass

k·p method - 3

These $u_{n0}(\mathbf{r})$ are therefore the solutions for the unit cell functions at $k=0$

(set $k=0$ in Eq. (8.61)).

Now comes a key step in this approach to band structure.

Because the $u_{n0}(\mathbf{r})$ are the solutions to an eigen equation, Eq. (8.63),

they form a complete set for describing unit cell functions,

and so we can, if we wish, expand the $u_{n\mathbf{k}}(\mathbf{r})$ in them, i.e.,

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{nn'k} u_{n'0}(\mathbf{r}) \tag{8.64}$$

i.e., we are expanding

the unit cell function in band n and wavevector $\mathbf{k}$

in the set of unit cell functions of all the bands for $k=0$.

The expansion Eq. (8.64) is sometimes known as the Luttinger-Kohn representation.

This expansion is over the bands n'.

When we have to add in some finite amount of the unit cell function from some particular band, $u_{n'0}(\mathbf{r})$, in the expansion Eq. (8.64),

we say we are mixing in some of that "band,"

strictly we are adding in some of the zone-center unit cell function from that band.

k·p method - 4

Thus far, we have merely rewritten the Schrödinger equation for the electron given its known Bloch form.

- ***Now presume (or pretend) that we know the wavefunctions $u_{n0}(r)$ and energies $E_n(0)$ at $\mathbf{k} = 0$.***
  - **Though we do not really know the wavefunctions,**
    - *we will only need some specific matrix elements using these wavefunctions,*
      - and these matrix elements can be deduced from other experimental measurements.
- ***With this presumption,***
  - **we could treat the $\mathbf{k} \cdot \mathbf{p}$ term as a perturbation,**
    - *and use perturbation theory to deduce effective masses and other properties.*
  - **We will not take such a perturbative approach, though it can be done.**
    - *Instead, more generally useful results can be obtained by*
      - "pretending" that we only need to consider a small number of basis functions, $u_{no}(\mathbf{r})$, to analyze the problem,
      - this is a "finite basis set approximation."
    - *This enables us to get exact results for a somewhat artificial problem;*
      - if we have chosen our limited set of basis functions properly, we will have a good first approximation to the actual problem,
      - and then we could add in other terms as perturbations.

k·p *model for a two-band semiconductor - 1*

We will look at the simplest model of this kind

to show how such methods work,

and the kinds of results they can give.

This simple model is for an idealized "two-band" semiconductor.

In general, if we substitute the expansion, Eq. (8.64) into the rewritten Schrödinger equation, Eq. (8.61), we have,

$$\left[\hat{H}_o + \frac{\hbar}{m_o}\mathbf{k}\cdot\hat{\mathbf{p}}\right]\sum_{n'} a_{n'} u_{n'0}(\mathbf{r}) = \left[E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_o}\right]\sum_{n'} a_{n'} u_{n'0}(\mathbf{r}) \tag{8.65}$$

Multiplying on the left by $u_{n0}^*(\mathbf{r})$ ***and integrating over a unit cell, we have***

$$\sum_{n'}\left\{\left[E_n(0) + \frac{\hbar^2 k^2}{2m_o}\right]\delta_{nn'} + \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}_{nn'}\right\} a_{n'} = E_n(\mathbf{k}) a_n \tag{8.66}$$

where we have used the orthonormality of the $u_{n0}(\mathbf{r})$**, and where**

$$\mathbf{p}_{nn'} \equiv \int_{\substack{unit\\cell}} u_{n0}^*(\mathbf{r})\,\hat{\mathbf{p}}\,u_{n'0}(\mathbf{r})\,d^3\mathbf{r} \tag{8.67}$$

k·p *model for a two-band semiconductor - 2*

Up to this point, we have made no approximations.

Eq. (8.66) is a complete statement of the Schrödinger wave equation for a periodic potential and periodic boundary conditions.

Now we presume that only two bands are important.

We will presume (as is usually the case) that the $u_{n0}(\mathbf{r})$ have definite parity,

so $\mathbf{p}_{nn} = 0$

Hence, now writing Eq. (8.66) in matrix form for the two bands of interest, 1 and 2, we have

$$\begin{bmatrix} E_1(0) + \dfrac{\hbar^2 k^2}{2m_o} & \dfrac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}_{12} \\ \dfrac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}_{21} & E_2(0) + \dfrac{\hbar^2 k^2}{2m_o} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E(\mathbf{k}) \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \tag{8.68}$$

k·p *model for a two-band semiconductor - 3*

To solve this equation for the eigen energies of the two bands, we set the appropriate determinant to zero, i.e.,

$$\begin{vmatrix} E_1(0) + \frac{\hbar^2 k^2}{2m_o} - E(\mathbf{k}) & \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}_{12} \\ \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}_{21} & E_2(0) + \frac{\hbar^2 k^2}{2m_o} - E(\mathbf{k}) \end{vmatrix} = 0 \qquad (8.69)$$

The operator $\mathbf{p}$ is Hermitian, and so $\mathbf{p}_{12} = \mathbf{p}_{21}^*$.

Let us also presume for simplicity here

(i) that we know for some reason that $\mathbf{p}_{12}$ is isotropic,

(ii) that $\hbar^2 k^2 / 2m_o$ is negligible compared to $E(\mathbf{k})$

as will be the case if the resulting bands turn out to have very light effective masses.

Hence we have

$$\begin{vmatrix} E_1(0) - E(\mathbf{k}) & \frac{\hbar}{m_o} k p_{12} \\ \frac{\hbar}{m_o} k p_{12}^* & E_2(0) - E(\mathbf{k}) \end{vmatrix} \cong 0 \qquad (8.70)$$

k·p *model for a two-band semiconductor - 4*

We choose the energy origin as $E_1(0)=0$,

and we write $E_2(0)-E_1(0)=E_g$**.**

We also define the parameter E_p as

$$E_p = \frac{2}{m_0}\left|p_{12}\right|^2, \tag{8.71}$$

Hence we have, from Eq. (8.70),

$$-E(k)\big(E_g - E(k)\big) - E_p\frac{\hbar^2 k^2}{2m_o} = 0 \tag{8.72}$$

which is a quadratic with two solutions.

For small k, we have

$$E(k) = E_g + \frac{E_p}{E_g}\frac{\hbar^2 k^2}{2m_o} \tag{8.73}$$

or

$$E(k) = -\frac{E_p}{E_g}\frac{\hbar^2 k^2}{2m_o} \tag{8.74}$$

k·p *model for a two-band semiconductor - 5*

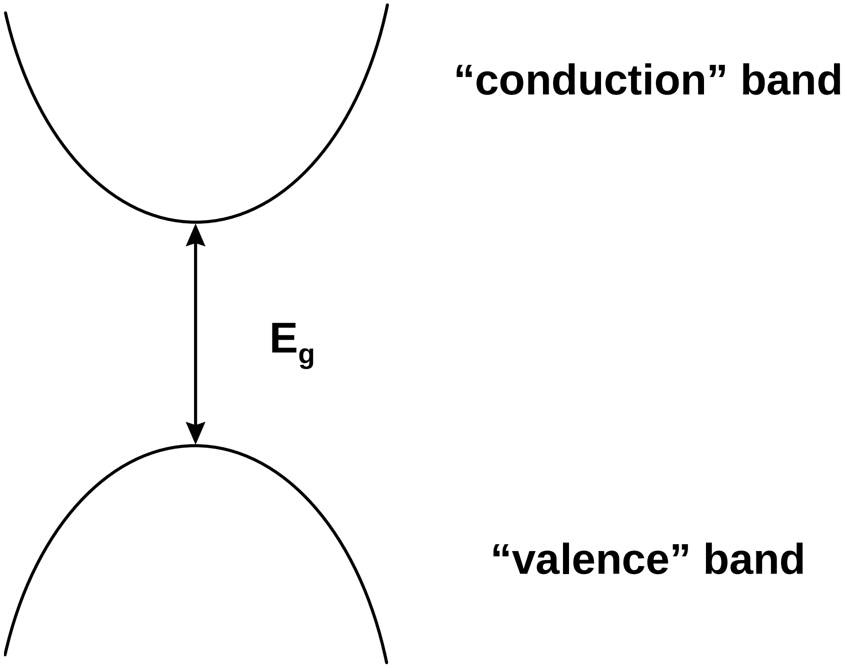
Hence the band structure calculated from this simple set of assumptions consists of two bands,

a conduction-like band starting at energy E_g, with a positive effective mass

$$m_{eff2} = m_o \frac{E_g}{E_p} \qquad (8.75)$$

and a valence-like band starting at energy 0, with a negative (i.e., hole-like) effective mass

$$m_{eff1} = -m_o \frac{E_g}{E_p} \qquad (8.76)$$



Note the effective masses depend proportionately on the energy gap, E_g.

Note the effective mass is "caused" by the "interaction between the bands."

If the $\mathbf{p}_{12}$ and $\mathbf{p}_{21}$ matrix elements were zero,

then the matrix in Eq. (8.68) would simply be diagonal,

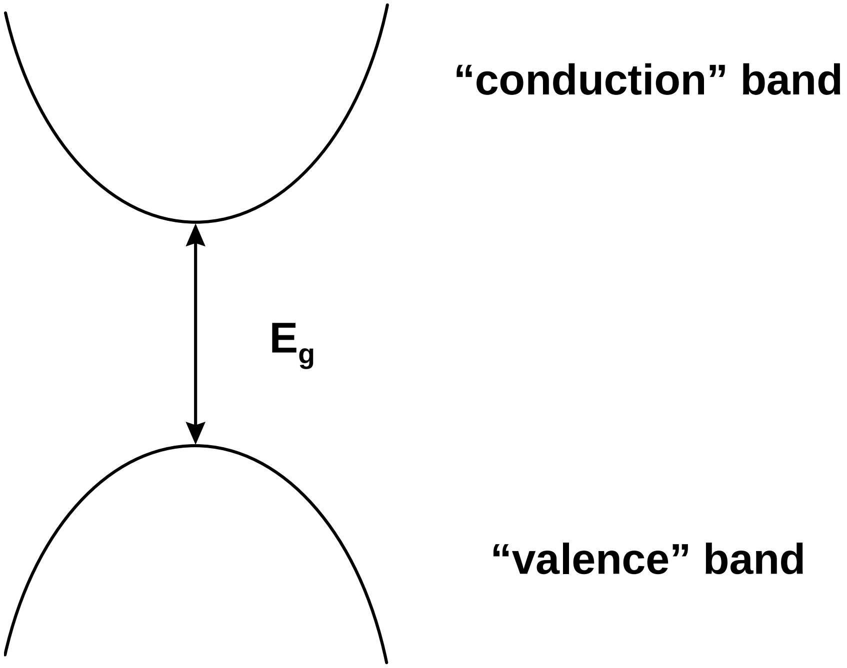
and both bands would simply have the free electron mass.

k·p *model for a two-band semiconductor - 6*

Having worked out the eigenenergies, it is now a simple matter to work out the eigenvectors or eigenfunctions.

With the simplifying approximations and definitions we made, for example, the matrix equation, Eq. (8.68), is

$$\begin{bmatrix} 0 & \frac{\hbar}{m_o}kp_{12} \\ \frac{\hbar}{m_o}kp_{12}^* & E_g \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E(\mathbf{k})\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad (8.77)$$



Hence, for the upper band (band 2), we have, using the eigenenergy solution, Eq. (8.73)

$$\begin{bmatrix} -E_g - \frac{E_p}{E_g}\frac{\hbar^2k^2}{2m_o} & \frac{\hbar}{m_o}kp_{12} \\ \frac{\hbar}{m_o}kp_{12}^* & -\frac{E_p}{E_g}\frac{\hbar^2k^2}{2m_o} \end{bmatrix}\begin{bmatrix} a_{21k} \\ a_{22k} \end{bmatrix} = 0 \quad (8.78)$$

k·p *model for a two-band semiconductor - 7*

Explicitly the expansion of Eq. (8.64) is, in this simple two band case,

$$u_{2\mathbf{k}}(\mathbf{r}) = a_{21k}u_{10}(\mathbf{r}) + a_{22k}u_{20}(\mathbf{r})$$

(8.79)

To deduce the unit cell wavefunctions as a function of k in this band 2,

we solve equation Eq. (8.78) for the coefficients a_{21k} and a_{22k}.

For the simple case of $k = 0$,

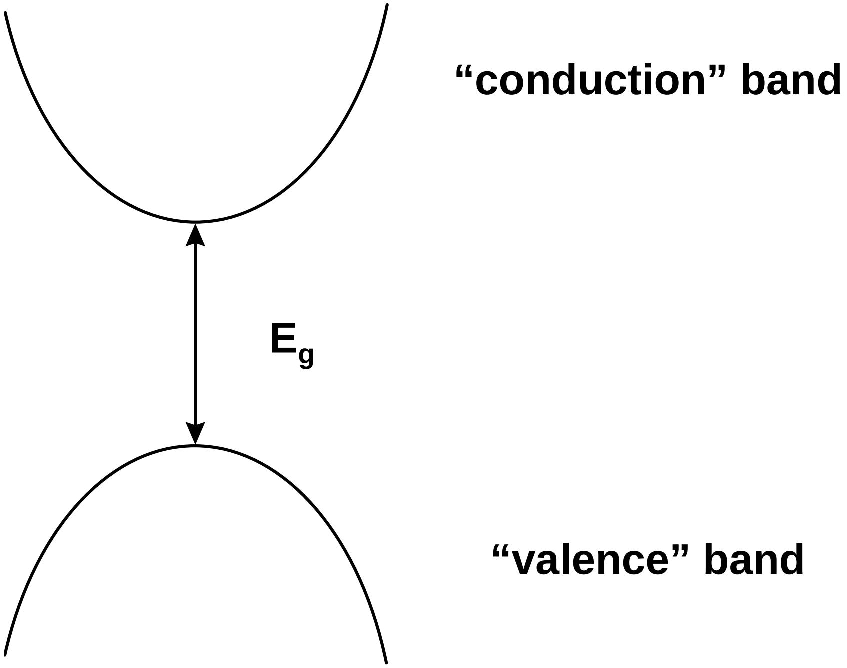
the only non-zero term is the upper left term,

which is then equal to $-E_g$.

As a result, we have $-E_g a_{21k} = 0$,

which means that $a_{21k} = 0$.

Hence, at $k = 0$, the unit cell wavefunction is $u_{20}(\mathbf{r})$ for the upper band, as we would have expected.



k·p *model for a two-band semiconductor - 8*

Away from $k = 0$, however,

the coefficients a_{21k} and a_{22k} deduced from Eq. (8.78) are both, in general, non-zero.

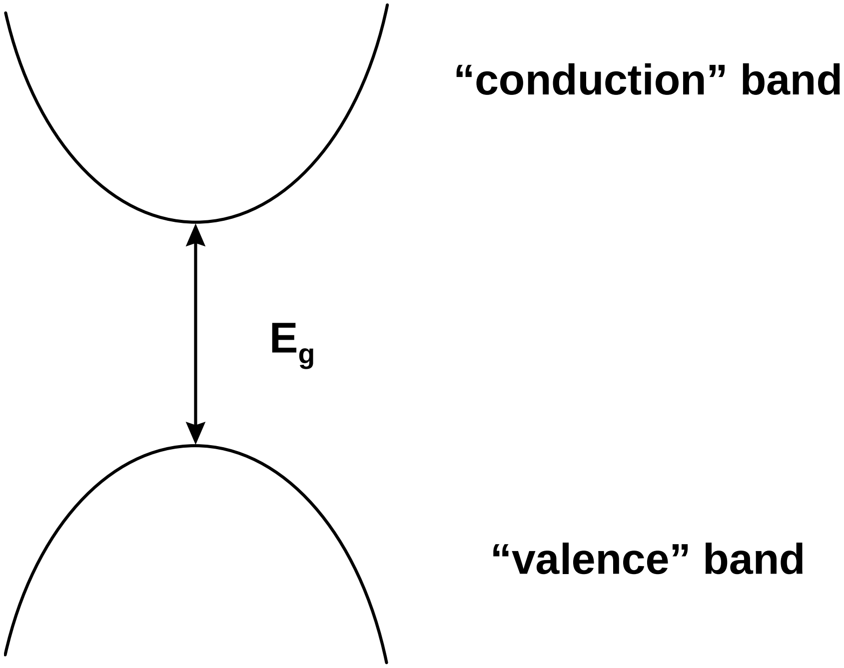
We would find a growing admixture of $u_{10}(\mathbf{r})$ as we move away from $k = 0$.

This is a simple example of "band mixing."

As we move away from $k = 0$,

the unit cell wavefunctions are no longer exactly the ideal functions,

with simple exact parities and symmetry properties, found at $k = 0$.



For "allowed" processes (“one photon” valence-conduction optical absorption), this mixing is not very important for small k,

"Forbidden" processes, i.e., ones disallowed at $k = 0$ by symmetry, can become progressively stronger as we move away from $k = 0$

Quantum mechanics in crystalline materials – 4

Reading – Section 8.10

Optical absorption in direct gap semiconductors

use of Fermi's Golden Rule

Optical absorption in direct gap semiconductors - 1

Now that we have a sufficient model for crystalline semiconductors,

we can use the most important result of time-dependent perturbation theory we derived before,

Fermi's Golden Rule (No. 2),

to calculate the optical absorption in direct gap semiconductors.

From Eq. (7.32),

$$w_{jm} = \frac{2\pi}{\hbar} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 \delta\left(E_{jm} - \hbar\omega\right)$$

we know that

the transition rate for absorption between

an initial electron state $\left|\psi_i\right\rangle$ in the valence band, with energy E_i,

and a final state $\left|\psi_f\right\rangle$ in the conduction band, with energy E_f,

in the presence of an oscillating perturbation of angular frequency ω, is

$$w_{abs} = \frac{2\pi}{\hbar} \left| \left\langle \psi_f \left| \hat{H}_{po} \right| \psi_i \right\rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right) \quad (8.80)$$

Optical absorption in direct gap semiconductors - 2

$\hat{H}_{po}$ **is of the form defined by Eq. (7.15)**

$$\hat{H}_p(t) = e\mathrm{E}(t)z = \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right]$$

In the present context

where we are interested also in the spatial variation of the perturbation,

here through the spatial dependence of the amplitude of an electromagnetic wave,

$$\hat{H}_p(\mathbf{r},t) = \hat{H}_{po}(\mathbf{r})\left[\exp(-i\omega t) + \exp(i\omega t)\right] \tag{8.81}$$

while the oscillatory field is "turned on".

$\left\langle \psi_f \middle| \hat{H}_{po} \middle| \psi_i \right\rangle$ **can now be written explicitly as**

$$\left\langle \psi_f \middle| \hat{H}_{po} \middle| \psi_i \right\rangle = \int \psi_f^*(\mathbf{r})\hat{H}_{po}(\mathbf{r})\psi_i(\mathbf{r})\,d^3\mathbf{r} \tag{8.82}$$

where $\psi_i(\mathbf{r})$ ***and*** $\psi_f(\mathbf{r})$ ***are, respectively, the wave functions of the initial and final states***

Form of the perturbing Hamiltonian for an electromagnetic field

For the case of an electron in an electromagnetic field,

the usual form presumed for $\hat{H}_p(\mathbf{r},t)$ is (see Appendix E)

$$\hat{H}_p(\mathbf{r},t) \cong -\frac{e}{m_0}\mathbf{A}\cdot\hat{\mathbf{p}} \tag{8.83}$$

where

m_0 **is the mass of the free electron**

$\hat{\mathbf{p}}$ **is the momentum operator $-i\hbar\nabla$, and**

$\mathbf{A}$ **is the electromagnetic vector potential corresponding to a wave of (angular) frequency ω**

$$\mathbf{A} = \mathbf{e}\left\{\frac{A_0}{2}\exp\left[i\left(\mathbf{k}_{op}\cdot\mathbf{r}-\omega t\right)\right]+\frac{A_0}{2}\exp\left[-i\left(\mathbf{k}_{op}\cdot\mathbf{r}-\omega t\right)\right]\right\} \tag{8.84}$$

Here $\mathbf{k}_{op}$ is the wave vector of the optical field inside the material, and we have taken the field to be linearly polarized with its electric vector in the direction of the unit vector $\mathbf{e}$.

Retaining only the $\exp(-i\omega t)$ term because only it corresponds to absorption, we therefore have

$$\hat{H}_{po}(\mathbf{r}) = -\frac{e\,A_0\exp\left(i\mathbf{k}_{op}\cdot\mathbf{r}\right)}{2m_0}\mathbf{e}\cdot\hat{\mathbf{p}} \tag{8.85}$$

i.e., we are using $\hat{H}_p(\mathbf{r},t) = \hat{H}_{po}\exp(-i\omega t)$ with $\hat{H}_{po}(\mathbf{r})$ as in Eq. (8.85)

Direct valence to conduction band absorption - 1

To proceed further, we need to know $\psi_i(\mathbf{r})$ and $\psi_f(\mathbf{r})$.

We presume that we can use the "single-electron" Bloch states deduced.

We are most interested in the transitions between

an initial state in the valence band and

a final state in the conduction band.

We will want to use normalized wave functions in the calculation below, and so we will define

$$\psi_i(\mathbf{r}) = B_i u_v(\mathbf{r}) \exp(i\mathbf{k}_v \cdot \mathbf{r}) \tag{8.86}$$

and

$$\psi_f(\mathbf{r}) = B_f u_c(\mathbf{r}) \exp(i\mathbf{k}_c \cdot \mathbf{r}) \tag{8.87}$$

where B_i and B_f are normalization constants

Here, and below, we omit the subscript $\mathbf{k}$ on $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$ for simplicity.

Note that we are now explicitly allowing the conduction ($u_c(\mathbf{r})$) and valence ($u_v(\mathbf{r})$) unit cell functions to be different.

We do, however, presume that they do not depend on $\mathbf{k}$, which is in practice a good approximation for an "allowed" process.

Direct valence to conduction band absorption - 2

In our normalization calculation, first we choose $u_v(\mathbf{r})$ and $u_c(\mathbf{r})$ to be normalized over a unit cell, i.e.,

$$\int_{unit\ cell} u_v^*(\mathbf{r})\, u_v(\mathbf{r})\, d^3\mathbf{r} = 1 \qquad (8.88)$$

and similarly for $u_c(\mathbf{r})$.

Hence, normalizing $\psi_i(\mathbf{r})$ and $\psi_f(\mathbf{r})$, we have, for ψ_i

$$\begin{aligned}\int_V \psi_i^*(\mathbf{r})\, \psi_i(\mathbf{r})\, d^3\mathbf{r} &= 1 \\ &= B_i^2 \int_V u_v^*(\mathbf{r}) \exp\left(-i\mathbf{k}_v \cdot \mathbf{r}\right) u(\mathbf{r}) \exp\left(i\mathbf{k}_v \cdot \mathbf{r}\right) d^3\mathbf{r} \\ &= B_i^2 \int_V u_v^*(\mathbf{r}) u_v(\mathbf{r})\, d^3\mathbf{r} = B_i^2 N \int_{unit\ cell} u_v^*(\mathbf{r}) u_v(\mathbf{r})\, d^3\mathbf{r} \\ &= B_i^2 N \end{aligned} \qquad (8.89)$$

where N is the number of unit cells and V is the volume of the crystal, and similarly for $\psi_f(\mathbf{r})$.

Hence we have

$$B_i = B_f = \frac{1}{\sqrt{N}} \qquad (8.90)$$

Direct valence to conduction band absorption - 3

With the choice of a valence band initial state and a conduction band final state, the matrix element of interest is now, from Eq. (8.82)

$$\left\langle \psi_f \middle| \hat{H}_{po}(\mathbf{r}) \middle| \psi_i \right\rangle = -\frac{eA_0}{2m_0 N} \int_V \left[u_c^*(\mathbf{r}) \exp(-i\mathbf{k}_c \cdot \mathbf{r}) \right] \exp\left(i\mathbf{k}_{op} \cdot \mathbf{r}\right) \mathbf{e} \cdot \hat{\mathbf{p}} \left[u_v(\mathbf{r}) \exp(i\mathbf{k}_v \cdot \mathbf{r}) \right] d^3\mathbf{r} \tag{8.91}$$

We are interested in transitions involving states near the center of the Brillouin zone, so

$|\mathbf{k}_v|$ ***and*** $|\mathbf{k}_c|$ ***are both*** $<< \pi / a$

(π / a **corresponds to the edge of the zone).**

Strictly,

$\hat{\mathbf{p}}$ ***operates on the product*** $u_v(\mathbf{r}) \exp(i\mathbf{k}_v \cdot \mathbf{r})$***,***

but $\exp(i\mathbf{k}_v \cdot \mathbf{r})$ **changes very slowly compared to the rate of change of** $u_v(\mathbf{r})$**,**

i.e., $\left| \nabla \exp(i\mathbf{k}_v \cdot \mathbf{r}) \right| \sim k_v << \left| \nabla u_v(\mathbf{r}) \right| \sim \pi / a$,

so we can neglect $\hat{\mathbf{p}}$ **operating on** $\exp(i\mathbf{k}_v \cdot \mathbf{r})$**, at least as a first approximation.**

Direct valence to conduction band absorption - 4

For definiteness, we choose $\mathbf{e}$ in the *x*-direction

- ***x will be one of the directions perpendicular to the propagation of the electromagnetic wave, and is the direction of polarization of the optical electric field.***

Rewriting, we have (neglecting the effect of $\hat{\mathbf{p}}$ on $\exp(i\mathbf{k}_v \cdot \mathbf{r})$)

$$\langle \psi_f | \hat{H}_{po}(\mathbf{r}) | \psi_i \rangle = -\frac{eA_0}{2m_0 N} \int_V \exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right) \cdot \mathbf{r}\right]\left[u_c^*(\mathbf{r})\, \hat{p}_x u_v(\mathbf{r})\right] d^3\mathbf{r} \qquad (8.92)$$

The optical wave vector $\mathbf{k}_{op}$ corresponds to the wavelengths (even inside the material) of 100s of nm or more,

- ***which means that $|\mathbf{k}_{op}| << \pi / a$.***

In fact, compared to the size scale of the Brillouin zone,

- $|\mathbf{k}_{op}|$ ***is almost totally negligible;***
  - **even with a 100 nm wavelength inside the material, $|\mathbf{k}_{op}| \sim 2\pi / 100\ \text{nm}^{-1}$,**
  - **while the edge of the Brillouin zone is $\pi / a \sim \pi / 0.5\ \text{nm}^{-1}$,**
    - *corresponding to $|\mathbf{k}_{op}| / (\pi / a) \sim 1\%$.*

Direct valence to conduction band absorption - 5

Hence, the entire factor $\exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{r}\right]$ varies very slowly over the length scale, a, of a unit cell.

As a result, we can approximately separate the above integral into a sum of integrals over a unit cell,

treating the value of $\exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{r}\right]$ as being approximately constant within a given unit cell, i.e.,

$$\left\langle\psi_f\left|\hat{H}_{po}(\mathbf{r})\right|\psi_i\right\rangle = -\frac{eA_0}{2m_0N}\langle c|\hat{p}_x|v\rangle \sum_{\substack{m\,(i.e.,\\ unit\,cells)}} \exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{R}_m\right] \tag{8.93}$$

where $\mathbf{R}_m$ is the position of (the center of) the *m*th unit cell in the crystal, and the summation is over all N unit cells.

Here

$$\langle c|\hat{p}_x|v\rangle \equiv \int_{\substack{unit\\ cell}} u_c^*(\mathbf{r})\,\hat{p}_x u_v(\mathbf{r})\,d^3\mathbf{r} \equiv p_{cv} \tag{8.94}$$

Direct valence to conduction band absorption - 6

The summation in Eq. (8.93)

$$\left\langle \psi_f \middle| \hat{H}_{po}(\mathbf{r}) \middle| \psi_i \right\rangle = -\frac{eA_0}{2m_0 N}\langle c|\hat{p}_x|v\rangle \sum_{\substack{m(i.e.,\\ unit\,cells)}} \exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{R}_m\right]$$

will average approximately to zero unless

$$\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op} = 0 \qquad (8.95)$$

because otherwise the function $\exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{r}\right]$ ***is oscillatory***

note, incidentally, that the condition Eq. (8.95) can be seen to correspond to conservation of "momentum" $(\hbar\mathbf{k})$**.**

In this case, the sum becomes

$$\sum_m \exp\left[i\left(\mathbf{k}_v - \mathbf{k}_c + \mathbf{k}_{op}\right)\cdot\mathbf{R}_m\right] = \sum_m \exp(0) = N \qquad (8.96)$$

Hence, we have

$$\left\langle \psi_f \middle| \hat{H}_{po}(\mathbf{r}) \middle| \psi_i \right\rangle = -\frac{eA_0}{2m_0} p_{cv} \qquad (8.97)$$

and the transition rate becomes

$$w_{abs} = \frac{2\pi}{\hbar}\frac{e^2 A_0^2}{4m_0^2}|p_{cv}|^2 \delta\left(E_f - E_i - \hbar\omega\right) \qquad (8.98)$$

Direct valence to conduction band absorption - 7

Eq. (8.98)

$$w_{abs} = \frac{2\pi}{\hbar}\frac{e^2 A_0^2}{4m_0^2}\left|p_{cv}\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

is therefore the restatement of Fermi's Golden Rule, Eq. (8.80),

$$w_{abs} = \frac{2\pi}{\hbar}\left|\left\langle\psi_f\left|\hat{H}_{po}\right|\psi_i\right\rangle\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

after we have made use of the facts that

(i) the electron wavefunctions in the crystalline semiconductor are in the Bloch form, and

(ii) the optical wavelength is much larger than the unit cell size.

Note that the concept of conservation of momentum emerged automatically,

and is consistent with $\hbar\mathbf{k}$ ***being the effective electron momentum in a Bloch state.***

Note also that the transition rate is proportional to

a (squared) matrix element, $\left|p_{cv}\right|^2$***,***

the optical intensity (which is proportional to A_o^2***),***

and hence to the average arrival rate of photons in the semiconductor (per unit area).

Total transition rate - 1

Eq. (8.98) $$w_{abs} = \frac{2\pi}{\hbar}\frac{e^2 A_0^2}{4m_0^2}\left|p_{cv}\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

represents the transition rate from

one particular initial valence band state with $\mathbf{k}$ vector $\mathbf{k}_v$

to a particular conduction band state

in this case, the state with wave vector $\mathbf{k}_c = \mathbf{k}_v + \mathbf{k}_{op}$.

The total transition rate, W_{TOT},

which we need to calculate the optical absorption coefficient, α,

is the sum of the transition rates between all possible initial states and all possible final states, i.e.,

$$W_{TOT} = \frac{2\pi}{\hbar}\sum_i \sum_f \left|\left\langle \psi_f \middle| \hat{H}_{po}(\mathbf{r}) \middle| \psi_i \right\rangle\right|^2 \delta\left(E_f - E_i - \hbar\omega\right) \quad (8.99)$$

Total transition rate - 2

We have shown above that,

for a given initial state with wave vector $\mathbf{k}_v$,

the only final state possible is the conduction band state with $\mathbf{k}_c = \mathbf{k}_v + \mathbf{k}_{op}$.

Since $\left|\mathbf{k}_{op}\right|$ is generally a very small fraction of the size of the Brillouin zone, we will henceforth neglect it, taking $\mathbf{k}_c = \mathbf{k}_v$

this negligible size of the optical wavevector means that the direct optical transitions are essentially "vertical" on the energy-momentum diagram.

Hence, for a given initial state $\mathbf{k}_v$,

only one term remains in the sum over the final states,

namely that with $\mathbf{k}_c = \mathbf{k}_v$.

Hence we have, substituting from Eq. (8.98), $w_{abs} = \frac{2\pi}{\hbar} \frac{e^2 A_0^2}{4m_0^2} \left|p_{cv}\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$

and dropping the suffix "v" (i.e., writing $\mathbf{k}$ instead of $\mathbf{k}_v$)

$$W_{TOT} = \frac{2\pi}{\hbar} \frac{e^2 A_0^2}{4m_0^2} \left|p_{cv}\right|^2 \sum_{\mathbf{k}} \delta\left[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega\right] \qquad (8.100)$$

In Eq. (8.100) we have additionally assumed $\left|p_{cv}\right|^2$ is independent of $\mathbf{k}$, which turns out to be a reasonable approximation for an "allowed" process.

Total transition rate - 3

Now we formally rewrite (considering unit volume)

$$\sum_{\mathbf{k}} \approx \int_{\mathbf{k}} g(\mathbf{k}) d^3\mathbf{k} \qquad (8.101)$$

where $g(\mathbf{k})$ is the density of states in k-space.

We next change variables in the integral to the energy $E_c(\mathbf{k}) - E_v(\mathbf{k})$.

Assuming parabolic bands, we can define E_J, the energy separation between the valence and conduction bands at a particular $\mathbf{k}$, as

$$E_J(\mathbf{k}) = E_c(\mathbf{k}) - E_v(\mathbf{k}) = \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_{effe}} + \frac{1}{m_{effh}}\right) + E_g = \frac{\hbar^2 k^2}{2\mu_{eff}} + E_g \qquad (8.102)$$

where m_{effe} is the effective mass of the electrons in the conduction band and m_{effh} is the effective mass of the holes in the valence band.

Hole masses

The electron effective mass at the top of the valence band is typically negative because we are at a typically at a maximum in the band.

Hole energy increases as we go down into the valence band, just as the potential energy of a bubble in water increases the deeper we push it.

Hence in terms of holes, the valence band effective mass is positive,

and it is this positive mass that we mean by m_{effh}.

Total transition rate - 4

The reduced effective mass we need for this problem, μ_{eff}, is given by

$$\frac{1}{\mu_{eff}} = \frac{1}{m_{effe}} + \frac{1}{m_{effh}} \tag{8.103}$$

Hence, we can follow the same argument as we followed above in deriving the energy density of states.

We define a "joint density of states" $g_J\left(E_J\right)$, including a factor of 2 for spin

$$g_J(E_J)dE_J = 2g(\mathbf{k})d^3\mathbf{k} \tag{8.104}$$

hence, for $E_J \geq E_g$,

$$g_J(E_J) = \frac{1}{2\pi^2}\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\left(E_J - E_g\right)^{1/2} \tag{8.105}$$

so, using Eqs. (8.100), (8.101), (8.104), and (8.105), per unit volume

$$W_{TOT} = \frac{2\pi}{\hbar}\frac{e^2A_0^2}{4m_0^2}\left|p_{cv}\right|^2 \int_{E_J \geq E_g} \frac{1}{2\pi^2}\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\left(E_J - E_g\right)^{1/2}\delta\left(E_J - \hbar\omega\right)dE_J \tag{8.106}$$

i.e.,

$$W_{TOT}(\hbar\omega) = \frac{2\pi}{\hbar}\frac{e^2A_0^2}{4m_0^2}\left|p_{cv}\right|^2 \frac{1}{2\pi^2}\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\left(\hbar\omega - E_g\right)^{1/2} \tag{8.107}$$

(for $\hbar\omega \geq E_g$).

Absorption coefficient - 1

The final step is to relate the absorption coefficient, α, to the total transition rate W_{TOT}.

α ***is the probability of absorption of a photon per unit length (in the direction of propagation).***

The number of photons incident per unit area per second is

$$n_p = \frac{I}{\hbar\omega} \tag{8.108}$$

where I *is the optical intensity (power per unit area), so*

$$\alpha = \frac{W_{TOT}}{n_p} = \frac{\hbar\omega W_{TOT}}{I}. \tag{8.109}$$

The intensity I can be written

$$I = \frac{n_r c \varepsilon_0 \omega^2 A_0^2}{2} \tag{8.110}$$

where n_r is the refractive index, c is the velocity of light, and ε_o is the permittivity of free space.

Absorption coefficient - 2

Hence

$$\alpha(\hbar\omega) = \frac{2\pi}{\hbar}\frac{e^2 A_0^2}{4m_0^2}\frac{1}{2\pi^2}\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\hbar\omega\frac{2}{n_r c\varepsilon_0\omega^2 A_0^2}\left|p_{cv}\right|^2\left(\hbar\omega - E_g\right)^{1/2}$$

(8.111)

$$= \frac{e^2}{2\pi m_0^2 c\varepsilon_o}\frac{1}{n_r\omega}\left|p_{cv}\right|^2\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\left(\hbar\omega - E_g\right)^{1/2}$$

In actual calculations, a parameter

$$E_p = \frac{2}{m_0}\left|p_{cv}\right|^2 \qquad (8.112)$$

which typically has a value of ~ 20 eV in many semiconductors,

is often used instead of $\left|p_{cv}\right|^2$ **, in which case we can rewrite Eq. (8.111) as**

$$\alpha\left(\hbar\omega\right) = \frac{\hbar e^2}{4\pi m_0 c\varepsilon_0}\frac{1}{n_r}\frac{E_p}{\hbar\omega}\left(\frac{2\mu_{eff}}{\hbar^2}\right)^{3/2}\left(\hbar\omega - E_g\right)^{1/2} \qquad (8.113)$$

or

$$\alpha\left(\hbar\omega\right) = \frac{\pi\hbar e^2}{2m_0 c\varepsilon_0}\frac{1}{n_r}\frac{E_p}{\hbar\omega}g_J\left(\hbar\omega\right) \qquad (8.114)$$

Absorption coefficient - 2

We can see that the absorption spectrum, $\alpha(\hbar\omega)$

follows the joint density of states,

rising (in this model) as $\left(\hbar\omega - E_g\right)^{1/2}$

and being zero for $\hbar\omega < E_g$.

The above model is very often used as a starting point for optical calculations in semiconductors.

The very simple model here does ignore some important spin effects,

which can be qualitatively important for polarization dependence.

It also completely neglects excitonic effects,

which are quantitatively and qualitatively quite important in optical absorption in direct gap semiconductors,

though we will not treat them here.

Angular momentum – 1

Reading – Section 9.1

Classical angular momentum

Angular momentum operators

Eigenfunctions of the angular momentum operators

Angular momentum

Thus far we have dealt primarily with

energy, position, and linear momentum,

and have proposed operators for each of these.

One other quantity that is important in classical mechanics,

angular momentum,

is particularly important also in quantum mechanics,

especially for the hydrogen atom.

Linear momentum eigenfunctions are functions of position along a specific spatial direction.

Angular momentum eigenfunctions are functions of angle or angles about a specific axis.

Note that angular momentum *always* has discrete eigenvalues.

This is associated with the fact that once we have gone an angle 2π about a particular axis, we are back to where we started.

Angular momentum operators - preview

Note that the operators corresponding to angular momentum about different orthogonal axes,

e.g., $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$,

will *not* commute with one another

in contrast to the linear momentum operators for the different orthogonal coordinate directions, for example.

We will, however, find another useful angular momentum operator,

$$\hat{L}^2,$$

which does commute with each of $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ separately.

The eigenfunctions for $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ are quite straightforward.

Those for $\hat{L}^2$,

the spherical harmonics,

though more complicated, can be understood relatively simply.

Classical angular momentum

The classical angular momentum

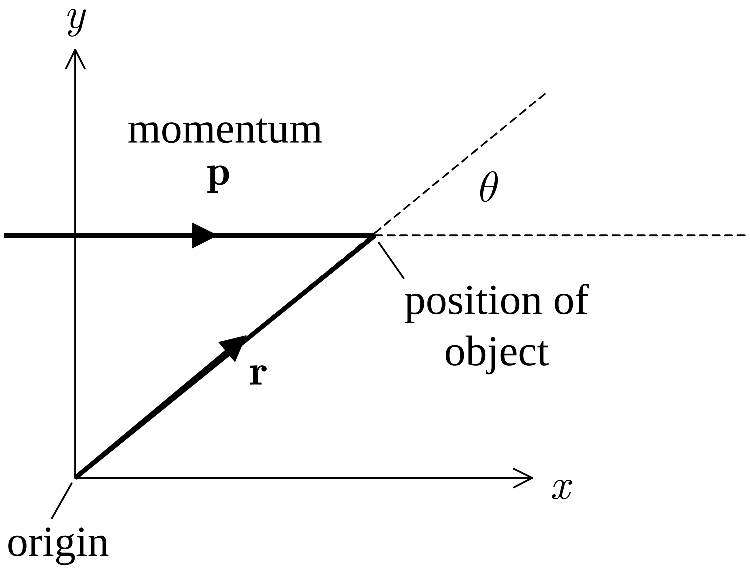
of a small object

centered at a point given by the vector displacement $\mathbf{r}$ relative to some origin,

of (vector) linear momentum $\mathbf{p}$

is

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{9.1}$$



Vector cross product

The vector cross product is defined as usual by

$$\mathbf{C} = \mathbf{A} \times \mathbf{B} \equiv \mathbf{c} AB \sin\theta \equiv \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$\equiv \mathbf{i}(A_y B_z - A_z B_y) - \mathbf{j}(A_x B_z - A_z B_x) + \mathbf{k}(A_x B_y - A_y B_x) \tag{9.2}$$

where $\mathbf{i}$, $\mathbf{j}$, ***and*** $\mathbf{k}$ ***are unit vectors in the*** x, y, ***and*** z ***coordinate directions,***

A_x ***is the component of*** $\mathbf{A}$ ***in the*** x ***direction (and similarly for*** x ***and*** y ***components).***

$\mathbf{C}$ ***is perpendicular to the plane of*** $\mathbf{A}$ ***and*** $\mathbf{B}$ ***just as the*** z ***axis is perpendicular to the plane containing the*** x ***and*** y ***axes for normal right-handed axes.***

θ ***is the angle between the vectors*** $\mathbf{A}$ ***and*** $\mathbf{B}$.

$\mathbf{c}$ ***is a unit vector in the direction of the vector*** $\mathbf{C}$

Note incidentally that

the ordering of the multiplications in the second line of Eq. (9.2) is chosen to work also for operators instead of numbers for one or other vector;

the sequence of multiplications in each term is always in the sequence of the rows from top to bottom.

Angular momentum vectors and quantum mechanical operator

Since the angular momentum is a vector quantity,

we can if we wish explicitly write out the various components, obtaining

$$L_x = yp_z - zp_y\,,\ L_y = zp_x - xp_z\,,\ L_z = xp_y - yp_x \tag{9.3}$$

In quantum mechanics,

we can propose an angular momentum operator $\hat{\mathbf{L}}$ by analogy with the classical angular momentum,

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar\left(\mathbf{r} \times \nabla\right) \tag{9.4}$$

with corresponding components

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{9.5}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{9.6}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{9.7}$$

These individual components of the angular momentum operator $\hat{\mathbf{L}}$ are each Hermitian and so, correspondingly, is the operator $\hat{\mathbf{L}}$ itself.

Commutation relations

The operators corresponding to individual coordinate directions obey commutation relations

$$\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = \left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \qquad (9.8)$$

$$\hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y = \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x \qquad (9.9)$$

$$\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z = \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y \qquad (9.10)$$

These individual commutation relations can be written in a more compact form as a shorthand,

$$\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar\hat{\mathbf{L}} \qquad (9.11)$$

Note, however, that,

unlike operators, $\hat{\mathbf{r}}$ ***for position and*** $\hat{\mathbf{p}}$ ***for linear momentum,***

the different components of this angular momentum operator do not commute with one another.

Though a particle can have simultaneously a well-defined position in both the x *and* y *directions, or have simultaneously a well-defined momentum in both the* x *and* y *directions,*

a particle cannot in general simultaneously have a well-defined angular momentum component in more than one direction.

Spherical polar coordinates

The eigenfunctions and eigenvalues of angular momentum operators are most usefully written using spherical polar coordinates.

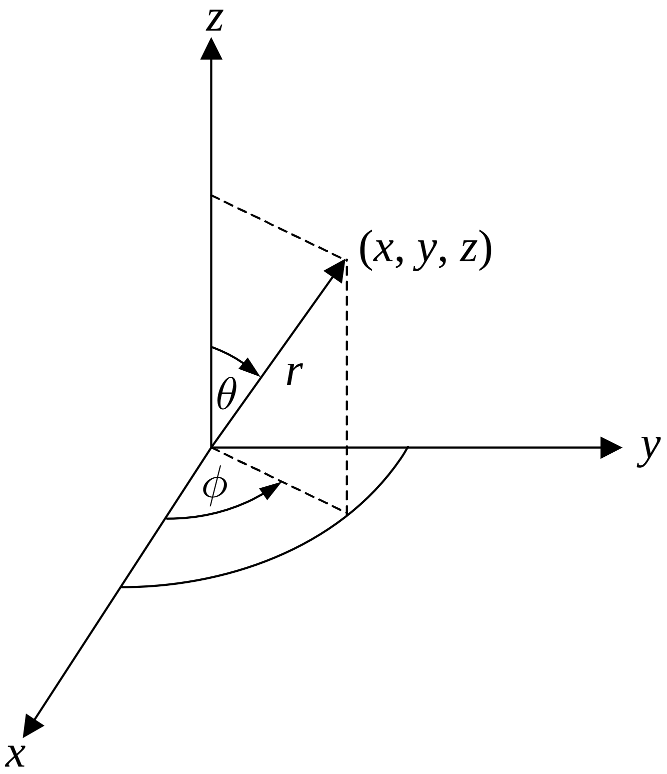
The relation between spherical polar and Cartesian coordinates is

$$x = r\sin\theta\cos\phi\ ,\quad y = r\sin\theta\sin\phi\ ,\quad z = r\cos\theta \qquad (9.12)$$

and, in inverse form

$$r = \sqrt{x^2+y^2+z^2}\ ,\ \theta = \sin^{-1}\left(\frac{\sqrt{x^2+y^2}}{\sqrt{x^2+y^2+z^2}}\right),$$

$$\phi = \tan^{-1}\left(\frac{y}{x}\right) \qquad (9.13)$$



θ is known as the polar angle, and

ϕ is the azimuthal angle.

Angular momentum operators in spherical polar coordinates

With these definitions of spherical polar coordinates,

and with standard partial derivative relations of the form

$$\frac{\partial}{\partial x} \equiv \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \qquad (9.14)$$

for each of the Cartesian coordinate directions,

it is straightforward to show from (9.5) - (9.7)

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{dy}\right),\ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{dz}\right),$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{dx}\right)$$

that

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \qquad (9.15)$$

$$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \qquad (9.16)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \qquad (9.17)$$

L_z eigenfunctions and eigenvalues

We can solve Eq. (9.17)

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

for the eigenfunctions and eigenvalues of $\hat{L}_z$.

The eigen equation is

$$\hat{L}_z \Phi(\phi) = m\hbar \Phi(\phi) \tag{9.18}$$

where $m\hbar$ is the eigenvalue to be determined.

The solution of this equation is

$$\Phi(\phi) = \exp(im\phi) \tag{9.19}$$

The requirements that the wavefunction and its derivative are continuous when we return to where we started,

i.e., for $\phi = 2\pi$,

means that m must be an integer (positive or negative or zero).

Hence we find that the angular momentum around the z axis is quantized,

with units of angular momentum of $\hbar$.

L_x, L_y, and L_z eigenfunctions

From this discussion,

we can understand that the eigenfunctions of the angular momentum about the different axes are not the same,

as required by the fact that the different angular momentum operators do not commute.

Our choice of the z axis was quite arbitrary –

we could equally well have chosen the x or y axes as the polar axes for our coordinate system,

in which case we would see quite clearly that the eigenfunctions of the $\hat{L}_x$ or $\hat{L}_y$ operators are of similar form to Eq. (9.19),

but in terms of the angles of rotation about the x or y axes respectively.

Hence the eigenfunctions of the angular momentum operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ are not the same.

Angular momentum – 2

Reading – Sections 9.2 – 9.5

L squared operator

Spherical harmonic functions

Notation for angular momentum states

Visualization of angular momentum

L^2 operator

In quantum mechanics it is also useful to consider another operator associated with angular momentum, the operator $\hat{L}^2$.

This should be thought of as the "dot" product as $\hat{\mathbf{L}}$ with itself, and is defined as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{9.20}$$

It is similarly straightforward to show then that

$$\hat{L}^2 = -\hbar^2 \nabla_{\theta,\phi}^2 \tag{9.21}$$

where the operator $\nabla_{\theta,\phi}^2$ is given by

$$\nabla_{\theta,\phi}^2 = \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{9.22}$$

This $\nabla_{\theta,\phi}^2$ operator is actually the θ and ϕ part of the Laplacian (∇^2) operator in spherical polar coordinates, hence the notation.

We will return to the full Laplacian in spherical polar coordinates when we examine the hydrogen atom.

Commutation of L^2

$\hat{L}^2$ **commutes with** $\hat{L}_x$**,** $\hat{L}_y$**, and** $\hat{L}_z$**.**

- ***It is easy to see from (9.22) and the form of*** $\hat{L}_z$ ***(Eq. (9.17)), that at least*** $\hat{L}^2$ ***and*** $\hat{L}_z$ ***commute.***
  - **The operation** $\partial / \partial\phi$ **has no effect on functions or operators depending on** θ **alone.**

Of course, the choice of the z **direction is quite arbitrary;**

- ***we could equally well have developed this problem considering the polar axis along the*** x ***or*** y ***directions,***
  - **in which cases it would similarly be obvious that** $\hat{L}^2$ **commutes with** $\hat{L}_x$ **or** $\hat{L}_y$**.**

Eigenfunctions of L^2

We are looking for eigenfunctions of $\hat{L}^2$ (or, equivalently, $\nabla^2_{\theta,\phi}$),

and so the equation we hope to solve is of the form

$$\nabla^2_{\theta,\phi} Y_{lm}(\theta,\phi) = -l(l+1) Y_{lm}(\theta,\phi) \tag{9.23}$$

We have anticipated the answer by writing the expected eigenvalue in the form $-l(l+1)$,

but for the moment we can consider this as an arbitrary number to be determined.

The notation $Y_{lm}(\theta,\phi)$ also anticipates the final answer,

though again for the moment it is an arbitrary function to be determined.

Separation of variables

We presume that the final eigenfunctions can be separated in the form

$$Y_{lm}(\theta,\phi)=\Theta(\theta)\Phi(\phi) \tag{9.24}$$

where $\Theta(\theta)$ only depends on θ and $\Phi(\phi)$ only depends on ϕ.

Substituting this form in Eq. (9.23) gives

$$\frac{\Phi(\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-l(l+1)\Theta(\theta)\Phi(\phi) \tag{9.25}$$

Multiplying both sides by $\sin^2\theta/\Theta(\theta)\Phi(\phi)$ and rearranging terms, we have

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-l(l+1)\sin^2\theta-\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) \tag{9.26}$$

The left hand side depends only on ϕ whereas the right hand side depends only on θ,

and so these must both equal a constant (the separation constant).

Anticipating the answer, we choose a separation constant of $-m^2$, where m is still to be determined.

ϕ *equation*

Taking the left hand side of

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-l(l+1)\sin^2\theta-\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)=-m^2$$

first, we now have an equation

$$\frac{d^2\Phi(\phi)}{d\phi^2}=-m^2\Phi(\phi) \qquad (9.27)$$

The solutions to an equation like this are of the form $\sin m\phi$***,*** $\cos m\phi$ ***or*** $\exp im\phi$***.***

We choose the exponential form so it is also a solution of the $\hat{L}_z$ eigen equation, Eq. (9.18)

We expect that it and its derivative are continuous.

As a result, this wavefunction must be cyclic every 2π of angle ϕ.

Hence, m must be an integer.

θ *equation*

Taking the right hand side of Eq. (9.26)

$$-l(l+1)\sin^2\theta-\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)=-m^2$$

we can now write an equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)-\frac{m^2}{\sin^2\theta}\Theta(\theta)+l(l+1)\Theta(\theta)=0 \qquad (9.28)$$

This is the associated Legendre equation,

and the solutions to it are the associated Legendre functions, $\Theta(\theta)=P_l^m(\cos\theta)$**.**

The solutions require that

$$l=0,1,2,3,\ldots \qquad (9.29)$$

$$-l\le m\le l \ (m \text{ integer}) \qquad (9.30)$$

The associated Legendre functions can conveniently be defined using Rodrigues' formula

$$P_l^m(x)=\frac{1}{2^l l!}\left(1-x^2\right)^{m/2}\frac{d^{l+m}}{dx^{l+m}}\left(x^2-1\right)^l \qquad (9.31)$$

Associated Legendre functions - 1

The first few of these functions $P_l^m(x)$ are, explicitly,

$$
\begin{aligned}
&P_0^0(x)=1\\
&P_1^0(x)=x\\
&P_1^1(x)=\left(1-x^2\right)^{1/2}\\
&P_1^{-1}(x)=-\frac{1}{2}\left(1-x^2\right)^{1/2}\\
&P_2^0(x)=\frac{1}{2}\left(3x^2-1\right)\\
&P_2^1(x)=3x\left(1-x^2\right)^{1/2}\\
&P_2^{-1}(x)=-\frac{1}{2}x\left(1-x^2\right)^{1/2}\\
&P_2^2(x)=3\left(1-x^2\right)\\
&P_2^{-2}(x)=\frac{1}{8}\left(1-x^2\right)
\end{aligned}
\tag{9.32}
$$

Associated Legendre functions - 2

We can see by inspection that these functions $P_l^m(x)$ have the following properties:

(i) the highest power of the argument x is always x^l;

(ii) the functions for a given l for $+m$ and $-m$ are identical (other than for differences in numerical prefactors).

Less obviously,

between –1 and +1,

and not including the values at those end points,

the functions have $l-|m|$ zeros.

$$P_0^0(x)=1$$

$$P_1^0(x)=x$$

$$P_1^1(x)=\left(1-x^2\right)^{1/2}$$

$$P_1^{-1}(x)=-\frac{1}{2}\left(1-x^2\right)^{1/2}$$

$$P_2^0(x)=\frac{1}{2}\left(3x^2-1\right)$$

$$P_2^1(x)=3x\left(1-x^2\right)^{1/2}$$

$$P_2^{-1}(x)=-\frac{1}{2}x\left(1-x^2\right)^{1/2}$$

$$P_2^2(x)=3\left(1-x^2\right)$$

$$P_2^{-2}(x)=\frac{1}{8}\left(1-x^2\right)$$

Eigenfunctions of L^2

From (9.21) and (9.23), the eigen equation is

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi) \qquad (9.33)$$

where $Y_{lm}(\theta,\phi)$ are referred to as the spherical harmonics,

which, after normalization, can be written

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta)\exp(im\phi) \qquad (9.34)$$

The allowed eigenvalues of $\hat{L}^2$ are $\hbar^2 l(l+1)$.

As is easily verified, these spherical harmonics are also eigenfunctions of the $\hat{L}_z$ operator.

Explicitly we have the eigen equation

$$\hat{L}_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi) \qquad (9.35)$$

with eigenvalues of $\hat{L}_z$ being $m\hbar$.

Visualization of spherical harmonic functions

We step away from the quantum mechanical problem for the moment,

and think instead of the modes of vibration of a thin spherical shell.

The only substantial mathematical difference between these two problems is that the shell’s vibrations must have real amplitudes,

and so, instead of complex functions $\exp(im\phi)$ ***with positive and negative*** m

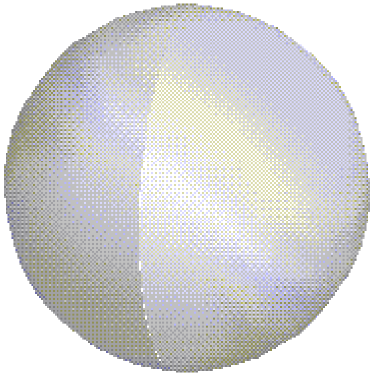
we use only positive m **but use both** $\sin m\phi$ **and** $\cos m\phi$ **solutions.**

Since the solutions corresponding to $\sin m\phi$ **and** $\cos m\phi$ **are merely rotated by 90º around the polar axis with respect to one another,**

we only need to understand one of these to understand the nature of the spherical harmonics.

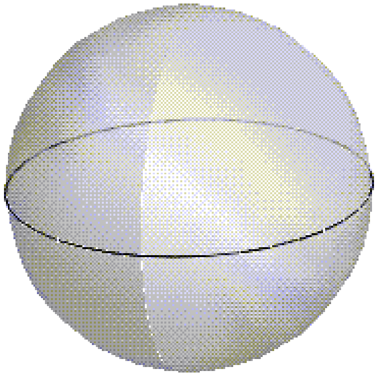
It is simple to construct the $\exp(im\phi)$ **solution from these.**

Illustration of the nodal circles for the spherical harmonics ($\cos\phi$ solutions shown) corresponding to the vibration modes of a spherical shell, for various cases



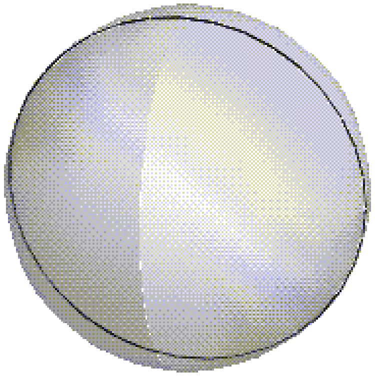
$l = 0$

$m = 0$



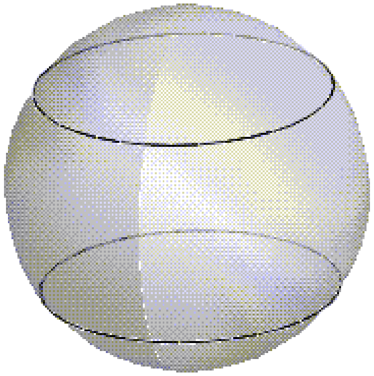
$l = 1$

$m = 0$



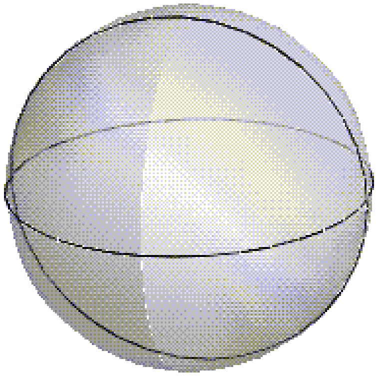
$l = 1$

$m = 1$



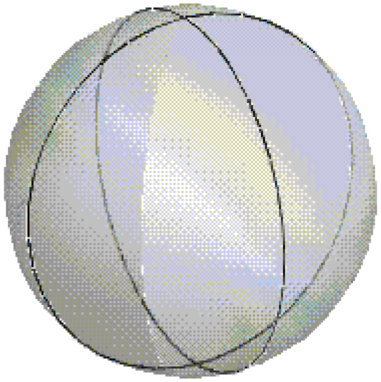
$l = 2$

$m = 0$



$l = 2$

$m = 1$



$l = 2$

$m = 2$

Click on the individual spheres for animations of the vibrations

Constructing spherical harmonics for the vibrating shell

The lowest solution ($l = 0, m = 0$) is the “breathing” mode

the spherical shell expands and contracts periodically

For all other solutions, there is one or more nodal circles on the sphere.

A nodal circle is one that is unchanged in that particular oscillating mode.

To understand the oscillations of the sphere in a given spherical harmonic, we can use the following rules.

(i) the surfaces on opposite sides of a nodal circle oscillate in opposite directions.

(ii) the total number of nodal circles is equal to l.

(iii) the number of nodal circles passing through the poles is m, and they divide the sphere equally in the azimuthal angle ϕ.

(iv) the remaining nodal circles are either equatorial or parallel to the equator, and are symmetrically distributed between the top and bottom halves of the sphere.

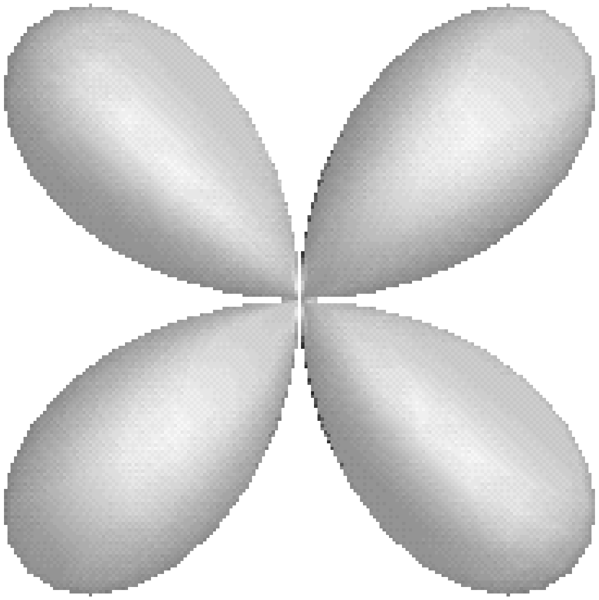
(Only the precise position of these circles is not immediately obvious from symmetry, and is determined by the zeros of the associated Legendre functions.)

Relation of spherical shell vibration modes to spherical harmonic functions

The visualization of a vibrating mode of a spherical shell is not itself the spherical harmonic function.

- ***The amplitude of the vibration at any given angle is the spherical harmonic function;***
  - **spherical harmonics are functions of angle only, not radius.**
    - *Hence, for the angles corresponding to the nodal circles,*
      - the spherical harmonic is zero.
  - **Note that the amplitude of the spherical harmonic may be positive for one range of angles and negative for another;**
    - *for example, for all the* $l=1$ *spherical harmonics,*
      - the function is positive on one hemispherical range of angle and negative on the other hemispherical range.

Parametric plot of spherical harmonic



The spherical harmonic for $l = 2$, $m = 1$. A polar circle of value zero pinches the function to zero in the vertical direction, and an equatorial circle of value zero pinches the function to zero in the horizontal direction. This polar parametric plot is the function given by the set of points (x, y, z) with

$$x = Y_{21}(\theta,\phi)\sin\theta\cos\phi,$$

$$y = Y_{21}(\theta,\phi)\sin\theta\sin\phi,$$

$$z = Y_{21}(\theta,\phi)\cos\theta.$$

The view is along the y axis.

Dirac notation

We will also commonly use the Dirac notation in writing equations associated with angular momentum,

in which case it is conventional to write

$$\hat{L}^2 |l,m\rangle = \hbar^2 l(l+1)|l,m\rangle \tag{9.36}$$

instead of Eq. (9.33), and

$$\hat{L}_z |l,m\rangle = m\hbar |l,m\rangle \tag{9.37}$$

instead of Eq. (9.35).

“s, p, d, f” notation

The spherical harmonics come up in the solution of the hydrogen atom problem.

Different values of l give rise to different sets of spectral lines that spectroscopists in the 19th century had identified empirically in their work on hydrogen.

In particular, they had identified what they called respectively

“spectral” (s)*,*

“principal” (p)*,*

“diffuse” (d)*, and*

“fundamental” (f)

groups of lines.

Each of these is now identified with the specific values of l as follows, where we also indicate the alphabetic extension to higher l values.

l	0	1	2	3	4	5
notation	*s*	*p*	*d*	*f*	*g*	*h*

It is also convenient to note that the *s* wavefunctions are all spherically symmetric,

even though the s of the notation originally had nothing to do with spherical symmetry.

S, X, Y, Z functions - 1

Many semiconductor crystals have crystalline structure that is based on a form of cubic crystal lattice.

The detailed calculation of the wavefunctions within the unit cell is difficult, but qualitative aspects

such as the polarization dependence of optical absorption,

can be understood from the symmetry of the unit cell wavefunctions.

The unit cell wavefunctions can have symmetries that are the same as, or similar to, the symmetries of atomic states;

the angular symmetries of atomic states are essentially those of the spherical harmonics.

For example,

the unit cell wavefunctions in the conduction band of materials such as GaAs and InP have approximately spherical symmetry (even though they are embedded in cubic unit cells),

just like the $l = 0$ *spherical harmonic function.*

this conduction band unit cell function is often written as $S(\mathbf{r})$**, where here** $\mathbf{r}$ **refers to the position within the unit cell.**

We do not know the actual detailed form of $S(\mathbf{r})$*, but we do know that it is approximately spherically symmetric within the unit cell.*

S, X, Y, Z functions - 2

The spherical harmonic for $l=1$, $m=0$, is antisymmetric about $z=0$.

The value of the function at a given point above the equator is minus that at the corresponding point below the equator.

This is the same symmetry as the function z itself.

A function with this symmetry can therefore be written as $Z(\mathbf{r})$.

There are two other spherical harmonics for $l=1$.

If we consider the real form of the spherical harmonics with $m=1$,

one of these (the $\cos m\phi$ one illustrated above) corresponds to a function that is antisymmetric about $x=0$.

A function with the same symmetry as this spherical harmonic can be written as $X(\mathbf{r})$.

Similarly, the $l=1$, $m=1$ spherical harmonic with the $\sin m\phi$ dependence corresponds to a function that is antisymmetric about $y=0$,

and a function with this symmetry can be written as $Y(\mathbf{r})$.

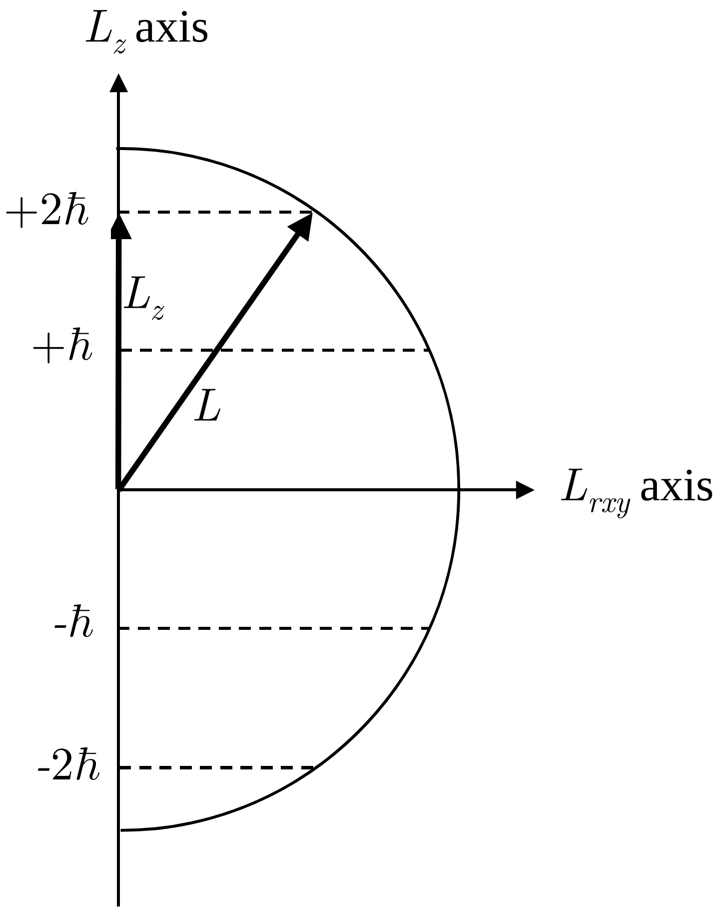
Functions with these $X(\mathbf{r})$, $Y(\mathbf{r})$, and $Z(\mathbf{r})$ symmetries are the p *atomic orbitals (shown as three orthogonal "dumbbells" in chemistry texts).*

The valence band states in materials such as GaAs and InP can be characterized by functions of these forms also,

even though the detailed form of these functions is not known with any accuracy.

Visualization of angular momentum

We can visualize the quantization of angular momentum as shown for $l = 2$.



We need to consider one more operator,

$$\hat{L}_{rxy}^2 = \hat{L}^2 - \hat{L}_z^2 \qquad (9.38)$$

where the subscript rxy refers to the radius $r_{xy} = \sqrt{x^2 + y^2}$ in the x-y plane.

Then we have

$$\hat{L}_{rxy}^2 |l,m\rangle = \hat{L}^2 |l,m\rangle - \hat{L}_z^2 |l,m\rangle$$
$$= \hbar^2 \left[l(l+1) - m^2 \right] |l,m\rangle = L_{rxy}^2 |l,m\rangle \qquad \text{`}(9.39)$$

The state $|l,m\rangle$ is also an eigenstate of this new operator, with eigenvalue $L_{rxy}^2 = \hbar^2 \left[l(l+1) - m^2 \right]$.

Hence we can plot the eigenstates and eigenvalues as on a circle.

The possible eigenstates correspond to the intersections of the horizontal straight lines, corresponding to the values of L_z, and spaced by $\hbar$, and the semicircle of radius $\hbar\sqrt{l(l+1)}$ (i.e., $\sqrt{6}\hbar$ for this example).

The hydrogen atom - 1

Reading – Sections 10.1 – 10.3 up to the start of “Bohr radius and Rydberg energy”

Multiple particle wavefunctions

Hamiltonian for the hydrogen atom problem

Coordinates for the hydrogen atom problem

The hydrogen atom

The hydrogen atom is a very important problem in quantum mechanics. It

- ***is mathematically exactly solvable***
- ***gives the basis for our understanding of atoms and molecules,***
  - **as well as much of the notation.**

In engineering

- ***the hydrogen atom solutions explain a phenomenon***
  - **Wannier excitonic effects**
- ***important in optical absorption in semiconductor optoelectronic devices.***

It is an excellent tutorial problem

- ***it takes us beyond simple one-dimensional spatial problems***
- ***it is a concrete example of angular momentum behavior***

It involves two particles (the electron and the proton), not just one.

- ***It gives an introduction to how we can handle more than one particle***

It illustrates series solution of differential equations.

Multiple particle systems

How should we tackle this problem of two particles (electron and proton)?

We generalize the Schrödinger equation.

We write quite generally for time-independent problems

$$\hat{H}\psi = E\psi \tag{10.1}$$

where now we mean that

the Hamiltonian $\hat{H}$ *is the operator representing the energy of the entire system, and similarly* ψ *is the wavefunction representing the state of the entire system.*

Multiple particle wavefunctions - 1

For the hydrogen atom, there are two particles,

the electron and the proton.

Each of these has a set of coordinates associated with it

x_e*,* y_e*, and* z_e *for the electron and*

x_p*,* y_p*, and* z_p *for the proton.*

The wavefunction will therefore in general be a function of all six of these coordinates.

In the simple single particle problems we considered before,

we could imagine that the wavefunction at any given time was a simple function in ordinary three dimensional space.

Now, however, the wavefunction is a function of six spatial coordinates,

and is really a wavefunction in what is called configuration space.

The dimensionality would grow even further if we had more particles;

three particles would require nine spatial coordinates.

A small lump of material would need ~ 10^{23} *coordinates*

Multiple particle wavefunctions - 2

Note that

the electron and the proton cannot be completely described separately,

each with wavefunctions given only by their own position coordinates.

Why this additional complexity for a multiple particle system?

Imagine we had a hydrogen atom in a box.

The hydrogen atom might be found anywhere in the box,

and hence the electron might be found anywhere in the box.

We might think an electron wavefunction describing the electron as being anywhere in the box would be sufficient.

Similarly, the proton might be found anywhere in the box,

and we might also think a proton wavefunction describing the proton as being anywhere in the box would be sufficient.

But that would not describe the relationship between the electron and the proton.

Multiple particle wavefunctions - 3

In particular, those two wavefunctions would not tell us

- ***if we find the electron at a particular position,***
  - **what is the probability that we will find the proton within 1 Å of that position.**
- ***Obviously, if the electron and proton are in a bound state of the hydrogen atom,***
  - **there is a large chance of finding the proton nearby**
- ***if the hydrogen atom was in a very high excited state, or an ionized state,***
  - **that probability would be quite low.**

Hence we see that

- ***simple, separate wavefunctions for electron and proton,***
  - **each a function only of that particle's own coordinates,**
- ***are not sufficient to describe the complete state of the pair or particles.***

Multiple particle wavefunctions - 4

We can sometimes find ways of separating the problem

- ***so that we do get back to a simple description,***
  - **with our six coordinate wavefunction being a product of two functions each of only three coordinates**
    - *and that is indeed the case for the hydrogen atom.*
  - **In general, we cannot hope to factor the wavefunction that simply, however.**

Note too that this configuration space is not the same as the Hilbert space we use to describe functions.

- ***Our configuration space has three dimensions for each particle (possibly four if we include time).***

- ***The Hilbert space has a possibly infinite number of dimensions for each degree of freedom (e.g., for each coordinate direction for each particle).***

Hamiltonian for the hydrogen atom problem - 1

The electron and proton each have a mass

m_e *and* m_p *respectively*

We expect

kinetic energy operators associated with each of these masses

potential energy from the electrostatic attraction of electron and proton

Hence, the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right) \quad (10.2)$$

where we mean

$$\nabla_e^2 \equiv \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \quad (10.3)$$

and similarly for ∇_p^2,

$$\mathbf{r}_e = x_e\mathbf{i} + y_e\mathbf{j} + z_e\mathbf{k} \quad (10.4)$$

is the position vector of the electron coordinates, and similarly for $\mathbf{r}_p$

Hamiltonian for the hydrogen atom problem - 2

The Coulomb potential energy

$$V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)=-\frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_e-\mathbf{r}_p\right|} \qquad (10.5)$$

depends on the distance $\left|\mathbf{r}_e-\mathbf{r}_h\right|$ ***between the electron and proton coordinates***

This will turn out to be very important in simplifying the solution

The Schrödinger equation with this Hamiltonian can now be written explicitly

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_p}\nabla_p^2+V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)\right]\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right)=E\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right) \qquad (10.6)$$

Solving the hydrogen atom problem

We want to break this problem up into more manageable parts.

- ***We do this by***
  - **an intelligent choice of coordinate systems, and by**
  - **separating the resulting differential equation.**

There are two questions in the choice of coordinate systems.

- ***(i) the coordinates of what?***
  - **With a single particle, it was obvious to choose the particle’s coordinates.**
  - **With two particles,**
    - *we might choose the separate coordinates of the individual particles.*
  - **In fact, the problem does not separate conveniently if we do that.**
    - *We will choose center-of-mass coordinates instead.*
- ***(ii) what axes?***
  - **For a problem with spherical symmetry, like the hydrogen atom,**
    - *we could make an intelligent guess that the problem would be simpler using spherical polar coordinates rather than simple Cartesian ones.*

Center-of-mass coordinates - 1

Note that the potential in this problem is only a function of the relative separation of the electron and proton, $\left|\mathbf{r}_e - \mathbf{r}_p\right|$.

We might therefore try to choose a new set of six coordinates in which three are the relative positions

$$x = x_e - x_p,\ \ y = y_e - y_p,\ \ z = z_e - z_p \tag{10.7}$$

i.e., with a relative position vector

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}\,, \tag{10.8}$$

from which we obtain

$$r = \sqrt{x^2 + y^2 + z^2} = \left|\mathbf{r}_e - \mathbf{r}_p\right| \tag{10.9}$$

What should we choose for the other three coordinates?

Center-of-mass coordinates - 2

Experience with related classical problems,

such as a moon orbiting a planet under gravitational attraction,

tells us that the position of the center of mass of the moon and the planet is not affected by the orbit of the moon round the planet –

each of them executes an orbit about the center of mass.

We therefore look for a similar approach here.

The position $\mathbf{R}$ ***of the center of mass is the same as***

the balance point of a light-weight beam with the two masses attached at opposite ends,

and so is the weighted average of the positions of the two individual masses, i.e.,

$$\mathbf{R} = \frac{m_e \mathbf{r}_e + m_p \mathbf{r}_p}{M} \qquad (10.10)$$

where M is the total mass

$$M = m_e + m_p \qquad (10.11)$$

Center-of-mass coordinates - 3

Now let us construct the differential operators we need in terms of these coordinates. With

$$\mathbf{R} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k} \tag{10.12}$$

we have, for example, for the new coordinates in the x-direction

$$X = \frac{m_e x_e + m_p x_p}{M}, \; x = x_e - x_p \tag{10.13}$$

and so the first derivatives in the x-direction can be written as

$$\begin{aligned}\left.\frac{\partial}{\partial x_e}\right|_{x_p} &= \left.\frac{\partial X}{\partial x_e}\right|_{x_p} \left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial x}{\partial x_e}\right|_{x_p} \left.\frac{\partial}{\partial x}\right|_{X} \\ &= \frac{m_e}{M} \left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial x}\right|_{X}\end{aligned} \tag{10.14}$$

and similarly

$$\begin{aligned}\left.\frac{\partial}{\partial x_p}\right|_{x_e} &= \left.\frac{\partial X}{\partial x_p}\right|_{x_e} \left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial x}{\partial x_p}\right|_{x_e} \left.\frac{\partial}{\partial x}\right|_{X} \\ &= \frac{m_p}{M} \left.\frac{\partial}{\partial X}\right|_{x} - \left.\frac{\partial}{\partial x}\right|_{X}\end{aligned} \tag{10.15}$$

(Here we have explicitly indicated the variables in the x-direction held constant in each partial differentiation to try to reduce confusion.)

Center-of-mass coordinates - 4

The second derivatives become

$$\left.\frac{\partial^2}{\partial x_e^2}\right|_{x_p} = \left.\frac{\partial}{\partial x_e}\right|_{x_p}\left(\left.\frac{\partial}{\partial x_e}\right|_{x_p}\right) = \frac{m_e}{M}\left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial x}\right|_{X}$$

$$= \left(\frac{m_e}{M}\right)^2 \left.\frac{\partial^2}{\partial X^2}\right|_{x} + \left.\frac{\partial^2}{\partial x^2}\right|_{X} + \frac{m_e}{M}\left(\left.\frac{\partial}{\partial x}\right|_{X}\left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial X}\right|_{x}\left.\frac{\partial}{\partial x}\right|_{X}\right) \tag{10.16}$$

and similarly

$$\left.\frac{\partial^2}{\partial x_p^2}\right|_{x_e} = \left(\frac{m_p}{M}\right)^2 \left.\frac{\partial^2}{\partial X^2}\right|_{x} + \left.\frac{\partial^2}{\partial x^2}\right|_{X} - \frac{m_p}{M}\left(\left.\frac{\partial}{\partial x}\right|_{X}\left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial X}\right|_{x}\left.\frac{\partial}{\partial x}\right|_{X}\right) \tag{10.17}$$

and so (dropping the explicit statement of variables held constant)

$$\frac{1}{m_e}\frac{\partial^2}{\partial x_e^2} + \frac{1}{m_p}\frac{\partial^2}{\partial x_p^2} = \frac{m_e + m_h}{M^2}\frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_e} + \frac{1}{m_p}\right)\frac{\partial^2}{\partial x^2}$$

$$= \frac{1}{M}\frac{\partial^2}{\partial X^2} + \frac{1}{\mu}\frac{\partial^2}{\partial x^2} \tag{10.18}$$

where μ *is the so-called reduced mass*

$$\mu = \frac{m_e m_p}{m_e + m_p} \tag{10.19}$$

Center-of-mass coordinates - 5

The same kinds of relations can be written for each of the other Cartesian directions, and so we have

$$\nabla_{\mathbf{R}}^2 \equiv \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \text{ and } \nabla_{\mathbf{r}}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (10.20)$$

Consequently, instead of Eq. (10.2), we can write the Hamiltonian in a new form with center of mass coordinates,

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \qquad (10.21)$$

which will now allow us to separate the problem.

Center-of-mass coordinates - 6

We first presume that the total wavefunction can be written as a product

$$\psi(\mathbf{R},\mathbf{r}) = S(\mathbf{R})U(\mathbf{r}) \tag{10.22}$$

Substituting this form in the Schrödinger equation (10.1) with the Hamiltonian in the form (10.21), we obtain

$$-U(\mathbf{r})\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) + S(\mathbf{R})\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = ES(\mathbf{R})U(\mathbf{r}) \tag{10.23}$$

Dividing by $S(\mathbf{R})U(\mathbf{r})$ *and moving some terms, we have*

$$-\frac{1}{S(\mathbf{R})}\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E - \frac{1}{U(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) \tag{10.24}$$

The left hand side depends only on $\mathbf{R}$*, and the right hand side depends only on* $\mathbf{r}$*, and so both must equal a constant, which we call* E_{CoM} *.*

Hence we now have two separated equations

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R}) \tag{10.25}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_H U(\mathbf{r}) \tag{10.26}$$

where

$$E_H = E - E_{CoM} \tag{10.27}$$

Center of Mass Motion

We can see immediately that the first of these equations, Eq. (10.25),

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R})$$

is the Schrödinger equation for a free particle of mass M ,

with wavefunction solutions

$$S(\mathbf{R}) = \exp(i\mathbf{K}\cdot\mathbf{R}) \qquad (10.28)$$

and eigenenergies

$$E_{CoM} = \frac{\hbar^2 K^2}{2M} \qquad (10.29)$$

This solution corresponds to the center of mass of the pair of particles

moving as a composite particle with mass equal to the total mass of the two particles –

i.e., this is the motion of the entire hydrogen atom.

Relative motion equation

The second of these equations, Eq. (10.26),

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_H U(\mathbf{r})$$

corresponds to the "internal" relative motion of the electron and proton,

and will give us the internal states of the hydrogen atom.

We now make use of the spherical symmetry of this equation,

and change to spherical polar coordinates.

(Henceforth, we drop the subscript $\mathbf{r}$ in the ∇^2 operator for simplicity)

In spherical polars, we have

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{10.30}$$

where the term in square brackets is the operator $\nabla_{\theta,\phi}^2 \equiv -\hat{L}^2/\hbar^2$ that we introduced above in discussing angular momentum.

Knowing the solutions to the angular momentum problem, we propose the separation

$$U(\mathbf{r}) = R(r)Y(\theta,\phi) \tag{10.31}$$

where $Y(\theta,\phi)$ will in the end be the appropriate spherical harmonic function.

The hydrogen atom - 2

Reading – Sections 10.3 from "Bohr radius and Rydberg energy" – 10.4 to the start of "Power series solution"

Solving for the internal states of the hydrogen atom

Bohr radius and Rydberg energy - 1

We will need dimensionless equations for subsequent mathematics,

and the corresponding units also have simple physical significance.

We presume that the hydrogen atom will have some characteristic size,

which is called the Bohr radius, a_o**.**

We expect that the "average" potential energy (strictly its expectation value) will therefore be

$$\langle E_{potential} \rangle \approx -\frac{e^2}{4\pi\varepsilon_o a_o} \quad (10.32)$$

For a reasonable smooth wavefunction of characteristic size a_o**,**

the second spatial derivative will be roughly $-1/a_o^2$ ***times the function***

(the minus sign comes about because the function is presumably peaked in the middle and falls off towards the sides – a reasonable guess at least for a lowest state – hence giving a negative second derivative).

Remembering that for a mass μ **the kinetic energy operator is** $-\left(\hbar^2/2\mu\right)\nabla^2$**,**

the "average" kinetic energy will therefore be

$$\langle E_{kinetic} \rangle \approx \frac{\hbar^2}{2\mu a_o^2} \quad (10.33)$$

Bohr radius and Rydberg energy - 2

For the lowest state of the system, in the spirit of a variational calculation we would minimize the total energy.

With our very simple model here, the total energy is

$$\begin{aligned}\langle E_{total} \rangle &= \langle E_{kinetic} \rangle + \langle E_{potential} \rangle \\ &\approx \frac{\hbar^2}{2\mu a_o^2} - \frac{e^2}{4\pi\varepsilon_o a_o}\end{aligned} \qquad (10.34)$$

The total energy is a balance between the potential energy,

which is made lower (more negative) by choosing a_o ***smaller,***

and the kinetic energy,

which is made lower (less positive) by making a_o ***larger.***

For the simple model represented in Eq. (10.34), simple differentiation shows that the choice of a_o **that minimizes the energy overall is**

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{e^2\mu} \cong 0.529 \text{ Å} = 5.29 \times 10^{-11} \text{ m} \qquad (10.35)$$

This equation, (10.35), is the standard definition of the Bohr radius.

We therefore see that the hydrogen atom is approximately 1 Å in diameter.

Bohr radius and Rydberg energy - 3

With this choice of a_o, the corresponding total energy of the state is, from Eq. (10.34),

$$\langle E_{total} \rangle = -\frac{\hbar^2}{2\mu a_o^2} = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2 \tag{10.36}$$

We can usefully define an energy unit that we call the "Rydberg", Ry,

$$Ry = \frac{\hbar^2}{2\mu a_o^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2 \cong 13.6 \text{ eV} \tag{10.37}$$

in which case $\langle E_{total} \rangle = -Ry$**.**

Though we have produced the Bohr radius a_o and the Rydberg Ry here by informal arguments,

they will turn out to be rigorously meaningful quantities once we have solved the complete hydrogen atom problem.

Specifically, the energy of the lowest hydrogen atom state will indeed turn out to be $-Ry$.

Internal states of the hydrogen atom - 1

It will make our mathematics simpler if we write this separation in the form

$$U(\mathbf{r}) = \frac{1}{r}\chi(r)Y(\theta,\phi) \tag{10.38}$$

where, obviously,

$$\chi(r) = rR(r) \tag{10.39}$$

With this choice we obtain the convenient simplification of the radial derivatives

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{\chi(r)}{r} = \frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2} \tag{10.40}$$

Hence, the Schrödinger equation (10.26) becomes

$$-\frac{\hbar^2}{2\mu}Y(\theta,\phi)\frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2} + \frac{\chi(r)}{r^3}\frac{1}{2\mu}\hat{L}^2Y(\theta,\phi) + Y(\theta,\phi)V(r)\frac{\chi(r)}{r} = E_H\frac{1}{r}\chi(r)Y(\theta,\phi) \tag{10.41}$$

Internal states of the hydrogen atom - 2

Dividing by $-\hbar^2\chi(r)Y(\theta,\phi)/2\mu r^3$ and rearranging, we have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi) \qquad (10.42)$$

In the usual manner for a separation argument,

we have arranged that the left hand side depends only on r,

and the right hand side depends only on θ and ϕ,

so both sides must be equal to a constant.

We already know what that constant is explicitly

i.e., we already know that $\hat{L}^2Y_{lm}(\theta,\phi)=\hbar^2 l(l+1)Y_{lm}(\theta,\phi)$,

so that the constant is $l(l+1)$.

i.e.,

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)=l(l+1)$$

Internal states of the hydrogen atom - 3

Hence, in addition to the $\hat{L}^2$ eigenequation (already solved), from our separation above

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)=l(l+1)$$

we obtain a radial equation for the hydrogen atom wavefunction

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r) \qquad (10.43)$$

which we can write as an ordinary differential equation because all the functions and derivatives are only in one variable, r.

Hence we have a Schrödinger-like wave equation for this radial part of the wavefunction,

with an additional effective potential energy term $l(l+1)/r^2$.

We remember that $l=0,1,2,\ldots$, and label the solutions with the l subscript.

Central Potentials

Note incidentally that,

though here we have a specific form for $V(r)$ in our assumed Coulomb potential in Eq. (10.5), ($V(|\mathbf{r}_e - \mathbf{r}_p|) = -\frac{e^2}{4\pi\varepsilon_o |\mathbf{r}_e - \mathbf{r}_p|}$)

the above separation works for any potential that is only a function of r

sometimes known as a central potential.

The precise form of the equation (10.43)

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} + \left(V(r) + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H \chi(r)$$

will be different for different central potentials, but the separation remains.

We can still separate out the $\hat{L}^2$ angular momentum eigenequation.

The solutions have specific L^2 values ($\hbar^2 l(l+1)$) and L_z values ($m\hbar$).

Hence we have proved that angular momentum (in the sense of L^2 and L_z values) is conserved in any of the eigenstates of this hydrogen atom,

or indeed of any problem with a central potential.

Note that we did not start by presuming conservation of angular momentum for such problems;

this conservation was a consequence of the solution to the problems.

Hydrogen atom radial equation short derivation - 1

Above, using the proposed separation of the wavefunction

$$U(\mathbf{r}) = R(r)Y(\theta,\phi) \tag{10.31}$$

and rewriting the radial part using

$$\chi(r) = rR(r) \tag{10.39}$$

we are therefore able to separate the wave equation, obtaining a radial part

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\varepsilon_o r} - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H\chi(r) \tag{10.48}$$

We choose to write our energies in the form

$$E_H = -\frac{Ry}{n^2} \tag{10.51}$$

where n for the moment it is simply an arbitrary real number,

We define a new distance unit

$$s = \alpha r \tag{10.52}$$

where the parameter α is

$$\alpha = \frac{2}{na_o} = 2\sqrt{-\frac{2\mu}{\hbar^2}E_H} \tag{10.53}$$

Hydrogen atom radial equation short derivation - 2

We therefore obtain an equation

$$\frac{d^2\chi}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right]\chi = 0 \tag{10.54}$$

Then we write

$$\chi(s) = s^{l+1}L(s)\exp(-s/2) \tag{10.55}$$

so we have, instead of (10.54),

$$s\frac{d^2L}{ds^2} - \left[s - 2(l+1)\right]\frac{dL}{ds} + \left[n - (l+1)\right]L = 0 \tag{10.56}$$

There are only normalizable solutions to this equation if

n is an integer,

and $n \geq l+1$ (10.62)

The solutions are the associated Laguerre polynomials

$$L_{n-l-1}^{2l+1}(s) = \sum_{q=0}^{n-l-1}(-1)^q \frac{(n+l)!}{(n-l-q-1)!(q+2l+1)!}s^q \tag{10.64}$$

where, equivalently $$L_p^j(s) = \sum_{q=0}^{p}(-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!}s^q \tag{10.65}$$

Detailed radial solution - Hydrogen radial wavefunction

We will solve for the radial hydrogen wavefunction.

This also illustrates a typical solution method for such differential equations.

- **Such methods are also used, for example, to solve**
  - *the harmonic oscillator problem and*
  - *other ordinary differential equation problems in quantum mechanics,*
- **and typically result in the known named polynomial functions**
  - *e.g., Legendre, Laguerre, Hermite.*

This method has typically two basic steps.

First,

- **we rewrite the differential equation for a new function where key underlying behaviors have been removed**

Second step,

- **we solve this new differential equation by postulating a finite power series (polynomial) as a solution,**
  - *and deduce the coefficients and hence deduce the function.*
- **Typically, it is in the finite length of the power series that the quantization appears for discrete eigen solutions.**

Detailed radial solution - Rationale for new function for differential equation

We look for what must be the behavior of the solution in asymptotic situations

here we will look at both $r \to 0$ *and* $r \to \infty$.

This will suggest underlying functional forms that should be present in the full solution.

We especially want to identify underlying functions with infinite power series,

such as exponentials.

At this stage, we can make all kinds of assumptions and approximations –

we are only trying to identify underlying functional forms, not yet solve the actual equation.

We construct a solution incorporating these forms,

substitute it in the differential equation,

and obtain a new differential equation for the remaining unknown part of the function.

A goal of this part of the solution method is to end up with an equation that will have a solution that can be defined as a polynomial with a finite number of terms.

Detailed radial solution - asymptotic behavior as $r \to 0$ - 1

Examining Eq. (10.43),

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

we see that we should likely presume that $\chi(r) \to 0$ as $r \to 0$.

Both

the actual Coulomb potential and

the additional effective potential in this equation

are tending towards infinite magnitude as $r \to 0$.

The only way we could keep the equation satisfied for finite $\chi(r)$ and finite E_H as $r \to 0$ is if

$$\chi(r) \to 0.$$

(From the point of view of solving Eq. (10.43) for $\chi(r)$, it is as if there were an infinite potential barrier for $\chi(r)$at $r = 0$.)

Detailed radial solution - asymptotic behavior as $r \to 0$ - 2

As we approach $r = 0$*,*

the dominant term in the effective potential is the term in $1/r^2$, which at sufficiently small r, becomes arbitrarily larger than the Coulomb potential.

Hence, very near to $r = 0$*, from Eq. (10.43) we can write*

$$-\frac{d^2\chi}{dr^2} + \frac{l(l+1)}{r^2}\chi = 0 \tag{10.44}$$

We now presume that $\chi(r)$ *must be an analytic function,*

and we can consequently postulate a power series form for it.

At small r*, we consider the lowest power in the power series*

(for sufficiently small r*, the lowest power in the series will always dominate).*

We will not, however, presume that the lowest power is r^0,

and instead presume we start with some power r^p *with* p *to be determined.*

i.e., at small r

$$\chi(r) \sim r^p \tag{10.45}$$

Substituting this form in Eq. (10.44), we obtain

$$-p(p-1)r^{p-2} + l(l+1)r^{p-2} = 0 \tag{10.46}$$

This must be true for all (very small) r*, and so we presume that* $p = l + 1$

Hence we expect that, for very small r

$$\chi(r) \sim r^{l+1} \tag{10.47}$$

Detailed radial solution - asymptotic behavior as $r \to \infty$

Now we will explicitly use the Coulomb attraction of the electron and proton as the potential from Eq. (10.5),

so Eq. (10.43) becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\varepsilon_o r} - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H \chi(r) \qquad (10.48)$$

For very large r, both the $1/r$ term and the $1/r^2$ term become arbitrarily small, and so we have approximately

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} \cong E_H \chi(r) \qquad (10.49)$$

For any bound state of the system, the eigenenergy E_H will be negative.

This asymptotic equation therefore has the simple solution for large r,

$$\chi \propto \exp\left(-\sqrt{-\frac{2\mu}{\hbar^2}E_H}\, r\right) \qquad (10.50)$$

This solution physically corresponds to the electron tunneling away from the proton into the potential barrier, which at large r simply is a barrier of height $|E_H|$ for a state of (negative) energy E_H.

Detailed radial solution - Recasting the problem - 1

Now we can rewrite the mathematical problem to be solved, Eq. (10.43),

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

using our new units and the asymptotic forms.

We choose to write the eigenenergy E_H of some state of interest as

$$E_H=-\frac{Ry}{n^2} \qquad (10.51)$$

Here n is the parameter we will evaluate to deduce the eigenenergy.

For the moment it is simply an arbitrary real number,

though we will prove later that it is an integer.

We choose to define a new, dimensionless radial distance, s,

$$s=\alpha r \qquad (10.52)$$

where the parameter α is

$$\alpha=\frac{2}{na_o}=2\sqrt{-\frac{2\mu}{\hbar^2}E_H} \qquad (10.53)$$

Detailed radial solution - Recasting the problem - 2

Using this distance unit $s = \alpha r$, we can rewrite Eq. (10.48),

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\varepsilon_o r} - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H\chi(r)$$

after some rearrangements, as

$$\frac{d^2\chi}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right]\chi = 0 \qquad (10.54)$$

Now we propose a functional form for $\chi(s)$ that incorporates what we deduced from the asymptotic behavior above.

Specifically, in terms of s, from the small r behavior of Eq. (10.47),

we will incorporate a factor s^{l+1},

and from the large r behavior of Eq. (10.50),

we obtain a factor $\exp(-s/2)$.

Hence the proposed form of the function is

$$\chi(s) = s^{l+1}L(s)\exp(-s/2) \qquad (10.55)$$

where $L(s)$ is now the function to be determined.

Detailed radial solution - Recasting the problem - 3

Having taken out the two asymptotic behaviors,

we hope that the function $L(s)$ can be some relatively simple function,

such as a low-order polynomial.

We ask only that $L(s)$ does not grow too fast with large s,

so that the function $\chi(s)$ can be normalized;

this restriction is actually the source of the quantization we will obtain.

Now we substitute this form $\chi(s) = s^{l+1}L(s)\exp(-s/2)$ into the Eq. (10.54),

$$\frac{d^2\chi}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right]\chi = 0$$

and obtain an equation for $L(s)$

$$s\frac{d^2L}{ds^2} - \left[s - 2(l+1)\right]\frac{dL}{ds} + \left[n - (l+1)\right]L = 0 \qquad (10.56)$$

which is the kind of form we need for the next part of this solution.

The hydrogen atom – 3

Reading – Section 10.4 from "Power series solution" – 10.6

Solving for the internal states of the hydrogen atom (continued)

Solutions of the hydrogen atom problem

Summary of the hydrogen atom solution

Detailed radial solution - Power series solution - 1

Next we propose that,

since $L(s)$ is presumably an analytic function,

it can be described as a power series,

which we write formally as

$$L(s) = \sum_{q=0}^{\infty} c_q s^q \tag{10.57}$$

where the c_q are coefficients to be determined by solving the differential equation (10.56).

Substituting this power series form into Eq. (10.56),

$$\sum_{q=0}^{\infty} \left[q(q-1)c_q s^{q-1} - qc_q s^q + 2q(l+1)c_q s^{q-1} + \left[n-(l+1)\right]c_q s^q \right] = 0 \tag{10.58}$$

We can open up this sum to see explicitly how we will gather terms in specific powers of s. In the middle of the summation, we will have two successive terms from the above sum

$$\begin{aligned}
&\cdots + q(q-1)c_q s^{q-1} - qc_q s^q + 2q(l+1)c_q s^{q-1} + \left[n-(l+1)\right]c_q s^q \\
&+(q-1)(q-2)c_{q-1}s^{q-2} - (q-1)c_{q-1}s^{q-1} + 2(q-1)(l+1)c_{q-1}s^{q-2} + \left[n-(l+1)\right]c_{q-1}s^{q-1} \\
&+\cdots
\end{aligned}$$

Detailed radial solution - Power series solution - 2

We can now gather terms of the same power of s (specifically here for minor reasons of convenience in s^{q-1}) to show that we can gather terms of the same power of s to show that

$$\sum_{q=1}^{\infty}\left\{\left[q(q-1)+2q(l+1)\right]c_q-\left[(q-1)+(l+1)-n\right]c_{q-1}\right\}s^{q-1}=0 \qquad (10.59)$$

Of course, this relation must hold for all s,

and so what we have shown is that there is a relation between successive coefficients in the power series, i.e., explicitly

$$\left[q(q-1)+2q(l+1)\right]c_q=\left[(q-1)+(l+1)-n\right]c_{q-1} \qquad (10.60)$$

i.e.,

$$c_q=\frac{(q+l-n)}{q(q+2l+1)}c_{q-1} \qquad (10.61)$$

This kind of relation between successive terms in a series is called a recurrence relation.

Detailed radial solution - Power series solution - 3

We are now very close to a solution of the mathematical problem, but one important step remains.

Note that, for very large q,

the factors in successive terms in the series are smaller by a factor of about $1/q$,

so the factors themselves are approximately proportional to $1/q!$.

That is the behavior we would find in the power series for the exponential function $\exp(s)$.

Such behavior would cause the function $\chi(s)$ to grow with increasing s,

and hence not to be normalizable.

How do we get out of this difficulty?

We try to find the condition that will cause the series to terminate at a finite number of terms.

That will happen if and only if the factor $(q+l-n)=0$ for some $q \geq 1$.

(We make the restriction that q must be at least 1 so that we have at least one term (the term $c_0 s^0$) in the series – otherwise the function is zero and not of interest to us.)

Detailed radial solution - Power series solution - 4

Hence we require two things for termination of the series,

first that n *is an integer,*

and second that

$$n \geq l + 1 \tag{10.62}$$

This termination therefore is responsible mathematically for the quantization of the radial behavior of the wavefunction.

Next, we will discuss the actual polynomial functions that the recurrence relation (10.61) has defined for us.

Detailed radial solution - Associated Laguerre polynomials - 1

Not surprisingly, the polynomials that solve (10.56) and that are defined by

(i) the recurrence relation (10.61), and

(ii) the "stopping condition" of an integer n that satisfies (10.62),

are a standard set of known polynomials,

the associated Laguerre polynomials.

(It is not necessary that we know this to solve the problem, but this does connects with other relations that can be helpful in making, for example, normalization integrals easier.)

The only choice we need to make to define our polynomials completely is the first coefficient in the power series (c_0);

because the coefficients in the polynomial are constructed progressively from the preceding coefficient,

this coefficient merely multiplies the entire polynomial,

and is arbitrary as far as solving the equation (10.56) is concerned.

Detailed radial solution - Associated Laguerre polynomials - 2

To make a connection with the standard definition of the associated Laguerre polynomials, we choose

$$c_0 = \frac{(n+l)!}{(n-l-1)!(2l+1)!} \tag{10.63}$$

With this choice, our polynomials become, using the recursive relation Eq. (10.61),

$$L_{n-l-1}^{2l+1}(s) = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+l)!}{(n-l-q-1)!(q+2l+1)!} s^q \tag{10.64}$$

where we have introduced the notation for the associated Laguerre polynomials

$$L_p^j(s) = \sum_{q=0}^{p} (-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!} s^q \tag{10.65}$$

Solutions of the hydrogen atom problem - 1

Now we can work back through our argument and put the complete solution together.

We now have, from Eqs. (10.55) and (10.64), with the definition

$$L_p^j(s) = \sum_{q=0}^{p} (-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!} s^q \tag{10.65}$$

for the associated Laguerre polynomials, the function

$$\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \tag{10.66}$$

of the variable $s = (2/na_o)r$

Hence, changing back to the variable r **for the separation of the electron and the proton, from Eq. (10.39) (**$\chi(r) = rR(r)$**),**

$$\begin{aligned} R(r = na_o s/2) &\propto \frac{1}{r} s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \\ &\propto s^{l} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \end{aligned} \tag{10.67}$$

and introducing a normalization constant into the radial wavefunction,

$$R(r = na_o s/2) = \frac{1}{A} s^{l} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \tag{10.68}$$

Solutions of the hydrogen atom problem - 2

The full normalization integral of the wavefunction $U(\mathbf{r}) = R(r)Y(\theta,\phi)$ would be

$$1 = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left| R(r)Y(\theta,\phi) \right|^2 r^2 \sin\theta d\theta d\phi dr \tag{10.69}$$

but we have already normalized the spherical harmonics with the θ and ϕ integrals,

so we are left with the radial normalization

$$1 = \int_0^{\infty} R^2(r) r^2 dr \tag{10.70}$$

It is possible to show that

$$\int_0^{\infty} s^{2l} \left[L_{n-l-1}^{2l+1}(s) \right]^2 \exp(-s) s^2 ds = \frac{2n(n+l)!}{(n-l-1)!} \tag{10.71}$$

from which we can therefore conclude that the normalized radial wavefunction is

$$R(r) = \left[\frac{(n-l-1)!}{2n(n+l)!} \left(\frac{2}{na_o} \right)^3 \right]^{1/2} \left(\frac{2r}{na_o} \right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_o} \right) \exp\left(-\frac{r}{na_o} \right) \tag{10.72}$$

Hydrogen atom radial wavefunctions

We write the wavefunctions using the Bohr radius a_o as the unit of radial distance,

so we have a radial distance $\rho = r / a_o$,

and we introduce the subscripts n and l for the quantum numbers to index the various functions $R_{n,l}$.

$$R_{1,0}(\rho) = 2\exp(-\rho)$$

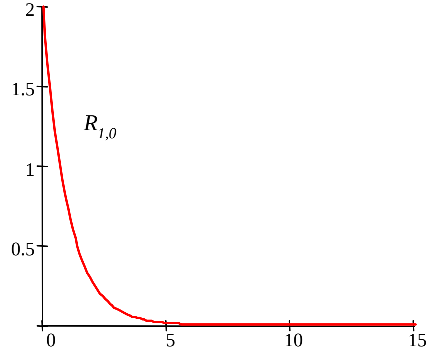
$$R_{2,0}(\rho) = \frac{\sqrt{2}}{4}(2-\rho)\exp(-\rho/2)$$

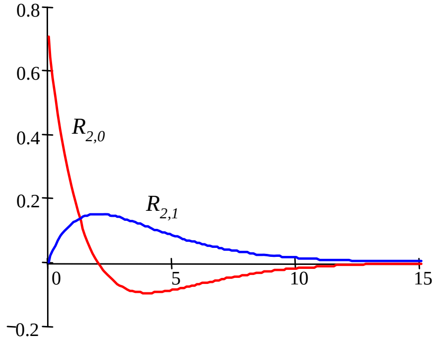
$$R_{2,1}(\rho) = \frac{\sqrt{6}}{12}\rho\exp(-\rho/2)$$

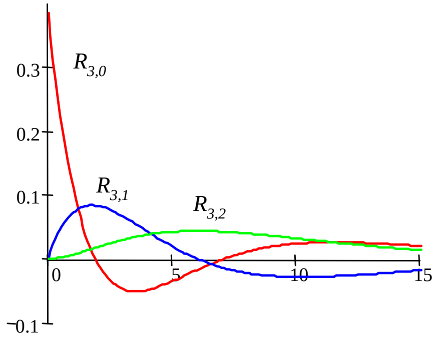
$$R_{3,0}(\rho) = \frac{2\sqrt{3}}{27}\left(3-2\rho+\frac{2}{9}\rho^2\right)\exp(-\rho/3)$$

$$R_{3,1}(\rho) = \frac{\sqrt{6}}{81}\rho\left(4-\frac{2}{3}\rho\right)\exp(-\rho/3)$$

$$R_{3,2}(\rho) = \frac{2\sqrt{30}}{1215}\rho^2\exp(-\rho/3) \qquad (10.73)$$







Behavior of the complete hydrogen atom solutions

(i) The overall "size" of the wavefunctions becomes larger with larger n.

(ii) The number of zeros in the wavefunction is $n-1$.

The radial wavefunctions have $n-l-1$ zeros,

and the spherical harmonics have l nodal "circles".

(The radial wavefunctions appear to have an additional zero at $r=0$ for all $l \geq 1$, but note that all the spherical harmonics have at least one nodal "circle" for all $l \geq 1$. As $r \to 0$, that nodal circle forces the wavefunction to be zero anyway, and so this zero is already counted.)

In summary of the quantum numbers,

for the so-called principal quantum number n

$$n = 1, 2, 3, \ldots \tag{10.74}$$

and

$$l \leq n-1 \tag{10.75}$$

(We have already deduced that l is a positive or zero integer.)

We also now know the eigenenergies of the hydrogen atom.

Knowing the possible values for n, we can write from Eq. (10.51)

$$E_H = -\frac{Ry}{n^2}, \; n = 1, 2, 3, \ldots \tag{10.76}$$

Summary of hydrogen atom solution - 1

Solution of the hydrogen atom problem

First,

we generalize the Schrödinger equation,

including terms for the kinetic energies of both the electron and the proton,

including the Coulomb potential energy that comes from the electrostatic attraction of the electron and the proton,

and allowing the wavefunction now to depend on the coordinates x_e, y_e, and z_e for the electron and x_p, y_p, and z_p for the proton, i.e.,

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_p}\nabla_p^2+V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)\right]\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right)=E\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right) \quad (10.6)$$

where

$$V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)=-\frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_e-\mathbf{r}_p\right|} \quad (10.5)$$

and

$$\nabla_e^2\equiv\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2} \quad (10.3)$$

is the Laplacian operator for the electron coordinates, and similarly for ∇_p^2.

Summary of hydrogen atom solution - 2

Solving this differential equation in six variables is hard,

so we look to separate variables,

to reduce it to two differential equations,

each in three variables.

We do this by first changing to a center-of-mass coordinate system, with relative position coordinates

$$x = x_e - x_p, \; y = y_e - y_p, \; z = z_e - z_p \tag{10.7}$$

giving a relative position vector

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}, \tag{10.8}$$

and a position vector for the center of mass

$$\mathbf{R} = \frac{m_e \mathbf{r}_e + m_p \mathbf{r}_p}{M} \tag{10.10}$$

where *M* is the total mass

$$M = m_e + m_p \tag{10.11}$$

We also define a reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \tag{10.19}$$

Summary of hydrogen atom solution - 3

After some algebra formally to change to this coordinate system, we can rewrite the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right) \equiv -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \qquad \text{(10.2) and (10.21)}$$

where $\nabla_{\mathbf{R}}^2 \equiv \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$ and $\nabla_{\mathbf{r}}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ (10.20)

With this new form of the Hamiltonian,

we now separate the variables by postulating that we can write

$$\psi(\mathbf{R},\mathbf{r}) = S(\mathbf{R})U(\mathbf{r}) \qquad (10.22)$$

leading to the separated equations

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R}) \qquad (10.25)$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_H U(\mathbf{r}) \qquad (10.26)$$

where

$$E_H = E - E_{CoM} \qquad (10.27)$$

Eq. (10.25) gives simple plane-wave solutions

$$S(\mathbf{R}) = \exp(i\mathbf{K}\cdot\mathbf{R}) \qquad (10.28)$$

that correspond to the motion of the entire hydrogen atom.

Summary of hydrogen atom solution - 4

Solving Eq. (10.26) will give the internal states of the hydrogen atom.

To solve it,

we transform to spherical polar coordinates,

in which the Laplacian operator becomes

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad (10.30)$$

The term in square brackets is the same as the operator $\nabla^2_{\theta,\phi} \equiv -\hat{L}^2/\hbar^2$ *that we introduced previously in discussing angular momentum, i.e.,*

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\nabla^2_{\theta,\phi} \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{1}{\hbar^2 r^2}\hat{L}^2$$

Noting this, we propose a separation of variables to solve Eq. (10.26),

$$U(\mathbf{r}) = R(r)Y(\theta,\phi) \equiv \frac{1}{r}\chi(r)Y(\theta,\phi) \qquad (10.31) \text{ and } (10.38)$$

where we have chosen to define a new function

$$\chi(r) = rR(r) \qquad (10.39)$$

for algebraic convenience.

Summary of hydrogen atom solution - 5

This separation of variables leads to two equations,

one of which

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi) \qquad (9.32)$$

we already solved in discussing angular momentum,

and the other of which becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} + \left(V(r) + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H \chi(r) \qquad (10.43)$$

This equation has solutions

$$\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \qquad (10.66)$$

where

$$L_p^j(s) = \sum_{q=0}^{p} (-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!} s^q \qquad (10.65)$$

are the associated Laguerre polynomials,

and *n*,

known as the principal quantum number in the hydrogen atom,

is a positive integer,

$$n = 1, 2, 3, \ldots \qquad (10.74)$$

and

$$l \le n-1 \qquad (10.75)$$

Summary of hydrogen atom solution - 6

The entire radial wavefunction solutions for the hydrogen atom then becomes

$$R_{n,l}(r)=\left[\frac{(n-l-1)!}{2n(n+l)!}\left(\frac{2}{na_o}\right)^3\right]^{1/2}\left(\frac{2r}{na_o}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_o}\right)\exp\left(-\frac{r}{na_o}\right) \qquad (10.72)$$

where $a_o=\frac{4\pi\varepsilon_o\hbar^2}{e^2\mu}\cong$ 0.529 Å = 5.29 x 10^{-11} m (10.35)

is known as the Bohr radius.

The angular parts of the total relative motion wavefunction

$$U_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi)$$

have already been solved as the spherical harmonics

$$Y_{lm}(\theta,\phi)=(-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)\exp(im\phi) \qquad (9.33)$$

The eigenenergies of these hydrogen atom solutions are

$$E_H=-\frac{Ry}{n^2},\ n=1,2,3,\ldots \qquad (10.76)$$

where Ry is the Rydberg $Ry=\frac{\hbar^2}{2\mu a_o^2}=\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o\hbar}\right)^2\cong$ 13.6 eV (10.37)

Methods for one-dimensional problems – 1

Reading – Sections 11.1 – 11.2, up to start of "Calculation of eigenenergies of bound states"

Tunneling

Transfer matrix technique

Methods for one-dimensional problems

Many quantum mechanical problems can be reduced to one-dimension

- ***because the problem, though truly three-dimensional, can be mathematically separated.***
  - **E.g., problems associated with electrons and planar surfaces or layered structures**
    - *field emission of electrons from planar metallic surfaces*
    - *most problems associated with semiconductor quantum well structures.*

One-dimensional problems can be solved by a number of techniques.

- ***Here we discuss one of these,***
  - **the transfer matrix technique**
- ***and we also derive one key result of the so-called "WKB" method.***

We will concentrate here on the use of such techniques for solving tunneling problems

Tunneling rates - 1

Remember the simple rectangular barrier.

Presume E is less than the barrier height V_o so that we have tunneling.

For any form of barrier,

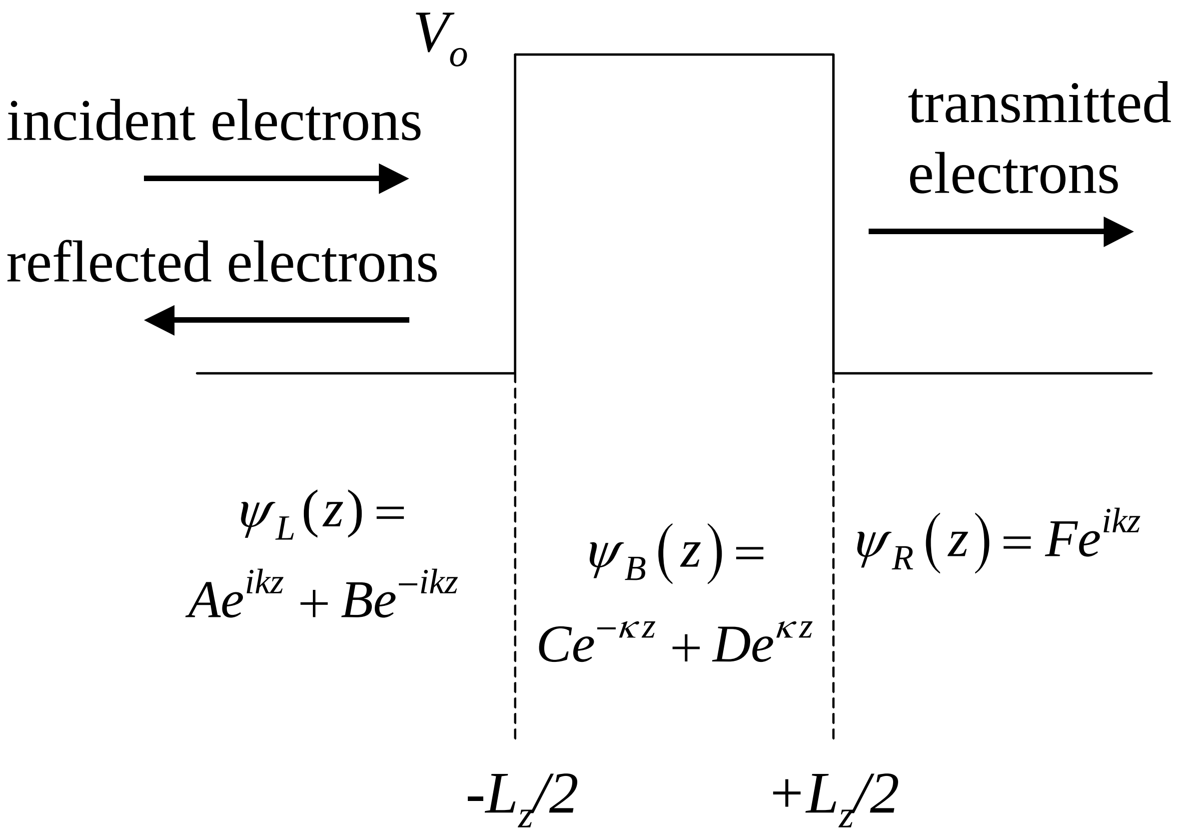
suppose we have found appropriate relations between the amplitudes of

the incident wave (A),

the reflected wave (B)

and the transmitted wave (F)

for some given energy of particle.



$$\psi_L(z) = Ae^{ikz} + Be^{-ikz}$$

$$\psi_B(z) = Ce^{-\kappa z} + De^{\kappa z}$$

$$\psi_R(z) = Fe^{ikz}$$

How do we relate this quantum mechanical problem to actual currents of electrons?

Tunneling rates - 2

For example, suppose we were solving the problem of tunneling emission of electrons from some solid.

- ***We will presume some thermal distribution of electrons on the left of the barrier,***
  - **and we will use a thermal argument to deduce how many electrons there are with a particular velocity v in the z direction (i.e., perpendicular to the barrier).**
    - *We will add up the results of all such electrons in the distribution to deduce the total emitted current.*

Hence, if we can find some way of deducing

- ***what fraction of electrons traveling at some velocity v in the z direction are transmitted by the barrier,***
  - **we will know the tunneling emission current.**

Formal evaluation of currents - 1

We previously discussed calculating particle current quantum mechanically,

concluding that the particle current density is

$$\mathbf{j}_p = \frac{i\hbar}{2m}\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right) \qquad (3.97)$$

where $\Psi = \Psi(\mathbf{r}, t)$ is the full time-dependent wavefunction.

If we presume here we are dealing with particles of well-defined energy E,

which is $E = \hbar^2 k^2 / 2m$ in the propagating regions,

the time-dependent factor $\exp(-iEt/\hbar)$ disappears in this current density equation because of the product of complex conjugates,

so in this case of well-defined energy we can write

$$j_p = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) \qquad (11.1)$$

where ψ is now the one-dimensional spatial wavefunction $\psi(z)$,

and we have dropped the vector character of the particle current density $\mathbf{j}_p$ because we are considering only currents in the z direction.

Formal evaluation of currents - 2

If we now consider, for example, the wavefunction on the right, $F\exp(ikz)$,

then we have from Eq. (11.1) ($j_p = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right)$)

$$j_p = |F|^2 \frac{\hbar k}{m} \qquad (11.2)$$

The quantity $\hbar k / m$ ***behaves like an effective classical velocity*** v***, with*** $E = \hbar^2 k^2 / 2m = (1/2)mv^2$**.**

For the particle current on the left,

we should proceed carefully,

remembering to deal with the whole wavefunction on the left in evaluating the particle current.

With the wavefunction $\psi(z) = A\exp(ikz) + B\exp(-ikz)$, we have from Eq. (11.1)

$$j_p = \frac{i\hbar}{2m}\left\{\begin{array}{l}\left[A\exp(ikz)+B\exp(-ikz)\right]\left[-ikA^*\exp(-ikz)+ikB^*\exp(ikz)\right] \\ -\left[A^*\exp(-ikz)+B^*\exp(ikz)\right]\left[ikA\exp(ikz)-ikB\exp(-ikz)\right]\end{array}\right\} \qquad (11.3)$$

$$= \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right)$$

because all of the spatially oscillating terms cancel.

Formal evaluation of currents - 3

Since we have deduced $j_p = \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right)$, we can therefore consider

$\hbar k|A|^2/m$ ***as the forward current on the left of the barrier, and***

$\hbar k|B|^2/m$ ***as the reflected or backward current,***

adding the two to get the net current.

Hence we find that we can identify the (particle) current densities as follows,

for particles of effective classical velocity $v = \hbar k/m$**.**

Incident current density $|A|^2 v$

Reflected current density $|B|^2 v$

Transmitted current density $|F|^2 v$

The fraction of incident particles that are transmitted by the barrier is

$$\eta = \left(|A|^2 - |B|^2\right)/|A|^2 \tag{11.4}$$

For the specific problem above where the medium on the left and the medium on the right have the same potential,

we can also write Eq. (11.4) in the form

$$\eta = |F|^2/|A|^2 . \tag{11.5}$$

Formal evaluation of currents - 4

We can use either Eq. (11.4) ($\eta = \left(|A|^2 - |B|^2\right)/|A|^2$) or Eq. (11.5) ($\eta = |F|^2 / |A|^2$).

The form involving only** A **and** B **remains valid regardless of the form of the potential to the right;

for example, in a field-emission tunneling problem,

where an electric field is applied perpendicular to a metal surface,

the potential in the barrier falls off linearly with distance,

and there is no region on the right of uniform potential,

making it harder to calculate the transmitted current directly.

It might seem above that we are merely proving the obvious.

Note, however, that

we have not used classical notions here to deduce the results,

though we have shown a connection to those notions.

We have instead rigorously deduced the current densities by a first-principles quantum mechanical argument.

We have been able to avoid trying to decide whether to use group velocities or phase velocities in considering the currents here, for example.

This argument clears the way for practical calculations of tunneling currents, including those with more complicated barriers.

Transfer matrix - 1

We previously analyzed simple problems, such as a square potential barrier.

In principle,

the simple methods we used before are extensible to multilayer structures

In practice

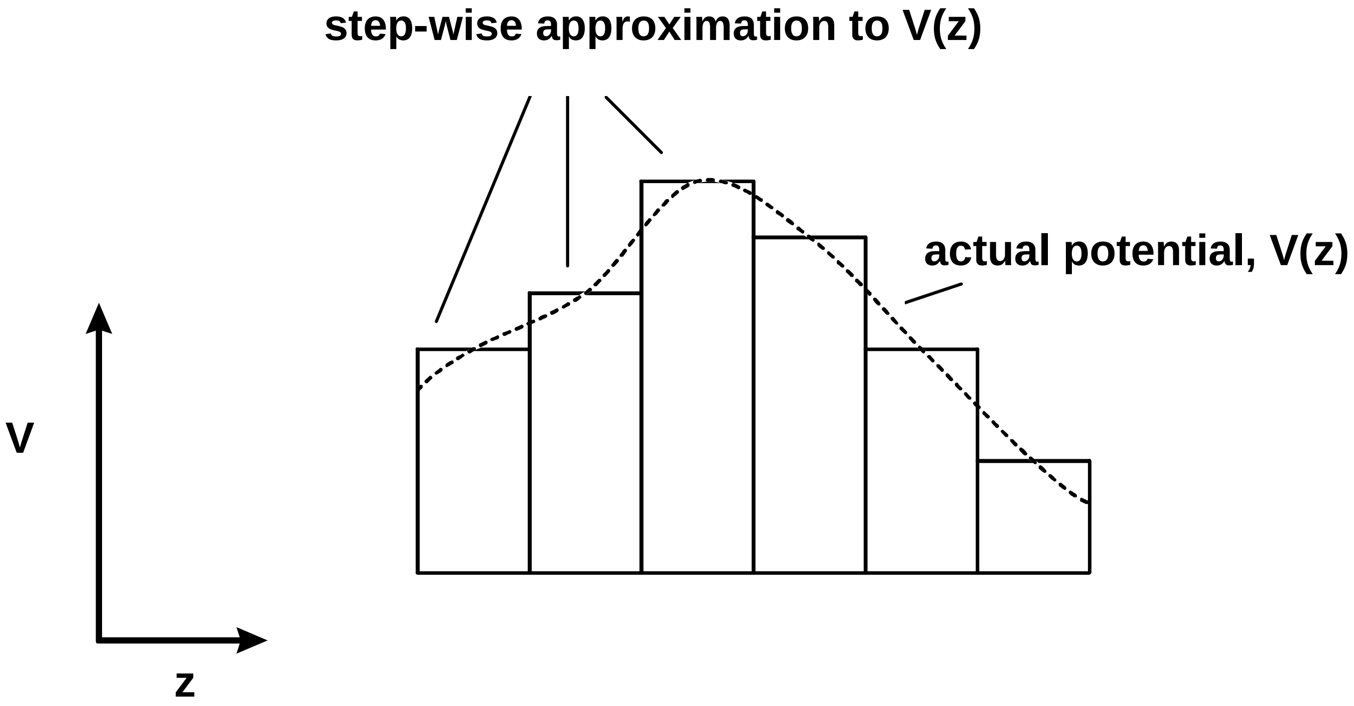
we need better mathematical techniques to keep track of the various coefficients.

We introduce the transfer matrix to handle all of the coefficients.

We presume that the potential is a series of steps.

This could be an actual step-like potential,

or we could be approximating some continuously varying potential



Transfer matrix - 2

We therefore reduce the problem to that of

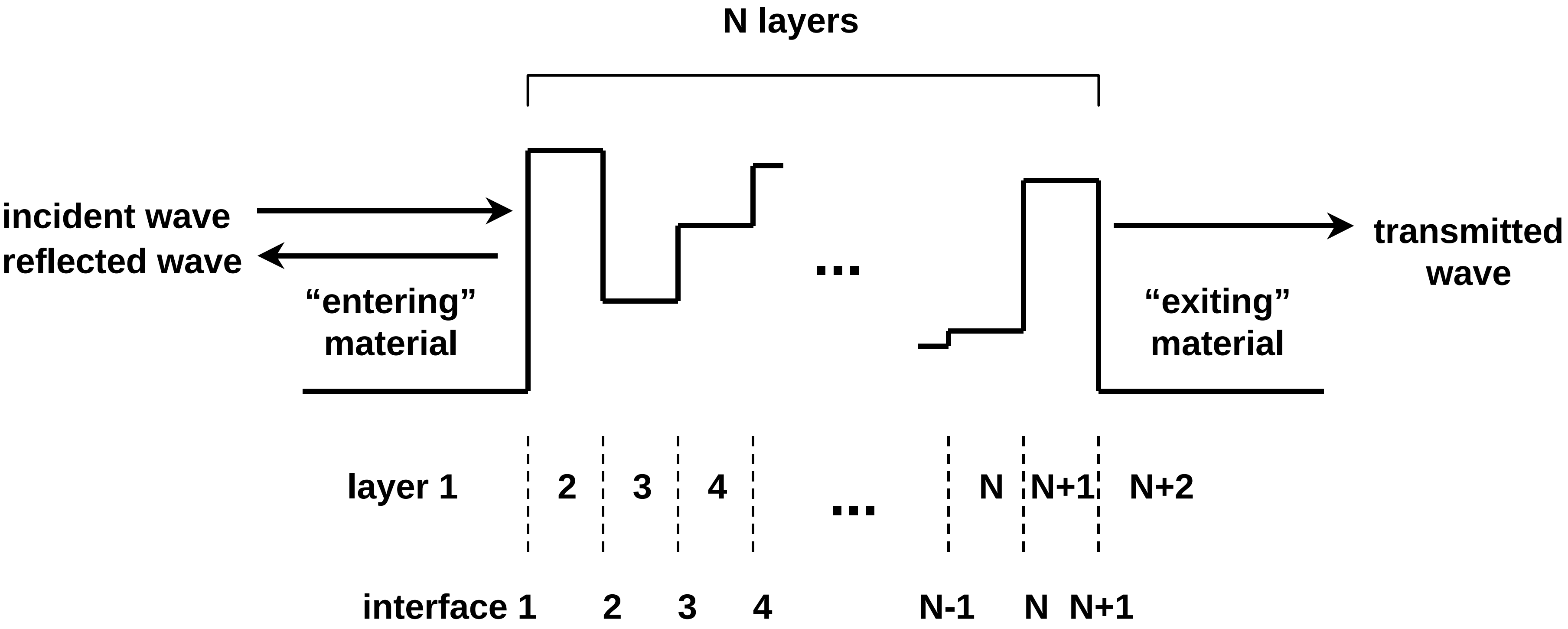
waves within a simple constant potential

which are either sinusoidal or exponential

together with appropriate boundary conditions to link the solutions in adjacent layers.

Imagine that we have an electron wave incident on the structure from one side, with a particular energy, E.

There will be some reflected wave and some transmitted wave.



Transfer matrix - 3

The approach we will take is, for each layer in the structure,

derive a matrix that relates the forward and backward amplitudes,

A_m *and* B_m*, just to the right of the (*m *- 1)th interface,*

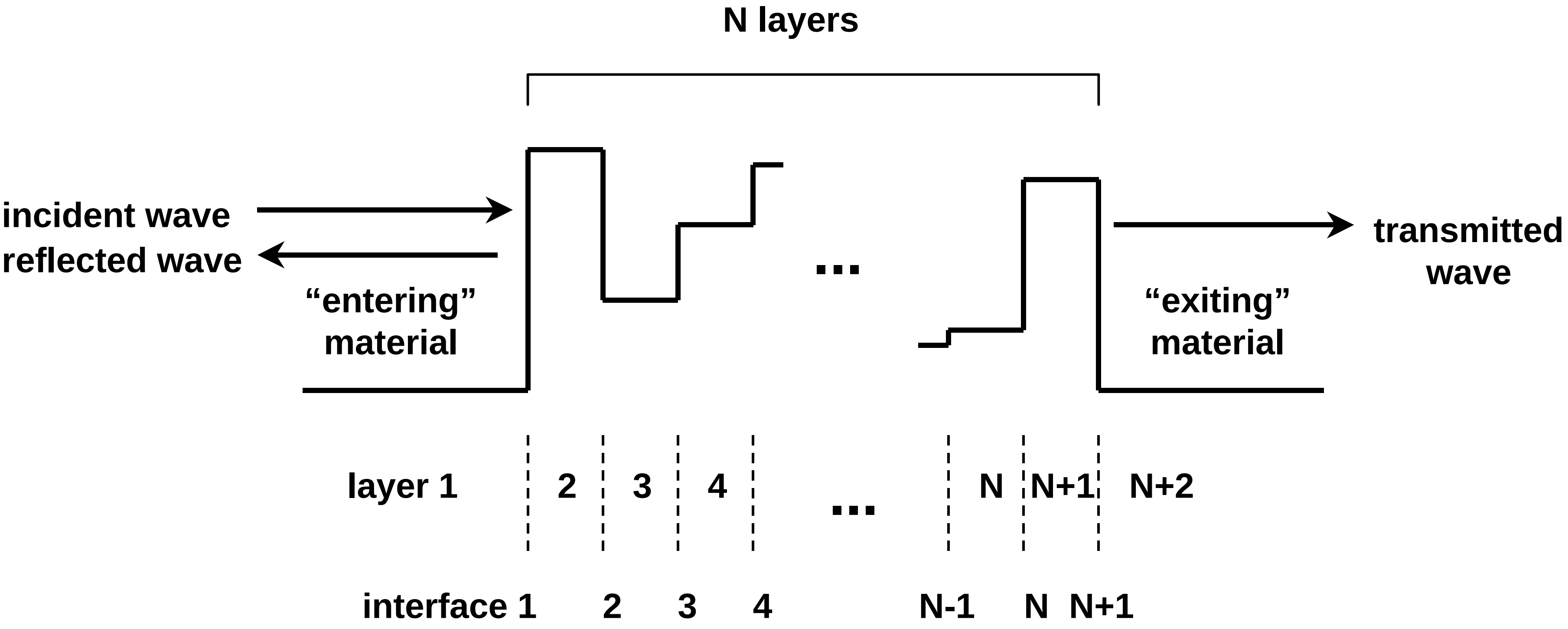
to the forward and backward amplitudes

A_{m+1} *and* B_{m+1}*, just to the right of the* m*th interface.*

By multiplying those matrices together for all of the layers,

we will construct a single "transfer matrix" for the whole structure,

which will enable us to analyze the entire multilayer structure.



Transfer matrix - 4

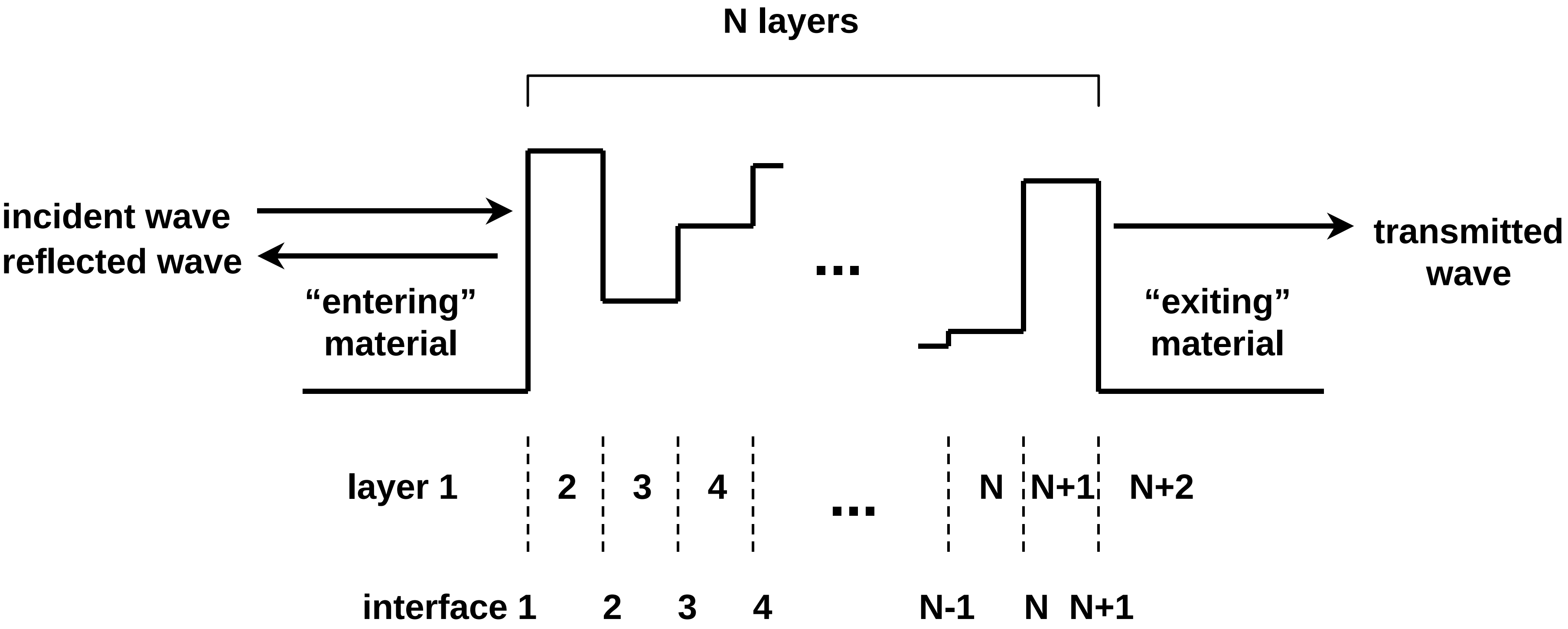
In this formalism, each layer m will have

a potential energy V_m, a thickness d_m,

and possibly a mass or effective mass, m_{fm}.

For interfaces 2 and higher (e.g., $z_2 = d_2$, $z_3 = d_2 + d_3$, etc.), the position of the mth interface, relative to the position of interface 1, is

$$z_m = \sum_{q=2}^{m} d_q \tag{11.6}$$



Transfer matrix - 5

In any given layer,

if $E > V_m$***,***

we know that we will in general have

a "forward" propagating wave

of the form $A = A_o \exp\left[ik_m\left(z - z_{m-1}\right)\right]$, and

a "backward" propagating wave

of the form $B = B_o \exp\left[-ik_m\left(z - z_{m-1}\right)\right]$,

where A and B are complex numbers representing the amplitude of the forward and backward waves, respectively.

In this case

$$k_m = \sqrt{\frac{2m_{fm}}{\hbar^2}\left(E - V_m\right)} \qquad (11.7)$$

where m_{fm} *is the mass of the particle in a given layer of the structure*

Transfer matrix - 6

Similarly,

if $V_m > E$*,*

we will have

a "forward" decaying “wave”

of the form $A = A_o \exp\left[-\kappa_m \left(z - z_{m-1}\right)\right]$, and

a "backward" decaying wave

of the form $B = B_o \exp\left[\kappa_m \left(z - z_{m-1}\right)\right]$, where

$$\kappa_m = \sqrt{\frac{2m_{fm}}{\hbar^2}\left(V_m - E\right)} \qquad (11.8)$$

Now, we note that,

if we use only the form (11.7),

$$k_m = \sqrt{\frac{2m_{fm}}{\hbar^2}\left(E - V_m\right)}$$

not only for the situation with $E > V_m$

but also for the case $V_m > E$*,*

we obtain imaginary k ***(***$\equiv i\kappa$***) for the*** $V_m > E$ ***case.***

Transfer matrix - 7

Mathematically,

as long as we choose the positive square root (either real or imaginary) in both cases,

we can work only with this k.

A forward propagating "wave" can then be written in the form

$$\exp\left[ik_m\left(z - z_{m-1}\right)\right]$$

for both the

$E > V_m$ *and*

$V_m > E$ *cases.*

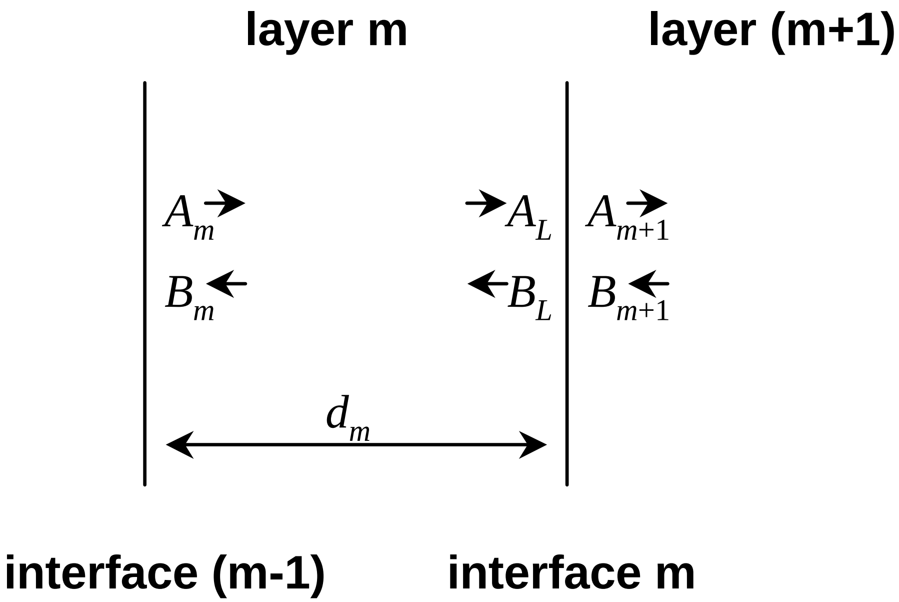
This will simplify our handling of the mathematics, allowing us to use the same formalism in all layers.

Now in *any* layer we have a wave that we can write as

$$\psi(z) = A_m \exp\left[ik_m\left(z - z_{m-1}\right)\right] + B_m \exp\left[-ik_m\left(z - z_{m-1}\right)\right] \tag{11.9}$$

where k can be either real or imaginary, and is given by Eq. (11.7) *($k_m = \sqrt{\frac{2m_{fm}}{\hbar^2}\left(E - V_m\right)}$).*

Boundary condition matrix - 1



Now let us look at the boundary conditions in going from

just inside one layer to the right of the boundary to

just inside the adjacent layer on the left of the boundary.

Using the notation of the above figure, we have,

for the continuity of the wavefunction, ψ, at the interface

$$\psi = A_L + B_L = A_{m+1} + B_{m+1}. \tag{11.10}$$

for the continuity of $d\psi / dz$

$$\frac{d\psi}{dz} = ik\left(A - B\right) \tag{11.11}$$

for the wave on either side of the boundary

Boundary condition matrix - 2

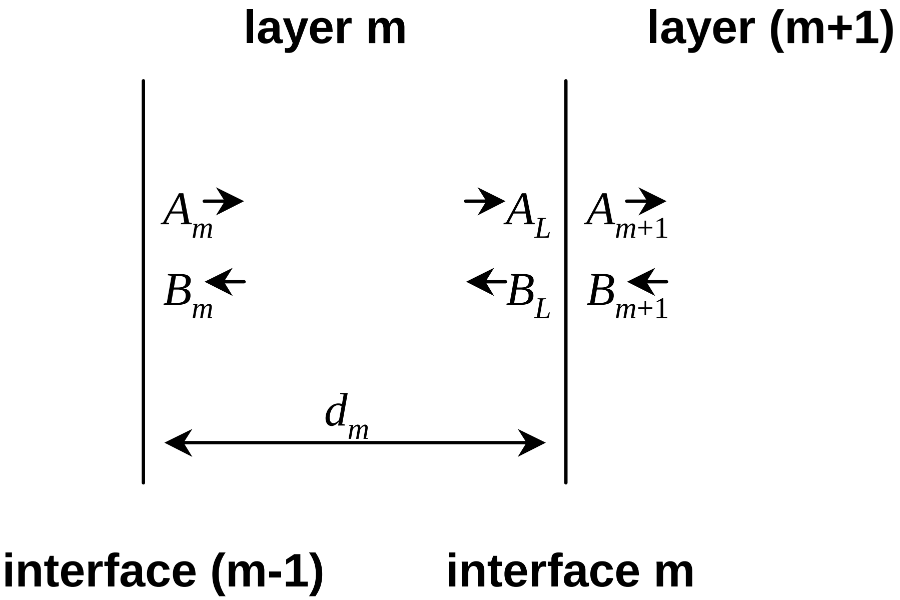
So we have, for the right boundary in the figure

$$A_L - B_L = \Delta_m \left(A_{m+1} - B_{m+1} \right) \qquad (11.12)$$

where

$$\Delta_m = \frac{k_{m+1}}{k_m} \qquad (11.13)$$

with the obvious notation that subscripts *m* and *m* + 1 refer to the values in the corresponding layers.



In a layered semiconductor structure in the effective mass approximation,

we might use continuity of $\left(1/m_f\right) d\psi/dz$ for the second boundary condition, in which case instead of Eq. (11.13) we would obtain

$$\Delta_m = \frac{k_{m+1}}{k_m} \frac{m_{fm}}{m_{fm+1}} \qquad (11.14)$$

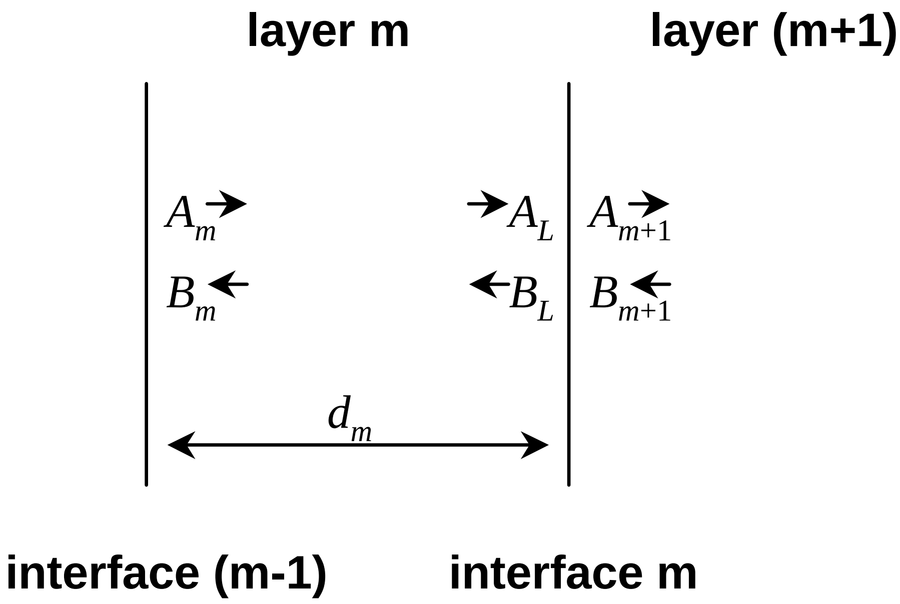
where m_{fm} is the (effective) mass in layer m,

and we would use this Δ_m in Eq. (11.12) and all subsequent equations.

Boundary condition matrix - 3

Using Eq. (11.10) ($\psi = A_L + B_L = A_{m+1} + B_{m+1}$)

and Eq. (11.12) ($\frac{d\psi}{dz} = ik\left(A - B\right)$) gives



$$A_L = A_{m+1}\left(\frac{1+\Delta_m}{2}\right) + B_{m+1}\left(\frac{1-\Delta_m}{2}\right) \qquad (11.15)$$

and

$$B_L = A_{m+1}\left(\frac{1-\Delta_m}{2}\right) + B_{m+1}\left(\frac{1+\Delta_m}{2}\right) \qquad (11.16)$$

which can be written in matrix form as

$$\begin{bmatrix} A_L \\ B_L \end{bmatrix} = \mathbf{D}_m \begin{bmatrix} A_{m+1} \\ B_{m+1} \end{bmatrix} \qquad (11.17)$$

where

$$\mathbf{D}_m = \begin{bmatrix} \frac{1+\Delta_m}{2} & \frac{1-\Delta_m}{2} \\ \frac{1-\Delta_m}{2} & \frac{1+\Delta_m}{2} \end{bmatrix} \qquad (11.18)$$

Propagation matrix

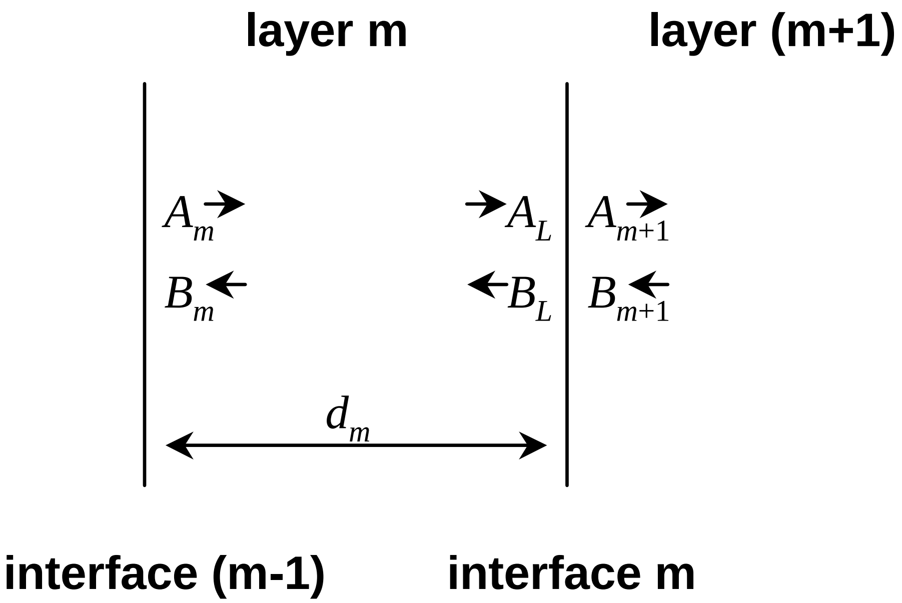
We now need to deal with the propagation that relates *A_m* and *B_m* to *A_L* and *B_L*.

(We have chosen, for a minor formal reason, to calculate the matrices for going "backwards" through the structure).

For the propagation in a given layer, *m*, whose layer thickness is *d_m*, we have

$$A_m = A_L \exp(-ik_m d_m) \qquad (11.19)$$

$$B_m = B_L \exp(ik_m d_m) \qquad (11.20)$$



corresponding to a matrix-vector representation

$$\begin{bmatrix} A_m \\ B_m \end{bmatrix} = \mathbf{P}_m \begin{bmatrix} A_L \\ B_L \end{bmatrix} \qquad (11.21)$$

with

$$\mathbf{P}_m = \begin{bmatrix} \exp(-ik_m d_m) & 0 \\ 0 & \exp(ik_m d_m) \end{bmatrix} \qquad (11.22)$$

Full transfer matrix

We can now write the full transfer matrix, $\mathbf{T}$, for this structure,

which relates the forward and backward wave amplitudes at the "entrance"

i.e., just to the left of the first interface

to the forward and backward wave amplitudes at the "exit"

i.e., just to the right of the last interface,

$$\begin{bmatrix} A_1 \\ B_1 \end{bmatrix} = \mathbf{T} \begin{bmatrix} A_{N+2} \\ B_{N+2} \end{bmatrix} \tag{11.23}$$

where

$$\mathbf{T} = \mathbf{D}_1 \mathbf{P}_2 \mathbf{D}_2 \mathbf{P}_3 \mathbf{D}_3 \cdots \mathbf{P}_{N+1} \mathbf{D}_{N+1} \tag{11.24}$$

Note that this transfer matrix depends on the energy E that we chose for the calculation of the k's in each layer.

Calculation of tunneling rates - 1

Given that we have calculated the transfer matrix for some structure and for some energy E

$$\mathbf{T} \equiv \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \tag{11.25}$$

we can now deduce the fraction of incident particles at that energy that are transmitted by the barrier.

We presume that there is no wave incident from the right,

so there is no backward wave amplitude on the right of the potential.

Hence we have,

for incident forward and backward amplitudes A and B respectively,

and a transmitted amplitude F,

$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} F \\ 0 \end{bmatrix} \tag{11.26}$$

Calculation of tunneling rates - 2

From this ($\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} F \\ 0 \end{bmatrix}$) we can see that

$$A = T_{11} F \tag{11.27}$$

and

$$B = T_{21} F \tag{11.28}$$

and hence, from Eq. (11.4), the fraction of particles transmitted by this barrier is

$$\eta = 1 - \frac{\left|T_{21}\right|^2}{\left|T_{11}\right|^2} \tag{11.29}$$

This technique can be used to give exact analytic results for layered potentials,

though such exact results become algebraically impractical for structures with even only quite small numbers of layers.

It is, however, particularly useful for numerical calculations, being straightforward to program.

It is therefore a very useful practical technique for investigating one-dimensional potentials and their behavior.

Calculation of wavefunctions - 1

Note that this method also enables us to calculate the wavefunction at any point in the structure.

We can readily calculate the forward and backward amplitudes, A_m and B_m respectively, at the left of each layer in the structure.

Obviously, we have

$$\begin{bmatrix} A_{N+1} \\ B_{N+1} \end{bmatrix} = \mathbf{P}_{N+1}\mathbf{D}_{N+1}\begin{bmatrix} A_{N+2} \\ B_{N+2} \end{bmatrix} \tag{11.30}$$

and similarly, we have in general for any layer within the structure

$$\begin{bmatrix} A_m \\ B_m \end{bmatrix} = \mathbf{P}_m\mathbf{D}_m \ldots \mathbf{P}_N\mathbf{D}_N\mathbf{P}_{N+1}\mathbf{D}_{N+1}\begin{bmatrix} A_{N+2} \\ B_{N+2} \end{bmatrix} \tag{11.31}$$

Given that we know the forward and backward amplitudes at the left of layer m,

then the wavefunction at some point z in that layer is the sum of the forward and backward wavefunctions as in Eq. (11.9).

$$\psi(z) = A_m \exp\left[ik_m(z - z_m)\right] + B_m \exp\left[-ik_m(z - z_m)\right]$$

Calculation of wavefunctions - 2

Note that we could set up a calculation so that these forward and backward amplitudes are calculated as intermediate results

if we progressively evaluate the forward and backward amplitudes for each successive layer as in

$$\begin{bmatrix} A_m \\ B_m \end{bmatrix} = \mathbf{P}_m \mathbf{D}_m \begin{bmatrix} A_{m+1} \\ B_{m+1} \end{bmatrix} \qquad (11.32)$$

rather than evaluating the transfer matrix $\mathbf{T}$ itself.

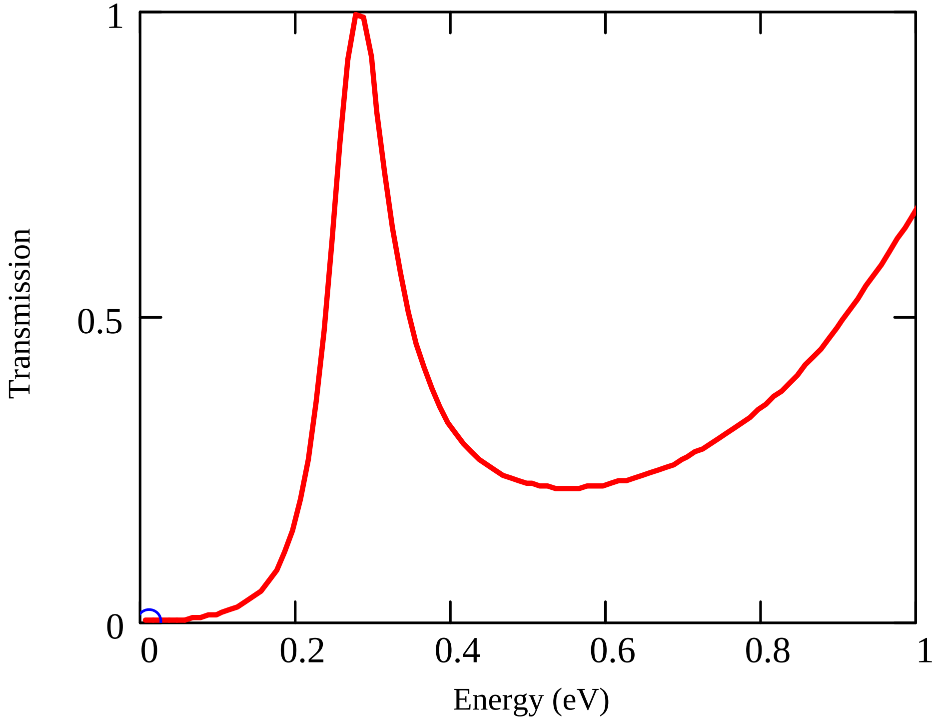
We can still calculate the transmission probability η using Eq. (11.4) rather than Eq. (11.29).

Example calculation – tunneling through a double barrier structure.

This structure shows a resonance in the tunneling probability (or transmission)

where the incident energy coincides with the energy of a resonance in the structure.

If the barriers were infinitely thick, there would be an eigenstate of the structure approximately at the energy where this resonance occurs.



Transmission probability as a function of incident particle energy for an electron incident on a double barrier structure consisting of two barriers of height 1 eV and thickness 0.2 nm on either side of a 0.7 nm thick region of zero potential energy. The regions on the left and the right of the entire structure are also assumed to have zero potential energy.

Click figure for animation

Methods for one-dimensional problems – 2

Reading – Sections 11.2 from start of "Calculation of eigenenergies of bound states" – 11.4

Transfer matrix technique (continued)

Penetration factor for slowly varying barriers

Electron emission with a potential barrier

Calculation of eigenenergies of bound states - 1

It is possible to use the transfer matrix itself to find eigenstates in cases of truly bound states.

For example, if

the first layer (layers 1) and last layer (layer $N+2$) are infinitely thick, and

their potentials are $V_1 > E$ *and* $V_{N+2} > E$,

there may be some values of *E* for which there are bound eigenstates.

Such states would only have exponentially decaying wavefunctions into the first and last layers from the multilayer structure.

Hence

$$A_1 = 0$$

i.e., no exponentially growing wave going out from the left of the structure,

and

$$B_{N+2} = 0$$

i.e., no exponentially growing wave going out from the right side of the structure.

Calculation of eigenenergies of bound states - 2

Therefore, if we have a bound eigenstate, we must have

$$\begin{bmatrix} 0 \\ B_1 \end{bmatrix} = \mathbf{T} \begin{bmatrix} A_{N+2} \\ 0 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} A_{N+2} \\ 0 \end{bmatrix} \tag{11.33}$$

This can only be the case if the element in the first row and first column of $\mathbf{T}$ ***is zero, i.e.,***

$$T_{11} = 0. \tag{11.34}$$

This condition can be used

to solve analytically for eigenenergies in simple structures, or

in a numerical search for eigenenergies through varying E***.***

Penetration factor for slowly varying barriers

When the barrier potential is slowly varying over the scale of the exponential attenuation length

- *it is possible to make some analytic approximations*

The rigorous analytic approach to such slowly varying potentials is known in quantum mechanics as

- *the WKB method.*

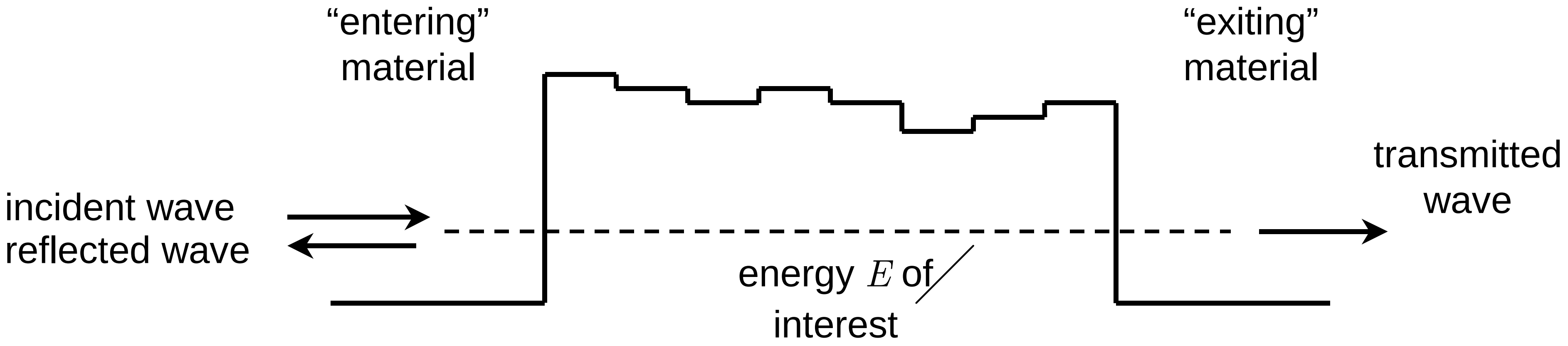
Here we will derive one important result that is usually obtained from the WKB approach

- *We will use the transfer matrix to derive this result,*
  - though the proper WKB derivation is arguably more rigorous for deriving this result.

Penetration factor for slowly varying barriers - 1

Consider a slowly varying potential approximated as a series of steps.

For simplicity of our algebra, we choose the entering and exiting materials as having the same energy.



We presume

$E << V_m$ *for each layer inside the structure, and that*

we have chosen the layers sufficiently thin in our calculation so that,

at least for interfaces within the structure, $k_m \cong k_{m+1}$**.**

Penetration factor for slowly varying barriers - 2

Then, for interfaces within the structure,

we can approximate the boundary condition matrix

$$\mathbf{D}_m = \begin{bmatrix} \dfrac{1+\Delta_m}{2} & \dfrac{1-\Delta_m}{2} \\ \dfrac{1-\Delta_m}{2} & \dfrac{1+\Delta_m}{2} \end{bmatrix}, \ \Delta_m = \frac{k_{m+1}}{k_m}$$

as the identity matrix

$$D_m \cong \begin{bmatrix} \sim 1 & \sim 0 \\ \sim 0 & \sim 1 \end{bmatrix} \qquad (11.35)$$

Since all of the internal boundary condition matrices have therefore been approximated by identity matrices,

we can omit them, and so the transfer matrix becomes

$$\mathbf{T} = \mathbf{D}_1\mathbf{P}_2\mathbf{P}_3\cdots\mathbf{P}_N\mathbf{P}_{N+1}\mathbf{D}_{N+1} \qquad (11.36)$$

(We have left in the boundary condition matrices for the beginning and end of the structure, where the potential may be quite discontinuous.)

Penetration factor for slowly varying barriers - 3

Since the propagation matrices are all diagonal, their product is

$$\mathbf{P}_2\mathbf{P}_3\cdots\mathbf{P}_N\mathbf{P}_{N+1}=\begin{bmatrix}1/G & \sim 0\\ \sim 0 & G\end{bmatrix} \tag{11.37}$$

where

$$G=\prod_{q=2}^{N+1}\exp(ik_q d_q)=\prod_{q=2}^{N+1}\exp(-\kappa_q d_q)=\exp\left(-\sum_{q=2}^{N+1}\kappa_q d_q\right) \tag{11.38}$$

Now, if we have chosen the layers to be sufficiently thin,

we may take the summation to be approximately equal to an integral, i.e.,

$$\sum_{q=2}^{N+1}\kappa_q d_q \cong \int_0^{z_{tot}}\kappa(z)\,dz \tag{11.39}$$

where $z_{tot}\ (=z_{N+1})$ **is the total thickness of the structure**

(which is taken to start on the left at $z=0$*).*

Hence we have

$$G\cong\exp\left(-\int_0^{z_{tot}}\kappa(z)\,dz\right)=\exp\left(-\int_0^{z_{tot}}\sqrt{\frac{2m_f}{\hbar^2}\left(V(z)-E\right)}\,dz\right) \tag{11.40}$$

where now $V(z)$ ***is the potential as a function of position*** z***.***

Penetration factor for slowly varying barriers - 4

If we now presume that

we have an amplitude F of forward wave leaving the right of the structure and no wave arriving from the right,

then, using the transfer matrix of Eq. (11.36) ($\mathbf{T} = \mathbf{D}_1 \mathbf{P}_2 \mathbf{P}_3 \cdots \mathbf{P}_N \mathbf{P}_{N+1} \mathbf{D}_{N+1}$)

and substituting for the propagation matrix product using Eq. (11.37),

$$\mathbf{P}_2 \mathbf{P}_3 \cdots \mathbf{P}_N \mathbf{P}_{N+1} = \begin{bmatrix} 1/G & \sim 0 \\ \sim 0 & G \end{bmatrix}$$

and the boundary condition matrices for the first and last interfaces,

we have for the forward wave amplitude

$$A \cong \frac{(1+\Delta_1)(1+\Delta_{N+1})}{4G} F \qquad (11.41)$$

giving the transmission probability from Eq. (11.5), $\eta = |F|^2 / |A|^2$ as

$$\eta \cong \frac{16}{\left|(1+\Delta_1)(1+\Delta_{N+1})\right|^2} \exp\left(-2 \int_0^{z_{tot}} \sqrt{\frac{2m_f}{\hbar^2}\left(V(z)-E\right)} dz \right) \qquad (11.42)$$

The prefactor contains the input and output boundary conditions

The exponential approximately gives the tunneling within the barrier

This approximation is frequently used in tunneling calculations.

Electron emission with a potential barrier - 1

Now we can complete the basic model for electron emission in the presence of a potential barrier.

- ***We have to introduce the thermal distribution of electrons, and perform an appropriate integration over that distribution.***

This approach enables us to calculate

- ***thermionic emission***
  - **the simple classical emission over a potential barrier because the particle has sufficient kinetic energy,**

and

- ***the corrections to that model resulting from the tunneling of particles through the barrier, such as***
  - **field-assisted thermionic emission,**
    - *where some of the particles without sufficient energy can tunnel through the barrier, or even*
  - **field-emission,**
    - *where the tunneling through the barrier dominates.*

Electron emission with a potential barrier - 2

The solution of problems of electron emission, such as

(i) from a metal into a vacuum

as is encountered, for example, with vacuum tubes of all kinds, including cathode ray tubes and field emission displays,

(ii) from a metal into a semiconductor

as in a Schottky barrier, or

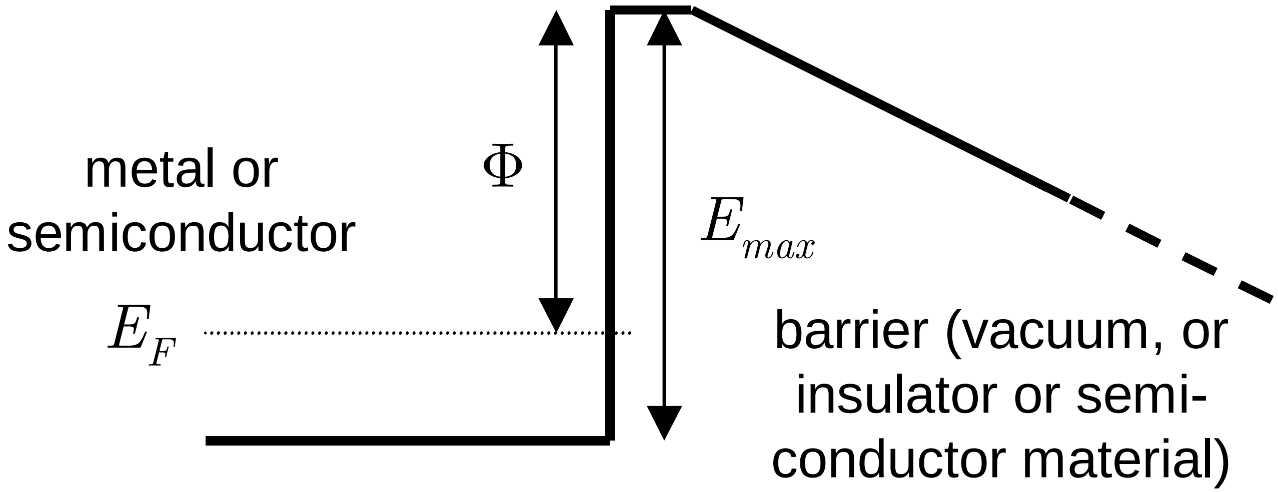
(iii) in electron emission across or "through" barriers in semiconductor devices,

such as leakage of current through barriers in semiconductor devices

e.g., through the gate oxide in silicon field effect transistors,

can all be handled by essentially the same approach.

Form of Potential Energy Diagram



E_{max} ***is***

- **the electron affinity if the barrier is the vacuum, or**
- **the band discontinuity if the barrier is an insulator or a semiconductor**
- **For this formalism,**
  - E_{max} *is the highest barrier potential seen by any electron from the left,*
  - even if it is not exactly at the interface with the metal or semiconductor on the left.

E_F ***is the Fermi energy***

- **it is not necessarily above the bottom of the band as shown here.**

Φ ***is the work function in the case of a metal-vacuum interface***

- **the separation between the Fermi energy and the vacuum level.**

Emission of electrons

In modeling thermionic or field emission,

- ***we presume that any electron that makes it through the barrier never comes back, and that***
- ***there is negligible current of any other electrons coming back into the metal or semiconductor from the barrier side.***
  - **Usually there is some electric field present that sweeps any emitted electrons away**

Such emission is not like a diffusion process,

- ***in which the electrons experience a net drift down a concentration gradient.***

In thermionic or field emission the situation is more severe than that –

- ***there are essentially no carriers coming back from right to left at all.***
  - **The concentration gradient in going from the metal or semiconductor into the barrier is essentially infinite.**

The current is simply limited then by how fast the emitted carriers can leave the emitting material.

Modeling emission - 1

Essentially,

if we figure out how many carriers are going to the right at a given energy and how fast they are going,

multiply that by the transmission probability associated with that energy, and

add up for all energies

the resulting total will be the emission current.

We construct a simple model

We presume that the emitting metal or semiconductor material on the left has

an isotropic parabolic band with mass m_f, which may be an effective mass.

For simplicity, we will assume we are dealing with electrons in a conduction band.

An electron in a given $\mathbf{k}$-state,

with components k_x, k_y, and k_z,

will have an energy, which we can think of as a kinetic energy

relative to the bottom of the band of

$$E_{KE} = \frac{\hbar^2}{2m_f}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad (11.43)$$

Modeling emission - 2

We presume that the particles are in a Fermi-Dirac thermal distribution

The probability that a state of any particular energy E_{KE} is occupied is

$$P_{FD}\left(E_{KE}\right)=\frac{1}{1+\exp\left[\left(E_{KE}-E_{F}\right)/k_{B}T\right]} \qquad (11.44)$$

where

E_F *is the Fermi energy,*

k_B *is Boltzmann's constant (~ 1.38 x 10^{-23} J/K), and*

T *is the temperature in degrees Kelvin.*

We also presume that the distribution remains a thermal one

even though we are continually extracting carriers in particular energy ranges.

In practice, that is usually a good assumption

gases of electrons tend to thermalize very quickly within themselves (e.g., << 1 ps).

Modeling emission - 3

We will only be interested in electrons with positive k_z

and hence positive effective classical velocities $v_z = \hbar k_z / m_f$

since those will be the only ones emitted to the right.

Any electron with positive k_z just on the left of the barrier therefore gives a contribution to the emitted (electrical) current of

$$e\eta\left(\hbar^2 k_z^2 / 2m_f\right) v_z ,$$

where $\eta(E_z)$ ***is the transmission probability of an electron with kinetic energy*** E_z ***associated with its motion in the*** z ***direction.***

Electrons with negative k_z and v_z do not enter the barrier,

and make no contribution to the emitted current,

and so must not be counted in the current.

Note that only the kinetic energy associated with the z motion enters the calculation of the transmission probability η.

The kinetic energies associated with the other directions, and the k_x ***and*** k_y ***values, make no difference to this transmission probability.***

Calculation of total emitted current density

The density of states in k space is $1/(2\pi)^3$ per unit real volume.

Including a factor of 2 for the two spin states of the electron,

the total emitted current density is therefore

$$J = 2\frac{e}{(2\pi)^3} \int_{k_x=-\infty}^{+\infty} \int_{k_y=-\infty}^{+\infty} \int_{k_z=0}^{+\infty} \eta\left(\hbar^2 k_z^2 / 2m_f\right) P_{FD}\left(E_{KE}\right) v_z dk_x dk_y dk_z \qquad (11.45)$$

Note explicitly that the integral is only over positive values of k_z

and hence over only positive values of $v_z = \hbar k_z / m_f$.

We can evaluate Eq. (11.45) now to calculate the total emission current,

including thermionic and field-assisted emission effects.

Applied electric fields E **simply give a potential barrier that falls off linearly to the right at a rate,** $e\mathrm{E}$**,**

resulting in a triangular barrier for tunneling.

Maxwell-Boltzmann approximation - 1

It is often the case in emission problems that only electrons with energies E_z near the top of the barrier or above make any substantial contribution to the emission current.

It is also usually the case that the barrier height, E_{max} is much larger than $k_B T$.

In such cases, we can approximate the Fermi-Dirac distribution to obtain

$$P_{FD}\left(E_{KE}\right) \simeq \exp\left(E_F / k_B T\right) \exp\left[-\frac{\hbar^2}{2m_f}\left(k_x^2 + k_y^2 + k_z^2\right)\right] \quad (11.46)$$

We can now deal with the k_x and k_y integrals separately

Mathematically we change to polar coordinates,

imagining that the integral over the k_x-k_y plane is performed by adding up rings of area $2\pi k_r dk_r$ (where $k_r^2 = k_x^2 + k_y^2$), giving

$$\int_{k_x=-\infty}^{+\infty} \int_{k_y=-\infty}^{+\infty} \exp\left[-\frac{\hbar^2}{2m_f} \frac{\left(k_x^2 + k_y^2\right)}{k_B T}\right] dk_x dk_y = 2\pi \int_{k_r=0}^{\infty} \exp\left[-\frac{\hbar^2}{2m_f} \frac{k_r^2}{k_B T}\right] k_r dk_r \quad (11.47)$$

Maxwell-Boltzmann approximation - 2

Now,

$$\int_0^\infty \exp\left(-a^2\right) a\,da = \frac{1}{2}\int_0^\infty \exp\left(-a^2\right) d\left(a^2\right) = \frac{1}{2}\int_0^\infty \exp\left(-b\right) db = \frac{1}{2} \tag{11.48}$$

Therefore,

$$\int_{k_x=-\infty}^{+\infty} \int_{k_y=-\infty}^{+\infty} \exp\left[-\frac{\hbar^2}{2m_f}\frac{\left(k_x^2+k_y^2\right)}{k_BT}\right] dk_x dk_y = 2\pi\frac{2m_f k_B T}{\hbar^2}\frac{1}{2}\int_0^\infty \exp\left(-b\right) db = \frac{2\pi m_f k_B T}{\hbar^2} \tag{11.49}$$

and so

$$J = 2\frac{e}{\left(2\pi\right)^3}\frac{2\pi m_f k_B T}{\hbar^2}\exp\left(\frac{E_F}{k_BT}\right)\int_{k_z=0}^{+\infty}\eta\left(\frac{\hbar^2 k_z^2}{2m_f}\right)\exp\left[-\frac{\hbar^2}{2m_f}\frac{k_z^2}{k_BT}\right] v_z dk_z \tag{11.50}$$

We can change variable in the integration. Noting that

$$v_z dk_z = \frac{\hbar}{m_f}k_z dk_z = \frac{\hbar}{2m_f}d\left(k_z^2\right) = \frac{1}{\hbar}dE_z \tag{11.51}$$

where

$$E_z \equiv \frac{\hbar^2 k_z^2}{2m_f} \tag{11.52}$$

is the kinetic energy associated with the z ***direction, we therefore have***

$$J = \frac{e m_f k_B T}{2\pi^2\hbar^3}\exp\left(\frac{E_F}{k_BT}\right)\int_{E_z=0}^{+\infty}\eta\left(E_z\right)\exp\left[-\frac{E_z}{k_BT}\right] dE_z \tag{11.53}$$

Maxwell-Boltzmann approximation - 3

Since our quantum mechanical analysis above enables us to work out $\eta(E_z)$ for quite arbitrary barrier forms,

- ***this expression (11.53) lets us evaluate electron emission through a barrier.***
  - **This expression includes both**
    - *tunneling current and*
    - *the current over the top of the barrier*
      - conventionally thought of as thermionic emission current.

- ***In principle, we have even accounted for the quantum mechanical partial reflection that can occur for particles with energy above the top of the barrier.***

Thermionic emission limit

Let us connect back to the conventional description of thermionic emission.

In semiclassical thermionic emission,

the transmission probability $\eta(E_z)$ is simply assumed to be

unity for $E_z > E_{max}$, and zero for $E_z < E_{max}$.

This neglects

tunneling, and the partial reflection that can occur for energies above the barrier.

In this simple case, the thermionic emission is therefore

$$J = \frac{em_f k_B T}{2\pi^2 \hbar^3} \exp\left(\frac{E_F}{k_B T}\right) \int_{E_z = E_{max}}^{+\infty} \exp\left[-\frac{E_z}{k_B T}\right] dE_z \qquad (11.54)$$

i.e.,

$$J = \frac{m_f}{m_o} A_0 T^2 \exp\left(-\frac{\Phi}{k_b T}\right) \qquad (11.55)$$

where A_0 is the Richardson constant $A_0 = \frac{em_o k_B^2}{2\pi^2 \hbar^3} \simeq 120.4 \text{ A cm}^{-2} \text{ K}^{-2}$ (11.56)

and $\Phi = E_{max} - E_F$ is the work function in the case of a metal-vacuum interface.

Eq. (11.55) is known as the Richardson-Dushman equation.

When the quantum mechanical effects of tunneling are added,

it is still common to use the Richardson constant, or an effective Richardson constant, in the final expressions.

Spin – 1

Reading – Sections 12.1 – 12.3

Angular momentum and magnetic moments

State vectors for spin angular momentum

Operators for spin angular momentum

Spin

Up to this point, we have presumed that the state of a system,

- ***such as an electron, or even a hydrogen atom,***

can be specified by a function in space and time,

- ***the wavefunction.***

This is not enough to describe quantum mechanical particles.

- ***We also need to specify amplitudes for the spin of the particle.***
  - **The magnitude of this spin is an intrinsic and unalterable property of the particle.**

Spin and its consequences are extremely important in quantum mechanics.

- ***Spin turns out to determine whether more than one particle can occupy a given state,***
  - **and is hence crucial to all of chemistry and solid state physics,**
    - *which both rely on the Pauli exclusion principle that only one electron can occupy a given state.*
- ***Magnetic effects in materials are almost entirely due to spin properties.***
- ***Electron spin effects are very important in determining polarization selection rules in optical absorption and emission.***

Angular momentum and magnetic moments - 1

To see just what the "spin" angular momentum of an electron is,

we can look at how the

energies of electron states or the

positions of electrons

are influenced by magnetic fields.

Charged particles with angular momentum have magnetic moments.

Classically, an electron orbiting with a

velocity v in a circular orbit of radius r,

as in the simple Bohr model of the hydrogen atom,

has an angular momentum of magnitude

$$L = m_o vr \tag{12.1}$$

We can also write angular momentum as a vector, i.e., classically,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times m_o \mathbf{v} \tag{12.2}$$

The electron takes a time $2\pi r / v$ to complete an orbit,

so the current corresponding to this orbiting electron is $I = ev / 2\pi r$

(this is the amount of charge that will pass any point in the loop per second).

The current loop corresponding to the orbit has an area πr^2.

Angular momentum and magnetic moments - 2

In magnetism, we define the *magnetic dipole* or *magnetic dipole moment*, μ_d

a quantity that is essentially the strength of a magnet.

For any closed current loop, $\mu_d = \text{current} \times \text{area}$**.**

So, with current $I = ev/2\pi r$ and area πr^2, an orbiting electron classically has

$$\mu_e = -evr/2 = -eL/2m_o \tag{12.3}$$

where the minus sign is because the electron charge is negative.

Magnetic moment is a vector quantity,

with vector axis along the polar axis of the magnet.

In the full vector statement, the magnetic dipole moment for a current loop is

$$\boldsymbol{\mu}_d = I\mathbf{a} \tag{12.4}$$

where I is the current in the loop,

and $\mathbf{a}$ is a vector whose magnitude is the area of the loop,

and whose direction is given by the right hand rule when considering the direction of current flow round the loop.

So, for a classical electron in a circular orbit,

$$\boldsymbol{\mu}_e = -\frac{e}{2}\mathbf{r} \times \mathbf{v} = -\frac{e\mathbf{L}}{2m_o} \tag{12.5}$$

Magnetic moments in magnetic fields

If we apply a magnetic field $\mathbf{B}$,

classically the energy of an object with magnetic moment $\boldsymbol{\mu}_d$ changes by

$$E_\mu = -\boldsymbol{\mu}_d \cdot \mathbf{B} \tag{12.6}$$

Applying $\mathbf{B}$ along the z-direction to a hydrogen atom will define the z-direction as the quantization axis,

making the angular momentum quantized around the z-direction,

with quantum number m,

where the allowed values of m go in integer steps from -l to +l.

with corresponding angular momenta $m\hbar$, or in vector form $m\hbar\hat{\mathbf{z}}$.

So, we expect corresponding magnetic moments for these electron orbits of

$$\boldsymbol{\mu}_e = -\frac{em\hbar\hat{\mathbf{z}}}{2m_o} \equiv -m\mu_B\hat{\mathbf{z}} \tag{12.7}$$

where μ_B is called the Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_o} \tag{12.8}$$

Hence, we would expect energy changes for these states of

$$E_m = m\mu_B B \tag{12.9}$$

as a result of applying the magnetic field.

Zeeman effect in hydrogen

So, in a hydrogen atom, we might expect an applied magnetic field to

- ***split the $2l+1$ degenerate levels (e.g., of a p state, with $l=1$)***
  - **into $2l+1$ different energy levels.**

We should do this calculation quantum mechanically

- ***e.g., using degenerate perturbation theory***
  - **with a perturbing Hamiltonian operator $\hat{H}_p = \left(e/2m_o\right)B\hat{L}_z$,**
- ***but the result (neglecting spin) would still be $2l+1$ different energy levels appearing, with splitting energies $m\mu_B B$.***

This splitting of atomic levels with magnetic fields is the Zeeman effect.

Counting angular momentum states of the electron with magnetic-field-induced separations

Magnetic moments of particles also lead to deflections in non-uniform magnetic fields,

as in the Stern-Gerlach experiment (see Section 3.8).

For particles with arbitrary initial values of m,

repeating the experiment many times should lead to $2l+1$ *different deflection angles emerging.*

Hence, we expect

a Zeeman splitting experiment or

a Stern-Gerlach experiment

to show

how many different values of the z component of the angular momentum are allowed in a magnetic field in the z direction in a given state.

What happens if we look at an electron itself in a magnetic field, especially when it has no orbital angular momentum?

How many different values of the z *component of the angular momentum do we see?*

The answer is, surprisingly, 2

and we ascribe these 2 results to spin

Spin angular momentum - 1

To distinguish spin angular momentum from orbital angular momentum,

we use the quantum numbers

s **rather than** l**, and**

σ **rather than** m**.**

To reconcile this with the quantum mechanics of angular momentum,

to get $2s+1=2$*,*

we need $s=1/2$**.**

Hence we assign total angular momentum $\hbar s=\hbar/2$ *to the electron.*

We say that σ **can take values in integer steps from -**s **to +**s**,**

so $\sigma=-1/2$ *or* $+1/2$ *, and the corresponding* z *angular momentum component in the* z *direction is* $\sigma\hbar$*.*

From our previous understanding of angular momentum,

this value of ½ is bizarre.

Angular momentum associated with wave functions has to have an integer for the m **quantum number,**

otherwise the spatial wavefunction would not be single-valued after a complete rotation about the z *axis.*

How then can we have the σ **quantum number be a half integer?**

Spin angular momentum - 2

The answer to which we are forced is that

the eigenfunctions associated with this internal angular momentum of the electron are not functions in space.

We cannot describe the behavior of an electron, including its spin, only in terms of one function amplitude in space.

For a complete description, we need another degree of freedom, the electron spin.

Incidentally, and somewhat confusingly,

the spin magnetic moment of the electron is not simply $\sigma\mu_B$***, but is instead***

$$\mu_e = g\sigma\mu_B \qquad (12.10)$$

where the so-called *gyromagnetic factor* $g \simeq 2.0023$**, often approximated as a factor 2.**

There is no radius of classical orbit of an electron that will give it both

an angular momentum of $\hbar/2$ ***and***

a magnetic moment of $\pm g\mu_B/2$***,***

further confirming that spin cannot be considered as corresponding to a classical orbit of any kind.

State vectors for spin angular momentum - 1

Suppose for the moment that we are only interested in the spin properties of the electron.

Let us go back and consider

how we would have described an angular momentum state in the orbital angular momentum case

without describing it explicitly as a function in angle in space.

Suppose, for example, that we considered only states with a specific value of l**, which we can write as** $|l\rangle$

In general, such a state would be some linear combination of the basis states $|l,m\rangle$ ***corresponding to any of the specific allowed values of*** m***, i.e.,***

$$|l\rangle = \sum_{m=-l}^{l} a_m |l,m\rangle \quad (12.11)$$

In the case of these states,

each of the states $|l,m\rangle$ ***can also be written as one of the spherical harmonic functions in space,***

and the resulting linear combination $|l\rangle$ **can also therefore be written as a function of angle in space.**

State vectors for spin angular momentum - 2

We could also, if we wish, write $|l\rangle$ explicitly as a vector of the coefficients a_m, i.e.,

$$|l\rangle \equiv \begin{bmatrix} a_l \\ a_{l-1} \\ \vdots \\ a_{-l+1} \\ a_{-l} \end{bmatrix} \qquad (12.12)$$

Note that

the set of functions corresponding to all of the possible values of m for a given l

is a complete set for describing any possible function with that value of l,

including even the eigenfunctions of L_x and L_y that are oriented around the other axes

In the case of the electron spin,

we cannot write the basis functions as functions of angle in space,

but we do expect that we can write them using the same kind of state and vector formalism as we use for other angular momenta.

State vectors for spin angular momentum - 3

In the electron spin case, that formalism becomes very simple.

Instead of l, we have s,

which we know is ½,

and instead of m we have σ.

There are, however, now only two basis states,

$|1/2,1/2\rangle$ ***and*** $|1/2,-1/2\rangle$***,***

corresponding to $\sigma = 1/2$ and $\sigma = -1/2$ respectively.

Hence, if we choose to write our general spin state as $|s\rangle$, we have

$$|s\rangle = a_{1/2}|1/2,1/2\rangle + a_{-1/2}|1/2,-1/2\rangle \equiv a_{1/2}|\uparrow\rangle + a_{-1/2}|\downarrow\rangle \equiv \begin{bmatrix} a_{1/2} \\ a_{-1/2} \end{bmatrix} \tag{12.13}$$

where we have also indicated another common notation,

with $|\uparrow\rangle$ being the "spin-up" state $|1/2,1/2\rangle$, and

$|\downarrow\rangle$ being the "spin-down" state $|1/2,-1/2\rangle$.

(The "up" and "down" refer to the z direction, conventionally.)

State vectors for spin angular momentum - 4

Any possible spin state of the electron can presumably be described this way.

Rather obviously,

a state with its magnetic moment in the $+z$ direction (the "spin-up" state) will be the state $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$,

and a state with its magnetic moment in the $-z$ direction (the "spin-down" state) will be $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$.

We could also multiply these states by any unit complex number and they would still be spin-up and spin-down states respectively.

The choice of unit amplitudes for these states also assures they are normalized.

Normalization in this case means assuring that the sum of the modulus squared of the two vector elements is equal to one,

i.e., $\left|a_{1/2}\right|^2 + \left|a_{-1/2}\right|^2 = 1$.

State vectors for spin angular momentum - 5

The reader might think that these vectors,

$$\begin{bmatrix}1\\0\end{bmatrix} \text{ and } \begin{bmatrix}0\\1\end{bmatrix},$$

- ***can represent only spin-up and spin-down states, oriented along the z axis.***

In fact, that is not correct;

- ***these two basis vectors can represent any possible spin state of the electron,***
  - **including spin states with the magnetic moment oriented along the x direction or along the y direction.**
- ***This is readily shown once we have defined the operators for the various spin components.***

Operators for spin angular momentum

Now that we have found an appropriate way of writing spin states,

- ***we need to define operators for spin angular momentum.***

In the case of orbital angular momentum, we started by

- ***postulating operators associated with the components along the three coordinate axes, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$,***
  - **in terms of spatial position and spatial derivative operators,**
    - *an option that we do not have for the spin operators since the spin functions are not functions of space.*

We also, however, were able to write commutation relations for the orbital angular momentum operators.

- ***Here we might therefore start with the commutation relations,***
  - **and find a representation of spin operators to satisfy them.**

Some authors regard the commutation relations as the more fundamental statement of the operator properties.

- ***If one starts with the commutation relations for angular momentum operators,***
  - **one can prove that both integer and half integer values for angular momentum are possible,**
    - *and these are all that are possible.*

Commutation relations for spin operators - 1

We therefore expect the spin angular momentum operators,

which we write as $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$, by analogy with the angular momentum operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$,

to obey a set of commutation relations

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar \hat{S}_z \tag{12.14}$$

$$\left[\hat{S}_y, \hat{S}_z\right] = i\hbar \hat{S}_x \tag{12.15}$$

$$\left[\hat{S}_z, \hat{S}_x\right] = i\hbar \hat{S}_y \tag{12.16}$$

Commonly we work with the "dimensionless" operators $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$ from which the spin angular momentum magnitude $\hbar/2$ has been removed, i.e.,

$$\hat{\sigma}_x = 2\hat{S}_x/\hbar,\ \hat{\sigma}_y = 2\hat{S}_y/\hbar,\ \hat{\sigma}_z = 2\hat{S}_z/\hbar \tag{12.17}$$

giving the set of commutation relations

$$\left[\hat{\sigma}_x, \hat{\sigma}_y\right] = 2i\hat{\sigma}_z \tag{12.18}$$

$$\left[\hat{\sigma}_y, \hat{\sigma}_z\right] = 2i\hat{\sigma}_x \tag{12.19}$$

$$\left[\hat{\sigma}_z, \hat{\sigma}_x\right] = 2i\hat{\sigma}_y \tag{12.20}$$

Commutation relations for spin operators - 2

If we choose to represent the spin function in the vectors format,

then the operators become represented by matrices.

One set of matrix representations of these operators is

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \ \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{12.21}$$

Such matrix representations are known as Pauli spin matrices.

There is more than one way we could have chosen these

- in fact there is an infinite number of ways –

depending on what axis we choose for the spin.

This set, which we can call the z ***representation,***

is such that the spin-up and spin-down vectors defined previously are eigenvectors of the $\hat{\sigma}_z$ **operator.**

These operators do indeed obey the commutation relations (12.18) - (12.20).

Commutation relations for spin operators - 3

We can write the three different Pauli spin matrices as one entity, $\hat{\sigma}$,

which has components associated with each of the coordinate directions x, y, and z,

$$\hat{\boldsymbol{\sigma}} = \mathbf{i}\hat{\sigma}_x + \mathbf{j}\hat{\sigma}_{\mathbf{y}} + \mathbf{k}\hat{\sigma}_{\mathbf{z}} \equiv \mathbf{i}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \mathbf{j}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} + \mathbf{k}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (12.22)$$

For completeness in discussing the spin operators, we note that, by analogy with the $\hat{L}^2$ operator, we can also define an $\hat{S}^2$ operator

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \qquad (12.23)$$

or a $\hat{\sigma}^2$ operator.

$$\hat{\sigma}^2 = \hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2 \qquad (12.24)$$

From the definitions for the Pauli matrices, we see that

$$\hat{\sigma}^2 \equiv 3\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad (12.25)$$

and hence that

$$\hat{S}^2 \equiv \frac{3}{4}\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = s(s+1)\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad (12.26)$$

from which we see that any spin ½ vector is an eigenvector of the $\hat{S}^2$ operator,

with eigenvalue $s(s+1)\hbar^2 = (3/4)\hbar^2$.

Commutation relations for spin operators - 4

Incidentally,

for orbital angular momentum any linear combination of spherical harmonics corresponding to a given l value

is an eigenfunction of the $\hat{L}^2$ operator, with eigenvalue $l(l+1)\hbar^2$,

so the behaviors here are still analogous to the behavior of orbital angular momentum.

Spin – 2

Reading – Sections 12.4 – 12.7

Visualizing spin states – the Bloch sphere

Direct product spaces and wavefunctions with spin

Pauli equation

Where does spin come from?

Visualizing spin states - 1

Although have discussed spins using the z representation here,

with eigenfunctions corresponding to pure “spin-up” and “spin-down”,

this representation can also describe spins oriented

exactly along the x axis, or

exactly along the y axis, or

spins oriented at any angle.

A spin pointing in the x direction can be expressed as a linear combination of spin-up and spin-down states described in the z direction!

How can this be?

Note that the spin vector is* not *a vector in ordinary geometrical space.

It is a vector in a two-dimensional Hilbert space.

One way to find what are the two spin vectors corresponding to a spin oriented in the positive or negative x direction, for example,

is to find the eigenvectors of the $\hat{\sigma}_x$ Pauli spin matrix.

Visualizing spin states - 2

The general spin state can be visualized in a particularly elegant way.

There are four real numbers required to specify the electron spin vector

- ***a real and an imaginary part (or equivalently a magnitude and phase) for each of the two elements of the vector.***
  - **This is enough to specify the two angles and the complex amplitude (e.g., magnitude and phase) for a spin pointing in any specific direction.**

Since the magnitude of the vector is fixed for spin, and

- ***since we can choose the quantum mechanical phase of any single state arbitrarily without making any difference to measurable quantities***
  - **we only really need two numbers to describe a spin state.**

One way to specify those two numbers is as a pair of angles, θ and ϕ,

- ***in terms of which we can choose to write the general spin state as***

$$|s\rangle = \cos(\theta/2)|\uparrow\rangle + \exp(i\phi)\sin(\theta/2)|\downarrow\rangle \qquad (12.27)$$

Since $\cos^2(\theta/2) + \sin^2(\theta/2) = 1$,

- ***the magnitude of this vector is correctly guaranteed to be unity,***
  - **and the $\exp(i\phi)$ factor allows for any relative quantum-mechanical phase between the two components.**

The Bloch sphere

We now ask for the expectation value of the Pauli spin operator $\hat{\boldsymbol{\sigma}}$ with such a state,

obtaining as the result a "spin polarization" vector $\mathbf{P}_s$

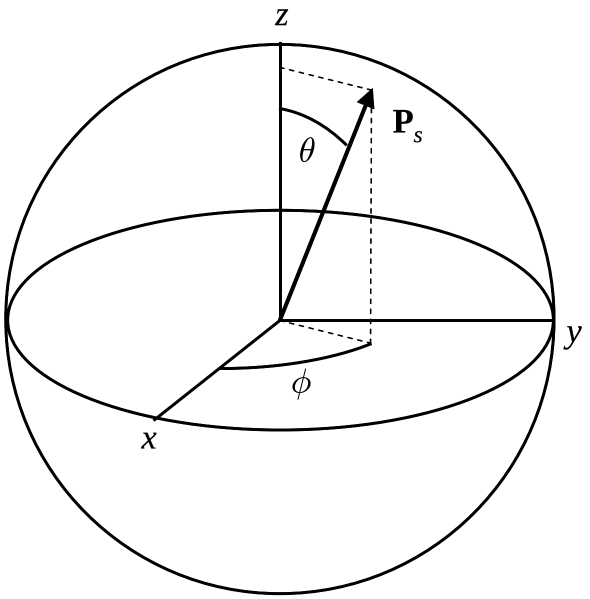
$$\begin{aligned}\mathbf{P}_s &= \langle s|\hat{\boldsymbol{\sigma}}|s\rangle = \mathbf{i}\langle s|\hat{\sigma}_x|s\rangle + \mathbf{j}\langle s|\hat{\sigma}_\mathbf{y}|s\rangle + \mathbf{k}\langle s|\hat{\sigma}_\mathbf{z}|s\rangle \\ &= \mathbf{i}\sin\theta\cos\phi + \mathbf{j}\sin\theta\sin\phi + \mathbf{k}\cos\theta\end{aligned} \tag{12.28}$$

$\mathbf{P}_s$ is a vector from the origin out to a point on a sphere of unit radius,

with angle relative to the North pole of θ*,*

and azimuthal angle ϕ*.*

The general spin state $|s\rangle$ can be visualized as a vector on a unit sphere.



The North pole corresponds to the state $|\uparrow\rangle$,

and the South pole to state $|\downarrow\rangle$.

This sphere is called the Bloch sphere,

with the angles θ *and* ϕ *on this sphere*

characterizing the spin state,

and the geometrical x*,* y*, and* z *directions*

corresponding to the directions of the eigenvectors of the corresponding spin operators.

Wavefunctions with spin

How can we obtain a description of the electron incorporating both spin and spatial behavior?

We allow the electron to have two spatial wavefunctions,

one associated with spin up and

the other associated with spin down.

We can write such a wavefunction as a vector in which the components vary in space.

Thus if $|\Psi\rangle$ is to be the most complete representation of the state of the electron,

including spin effects,

we might write

$$|\Psi\rangle \equiv \begin{bmatrix} \psi_{\uparrow}(\mathbf{r},t) \\ \psi_{\downarrow}(\mathbf{r},t) \end{bmatrix} \equiv \psi_{\uparrow}(\mathbf{r},t)\begin{bmatrix} 1 \\ 0 \end{bmatrix} + \psi_{\downarrow}(\mathbf{r},t)\begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (12.29)$$

A function of the form $\begin{bmatrix} \psi_{\uparrow}(\mathbf{r},t) \\ \psi_{\downarrow}(\mathbf{r},t) \end{bmatrix}$ is called a "spinor".

Hilbert spaces for different problems

For a spatial wavefunction,

- ***we needed an infinite dimensional Hilbert space,***
  - **with one dimension for each basis function.**
- ***The state vector in that Hilbert space was***
  - **the vector of the amplitudes of all the basis functions required to build up the desired function in space.**

For other problems,

- ***we can construct other Hilbert spaces.***

If we are only interested in electron spin,

- ***we have a two dimensional Hilbert space,***
  - **with the dimensions labeled spin-up and spin-down.**

We could have constructed a Hilbert space to represent any angular function associated with a specific total orbital angular momentum l.

- ***That space would have had $2l+1$ dimensions,***
  - **corresponding to the different possible values of m.**

Combining Hilbert spaces

What happens where we want to combine two Hilbert spaces

> ***e.g., the spatial and temporal Hilbert space describing ordinary spatial and temporal functions,***
>
> ***and the Hilbert space for spin***

to create a space that can handle any state in this more complicated problem?

In the present electron spin case,

> ***we want to have a space that is sufficient to represent two spatial (or spatial and temporal) functions at once.***
>
> > **Hence, where previously we only needed**
> >
> > > *one dimension, and*
> > >
> > > *one coefficient,*
> > >
> > > *associated with a particular spatial and temporal basis function,*
> >
> > **we now need two.**
>
> ***We have doubled the number of our dimensions.***

Basis functions in combined Hilbert spaces

The basis functions in our new Hilbert space are all the products of the basis functions in the original separate spaces.

For example, if the basis functions for the spatial and temporal function were

$$\psi_1(\mathbf{r},t),\ \psi_2(\mathbf{r},t),\ \ldots,\ \psi_j(\mathbf{r},t),\ \ldots$$

then the basis functions when we add spin into the problem are

$$\psi_1(\mathbf{r},t)\begin{bmatrix}1\\0\end{bmatrix},\ \psi_2(\mathbf{r},t)\begin{bmatrix}1\\0\end{bmatrix},\ \ldots,\ \psi_j(\mathbf{r},t)\begin{bmatrix}1\\0\end{bmatrix},\ \ldots,\ \psi_1(\mathbf{r},t)\begin{bmatrix}0\\1\end{bmatrix},\ \psi_2(\mathbf{r},t)\begin{bmatrix}0\\1\end{bmatrix},\ldots,\ \psi_j(\mathbf{r},t)\begin{bmatrix}0\\1\end{bmatrix},\ \ldots$$

Combining basis functions in Hilbert spaces for spatial problems

This concept of the new basis functions being the products of the elements two basis function sets is not exclusively a quantum mechanical one.

For example, if a spatial function in one dimensional box of size L_x can be represented as a Fourier series of the form

$$f(x) = \sum_n a_n \exp\left(i2n\pi x / L_x\right) \tag{12.30}$$

then a function in a two-dimensional rectangular box of sizes L_x and L_y in the respective coordinate directions can be represented as a Fourier series

$$g(x,y) = \sum_{n,p} a_{n,p} \exp\left(i2\pi nx / L_x\right) \exp\left(i2\pi py / L_y\right) \tag{12.31}$$

Here the new basis functions are the products of the basis functions of the two Hilbert spaces associated with the two separate problems of functions in x and functions in y.

Direct product spaces

A Hilbert space formed by

combining two other spaces

and making the new basis functions the products of the basis functions in the different spaces

is called a direct product space.

The spinors exist in such a direct product space formed by the multiplication of

the spatial and temporal basis functions and

the spin basis functions.

Dirac notation and direct product spaces

We can also write the new basis functions using Dirac notation.

In the electron spin case, we could write the basis functions as

$$\left|\psi_1\right\rangle\left|\uparrow\right\rangle, \left|\psi_2\right\rangle\left|\uparrow\right\rangle, \ldots\left|\psi_j\right\rangle\left|\uparrow\right\rangle, \ldots, \left|\psi_1\right\rangle\left|\downarrow\right\rangle, \left|\psi_2\right\rangle\left|\downarrow\right\rangle, \ldots, \left|\psi_j\right\rangle\left|\downarrow\right\rangle, \ldots$$

Here, we understand that

the $\left|\psi_j\right\rangle$ ***kets are vectors in one Hilbert space,***

the space that represents an arbitrary spatial and temporal function,

and the $\left|\uparrow\right\rangle$ ***and*** $\left|\downarrow\right\rangle$ ***kets are vectors in the other Hilbert space***

representing only spin functions.

The products $\left|\psi_j\right\rangle\left|\uparrow\right\rangle$ **and** $\left|\psi_j\right\rangle\left|\downarrow\right\rangle$ **are vectors in the direct product Hilbert space.**

We could also write these products, using the notations $\left|\psi_j \uparrow\right\rangle \equiv \left|\psi_j\right\rangle\left|\uparrow\right\rangle$ **and so on, as the basis functions of our direct product Hilbert space**

$$\left|\psi_1 \uparrow\right\rangle, \left|\psi_2 \uparrow\right\rangle, \ldots, \left|\psi_j \uparrow\right\rangle, \ldots, \left|\psi_1 \downarrow\right\rangle, \left|\psi_2 \downarrow\right\rangle, \ldots, \left|\psi_j \downarrow\right\rangle, \ldots$$

With our different notations, we could also write Eq. (12.29) ($\left|\Psi\right\rangle \equiv \begin{bmatrix}\psi_\uparrow(\mathbf{r},t)\\ \psi_\downarrow(\mathbf{r},t)\end{bmatrix} \equiv \psi_\uparrow(\mathbf{r},t)\begin{bmatrix}1\\0\end{bmatrix} + \psi_\downarrow(\mathbf{r},t)\begin{bmatrix}0\\1\end{bmatrix}$**) as**

$$\left|\Psi\right\rangle = \left|\psi_\uparrow\right\rangle\left|\uparrow\right\rangle + \left|\psi_\downarrow\right\rangle\left|\downarrow\right\rangle = \left|\psi_\uparrow \uparrow\right\rangle + \left|\psi_\downarrow \downarrow\right\rangle \qquad (12.32)$$

Direct product spaces and degrees of freedom

Direct product spaces occur any time in quantum mechanics that we add more

degrees of freedom or

“dynamical variables”

into the problem, including, for example,

adding more spatial dimensions, or

more particles, or

more attributes,

such as spin, for individual particles.

Pauli equation - 1

With the addition of spin,

the Schrödinger equation we have been using is obviously not enough.

At the very least,

we should add in the additional energy that an electron has from the interaction with a magnetic field $\mathbf{B}$.

Classically,

if we viewed the electron spin as a vector, $\boldsymbol{\sigma}$,

because it has direction, just as normal angular momentum does,

then we would expect an associated magnetic moment, in a simple vector generalization of Eq. (12.10), ($\mu_e = g\sigma\mu_B$)

$$\boldsymbol{\mu}_e = g\mu_B\boldsymbol{\sigma} \tag{12.33}$$

and the energy associated with that magnetic moment in the field $\mathbf{B} = \mathbf{i}B_x + \mathbf{j}B_y + \mathbf{k}B_z$ would be

$$E_S = \boldsymbol{\mu}_e \cdot \mathbf{B} = g\mu_B\boldsymbol{\sigma} \cdot \mathbf{B} \tag{12.34}$$

Pauli equation - 2

In the quantum mechanical case,

as usual we postulate the use of the operator instead of the classical quantity.

The quantum mechanical Hamiltonian corresponding to the energy E_S of Eq. (12.34) is therefore

$$\hat{H}_S = \frac{g\mu_B}{2}\hat{\boldsymbol{\sigma}}\cdot\mathbf{B} \equiv \frac{g\mu_B}{2}B_x\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} + \frac{g\mu_B}{2}B_y\begin{bmatrix}0 & -i\\i & 0\end{bmatrix} + \frac{g\mu_B}{2}B_z\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} \qquad (12.35)$$

where we have used $\hat{\boldsymbol{\sigma}}$ *as in Eq. (12.22)*

The factor ½ in this expression compared to the classical one is only because

we like to work with Pauli matrices with eigenvalues of unit magnitude

rather than the half integer magnitude associated with the spin itself

It does not express any other difference in the physics.

Pauli equation - 3

The Pauli equation includes this additional energy term.

The Pauli equation also treats electromagnetic effects on the electron,

and so it uses

$$\hat{\mathbf{p}} - e\mathbf{A}$$

instead of just the momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$

in constructing the rest of the energy terms in the equation

this point is discussed in Appendix E.

Hence, instead of the Schrödinger equation, we have the Pauli equation

$$\left[\frac{1}{2m_o}\left(\hat{\mathbf{p}} - e\mathbf{A}\right)^2 + V + \frac{g\mu_B}{2}\hat{\boldsymbol{\sigma}} \cdot \mathbf{B}\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (12.36)$$

Note here that $\Psi \equiv \begin{bmatrix} \psi_\uparrow(\mathbf{r},t) \\ \psi_\downarrow(\mathbf{r},t) \end{bmatrix}$ **is a spinor.**

The Pauli equation is therefore not one differential equation,

but is in general two coupled ones.

This equation is the starting point for investigating the effects of magnetic effects on electrons.

It can be used, for example, to derive the Zeeman effect rigorously, including the effects of spin.

Where does spin come from? - 1

Initially, spin and the mathematical framework of the Pauli spin matrices were postulated simply to explain experimental behavior.

- ***Later, Dirac showed that,***
  - **if one postulated a version of the quantum mechanics of an electron that was correct according to special relativity,**
- ***in his famous Dirac equation for the electron,***
  - **the spin behavior of the electron emerged naturally.**

In special relativity, it is essential that one treats space and time on a much more equal footing.

- ***Essentially, it was not possible to construct a relativistically invariant wave equation that is a first order differential equation in time***
  - **without introducing another degree of freedom in the formulation,**
    - *and that additional "dynamical variable" is spin.*

It is usually stated that spin therefore is a relativistic effect,

- ***though it is only necessary to require that the electron obeys a wave equation that treats time and space both with only first derivatives***
  - **rather than having time treated using a first derivative and space using a second derivative, as in the Schrödinger equation**
- ***to have the spin behavior emerge.***

Where does spin come from? - 2

One can, therefore, construct both relativistic and non-relativistic wave equations that treat time and space both through first derivatives,

and which have all of the solutions of the Schrödinger equation as solutions also,

but which also naturally incorporate spin.

If one takes this approach non-relativistically, one obtains an equation that can also be rewritten as the Pauli equation above.

Whether we were trying to construct a relativistic or non-relativistic equation for the electron,

simply put,

when we postulated Schrödinger's equation,

we got it wrong!

If we postulate the correct equation,

spin emerges naturally as a requirement,

and nature tells us we need to incorporate spin for a complete description of the electron.

Identical particles – 1

Reading – Section 13.1

Scattering of identical particles

Identical particles - 1

Suppose we have two electrons with the same spin,

which we imagine we can label as electron 1 and electron 2.

As far as we know, there is absolutely no difference between one electron and another.

They are absolutely interchangeable.

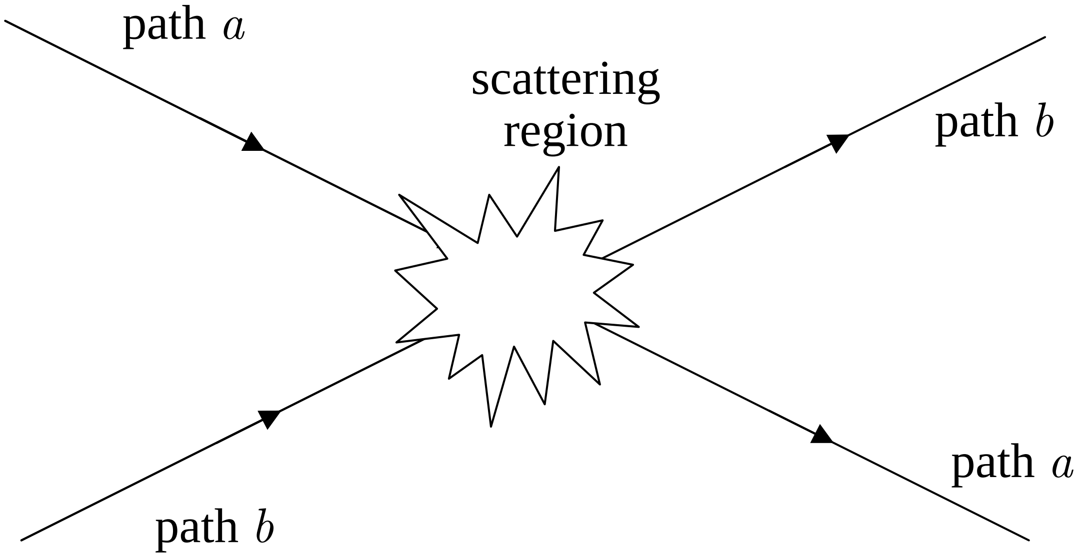
We might think,

because of something we know about the history of these electrons,

that it is more likely that we are looking at electron 1 rather than electron 2,

but there is no way by making a measurement that we can actually know for sure which one we are looking at.

Identical particles - 2



We could imagine that the two electrons were traveling through space,

each in some kind of wavepacket.

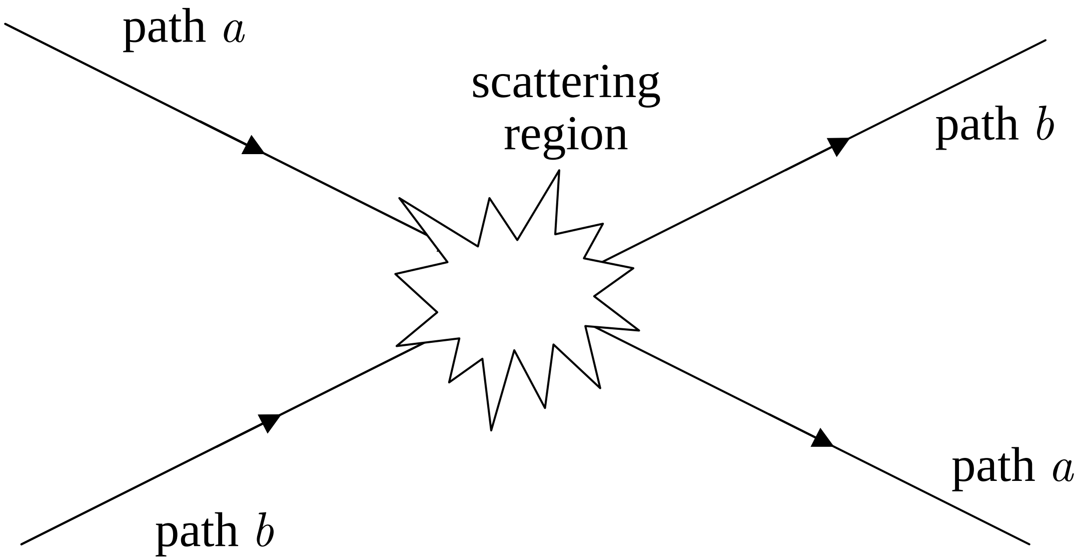
The wavepackets might each be quite localized in space at any given time.

These wavepackets will, however, each extend out arbitrarily far,

even though the amplitude will become small,

and hence the wavefunctions always overlap to some degree.

Identical particles - 3



We may find the following argument more convincing if we imagine that the wavepackets are initially directed towards one another,

and that these wavepackets substantially overlap for some period of time as they "bounce" off one another

Now, certainly on the right of the scattering region,

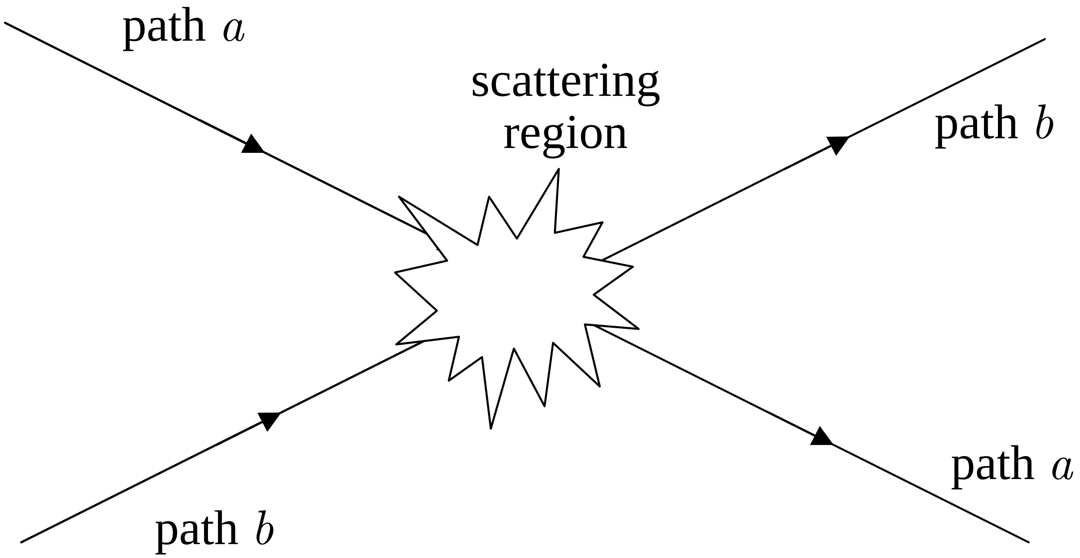
when we measure the electrons,

possibly finding one near path a and another near path b,

because two electrons are absolutely identical,

we have absolutely no way of knowing whether it is electron 1 or electron 2 that we find near any particular path.

Identical particles - 4



We might have good reason to believe,

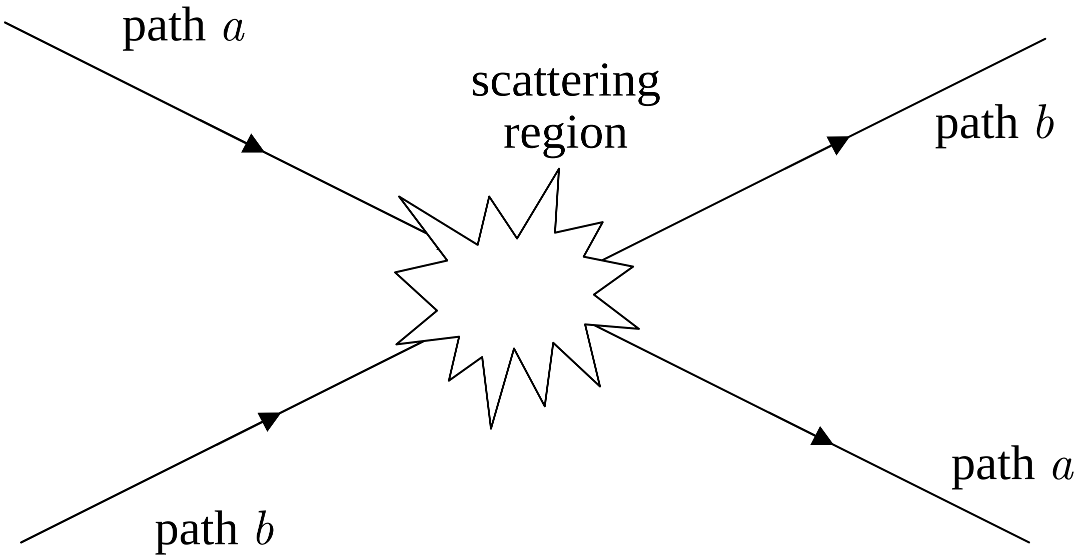
because of our understanding of the scattering process,

that if electron 1 started out on path a on the left,

it is relatively unlikely that electron 1 emerged into path b on the right,

but we have to accept that it is possible.

Identical particles - 5



Let us write the wavefunction,

$\psi_a(\mathbf{r})$, ***associated with path*** a***,***

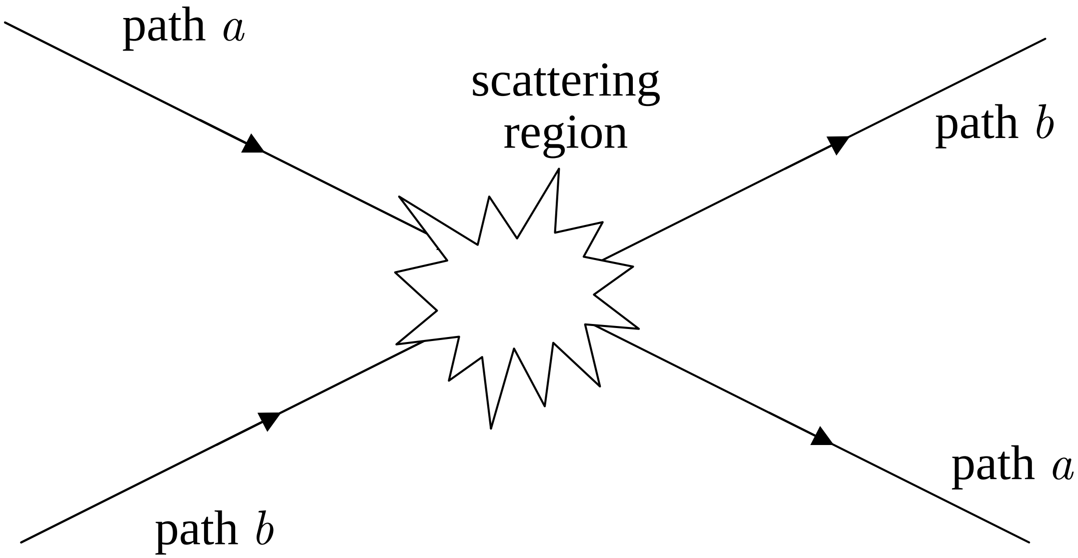
at least on the right of the scattering region,

and at some particular time,

and similarly write

$\psi_b(\mathbf{r})$ ***for the corresponding wavefunction on path*** b***.***

Identical particles - 6



Hence, we might expect that

the two particle wavefunction $\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)$ on the right can be written as some linear combination of the two possible outcomes

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right) = c_{12}\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right) + c_{21}\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right) \quad (13.1)$$

where c_{12} is the amplitude for the outcome that

it is electron 1 on path a and electron 2 on path b,

and oppositely for the amplitude c_{21}.

Identical particles - 7

But we believe electrons to be absolutely identical,

to the extent that it can make no difference to any measurable outcome if we swap the electrons.

We can never measure the wavefunction itself,

but we do expect to be able to measure $\left|\psi_{tp}\right|^2$***.***

Swapping the electrons changes

$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)$ ***into*** $\psi_{tp}\left(\mathbf{r}_2,\mathbf{r}_1\right)$***, and so we conclude that***

$$\left|\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)\right|^2=\left|\psi_{tp}\left(\mathbf{r}_2,\mathbf{r}_1\right)\right|^2 \tag{13.2}$$

which means that

$$\psi_{tp}\left(\mathbf{r}_2,\mathbf{r}_1\right)=\gamma\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right) \tag{13.3}$$

where γ is some complex number of unit magnitude.

We could of course swap the particles again.

Since the particles are absolutely identical,

this swapping process produces exactly the same result, and so

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\gamma\psi_{tp}\left(\mathbf{r}_2,\mathbf{r}_1\right) \tag{13.4}$$

Identical particles - 8

But we already know $\psi_{tp}(\mathbf{r}_2,\mathbf{r}_1)=\gamma\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2)$ from Eq. (13.3),

and so we have

$$\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2)=\gamma^2\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2) \tag{13.5}$$

which means,

assuming the wavefunction should be restored on this double swap

(this is actually a postulate of quantum mechanics)

that

$$\gamma^2=1 \tag{13.6}$$

and so we have only two possibilities for γ

$$\gamma=1 \tag{13.7}$$

or

$$\gamma=-1 \tag{13.8}$$

i.e.,

$$\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2)=\pm\psi_{tp}(\mathbf{r}_2,\mathbf{r}_1) \tag{13.9}$$

Identical particles - 9

Now we can substitute our general linear combination from Eq. (13.1)

$$\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2)=c_{12}\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+c_{21}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$

in Eq. (13.9) ($\psi_{tp}(\mathbf{r}_1,\mathbf{r}_2)=\pm\psi_{tp}(\mathbf{r}_2,\mathbf{r}_1)$), to get

$$c_{12}\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+c_{21}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)=\pm\left(c_{21}\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+c_{12}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right) \tag{13.10}$$

Rearranging, we have

$$\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)[c_{12}\mp c_{21}]=\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)[c_{12}\mp c_{21}] \tag{13.11}$$

But this must hold for all $\mathbf{r}_1$

and in general $\psi_a(\mathbf{r}_1)\neq\psi_b(\mathbf{r}_1)$

since they represent different and largely separate wavepackets,

and so we must have

$$c_{12}\mp c_{21}=0 \tag{13.12}$$

i.e.,

$$c_{12}=\pm c_{21} \tag{13.13}$$

Identical particles - 10

So given that the electrons emerge on paths a and b,

we have shown that there are only two possibilities for the nature of the wavefunction on the right of the scattering volume, either

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)=c\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)+\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right] \tag{13.14}$$

or

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)=c\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)-\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right] \tag{13.15}$$

where c is in general some complex constant.

We have therefore proved that, on the right,

the amplitudes of the function $\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)$

and the function $\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)$

are equal in magnitude (though possibly opposite in sign).

But, we might say,

for the electron on path a on the left,

the scattering probability into path a on the right is in general different from the scattering probability into path b on the right.

How therefore can we have the amplitudes of the two possibilities $\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)$ and $\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)$ being equal in magnitude?

Identical particles - 11

The resolution of this apparent problem is that,

even on the left of the scattering volume,

at some time before the scattering,

the wavefunction $\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2)$ *must also have had the two possibilities* $\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2)$ *and* $\psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)$ *being equal in magnitude,*

i.e. specifically, corresponding to the final situation of Eq. (13.14), of the form

$$\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2) = c_{before}\left[\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) + \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)\right] \quad (13.16)$$

or, corresponding to the final situation of Eq. (13.15), of the form

$$\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2) = c_{before}\left[\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) - \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)\right] \quad (13.17)$$

Identical particles - 12

Actually, we know from the basic linearity of quantum mechanical operators that this must be the case, as we can now show.

If we know the wavefunction on the left before scattering, $\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2)$,

we know in general that we could integrate the Schrödinger equation in time to deduce the wavefunction after scattering,

which we can in general call $\psi_{tpafter}(\mathbf{r}_1,\mathbf{r}_2)$.

The result of that integration is the same as some linear operator

$\hat{S}$ **(a time-evolution operator)**

acting on the initial state $\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2)$,

because the integration is just a sum of linear operations on the initial state.

Hence we can write

$$\psi_{tpafter}(\mathbf{r}_1,\mathbf{r}_2)=\hat{S}\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2) \tag{13.18}$$

Now, there is absolutely no difference in the effect of the Hamiltonian

on the state $\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2)$ and on the state $\psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)$

because the particles are absolutely identical

(if there were a difference, there would be a different energy associated with these two states, and hence we could distinguish between them).

Identical particles - 13

Hence, since $\hat{S}$ is derived from the Hamiltonian, the same holds true for it.

So, if

$$\hat{S}\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) = \psi_{aafter}(\mathbf{r}_1)\psi_{bafter}(\mathbf{r}_2) \tag{13.19}$$

then

$$\hat{S}\psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1) = \psi_{aafter}(\mathbf{r}_2)\psi_{bafter}(\mathbf{r}_1) \tag{13.20}$$

Now $\hat{S}$ is a linear operator, so

$$\begin{aligned}\hat{S}\psi_{tpbefore}(\mathbf{r}_1,\mathbf{r}_2) &= \hat{S}c_{before}\left[\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) \pm \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)\right] \\ &= c_{before}\hat{S}\left[\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) \pm \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)\right] \\ &= c_{before}\left\{\left[\hat{S}\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2)\right] \pm \left[\hat{S}\psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)\right]\right\} \\ &= c_{before}\left[\psi_{aafter}(\mathbf{r}_1)\psi_{bafter}(\mathbf{r}_2) \pm \psi_{aafter}(\mathbf{r}_2)\psi_{bafter}(\mathbf{r}_1)\right]\end{aligned} \tag{13.21}$$

Hence we have shown that,

if we start out with a linear combination of the form

$\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) \pm \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1)$ *on the left,*

we end up with a linear combination of the form

$\psi_{aafter}(\mathbf{r}_1)\psi_{bafter}(\mathbf{r}_2) \pm \psi_{aafter}(\mathbf{r}_2)\psi_{bafter}(\mathbf{r}_1)$ *on the right.*

Identical particles - 14

The Schrödinger equation can just as well be integrated backwards in time,

starting mathematically with a wavefunction on the right of the form

$$\psi_{aafter}(\mathbf{r}_1)\psi_{bafter}(\mathbf{r}_2) \pm \psi_{aafter}(\mathbf{r}_2)\psi_{bafter}(\mathbf{r}_1),$$

in which case we would get to an initial wavefunction of the form

$$\psi_{abefore}(\mathbf{r}_1)\psi_{bbefore}(\mathbf{r}_2) \pm \psi_{abefore}(\mathbf{r}_2)\psi_{bbefore}(\mathbf{r}_1).$$

The action of the scattering does not change this underlying property of the wavefunction.

Generality of argument on identical particles

In the argument above,

we have supposed the two electrons were scattering off one another.

The same conclusion can be drawn for any state of the pair of particles where the two particles overlap or interact,

including, for example, electrons in an atom or molecule.

We have discussed the pair of identical particles as if they were electrons with the same spin,

but we have not presumed any specific property of these particles other than that they are absolutely identical.

Thus we could apply the same quantum mechanical argument to protons with the same spin or neutrons with the same spin.

We can also apply this argument to photons.

Fermions and Bosons - 1

We find that a given kind of particle always corresponds to only one of the possible choices of γ.

All particles corresponding to $\gamma = +1$

i.e., a wavefunction for a pair of particles of the form

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right) = c\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right) + \psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right]$$

are called bosons.

Photons and all particles with integer spin

including also, for example, ^{4}He nuclei

are bosons.

We say that such particles have a wavefunction that is symmetric in the exchange of two particles.

Sometimes, loosely, we say the wavefunction is symmetric,

though the symmetry we are referring to here is a symmetry in the exchange of the particles,

not in the spatial distribution of the wavefunction.

Fermions and Bosons - 2

All particles corresponding to $\gamma = -1$

i.e., a wavefunction for a pair of particles of the form

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right) = c\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right) - \psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right]$$

are called fermions.

Electrons, protons, neutrons, and all particles with half integer spin are fermions.

Such particles have a wavefunction that is antisymmetric in the exchange of two particles.

Again, loosely, we sometimes say this wavefunction is antisymmetric,

though again we are not referring to its spatial distribution.

Identical particles - 2

Reading – Sections 13.2 – 13.5

Pauli exclusion principle

States, single-particle states, and modes

Exchange energy

Extension to more than two identical particles

Special properties of fermions

Fermions have one particularly unusual property compared to classical particles

a property that has no classical analog.

the Pauli exclusion principle

Very often with fermions

and occasionally also with bosons

we have to consider another non-classical phenomenon

exchange energy.

Pauli exclusion principle

For two fermions, we know the wavefunction is of the form (13.15).

Suppose now that we postulate that the two fermions are in the same single-particle state,

say state a**.**

Then the wavefunction becomes

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)=c\left[\psi_a\left(\mathbf{r}_1\right)\psi_a\left(\mathbf{r}_2\right)-\psi_a\left(\mathbf{r}_2\right)\psi_a\left(\mathbf{r}_1\right)\right]=0 \quad (13.22)$$

Note that this wavefunction is zero everywhere.

Hence, it is not possible for two fermions (of identical spin) to be in the same single-particle state.

This is the famous Pauli exclusion principle,

originally proposed to explain the occupation of atomic orbitals by electrons.

Only fermions show this exclusion principle, not bosons.

There is no corresponding restriction on the number of bosons that may occupy a given mode.

States, single-particle states, and modes

We need to clarify some definitions related to states.

When we say that

no two fermions can be in the one “state” or that

multiple bosons can be in the same “state”,

the “state” here is not the quantum mechanical state of the entire system.

There are three different concepts, which we can call

the quantum mechanical state (of the whole system)

single particle states (which we will use to refer to states of single fermions)

modes (which we will use to refer to a state that can be occupied by a boson)

Fermions and states

Consider an analogy, suitable for the fermion case.

The United States of America has 50 States (with a capital “S”).

Each State can have a Governor.

A State cannot have more than one Governor.

A Democratic exclusion principle means we cannot have more than one Governor in a State.

A State might have no Governor at some time.

We can write a column vector called the “state of the Governorships”

with 50 elements (one element per State), in alphabetical order,

with a “1” (Governor) or a “0” (no Governor) in the corresponding element.

The state of the Governorships (the 50 element vector)

is analogous to

the quantum mechanical state of the entire system (which we will often just refer to as the “state”, with a small “s”)

a State (which can be occupied by no more than one governor)

is analogous to

a single-particle (fermion) state

Bosons and states

Consider an analogy, suitable for the boson case.

The United States of America has 50 States (with a capital "S").

Each State can have citizens.

There is no limit to the number of citizens in a State.

We can write a column vector called the "state of the citizenships"

with 50 elements (one element per State), in alphabetical order,

with the number of citizens in the corresponding element.

The state of the citizenships (the 50 element vector)

is analogous to

the quantum mechanical state of the entire system (which we will often just refer to as the "state", with a small "s")

A State (which can be occupied by any number of citizens)

is analogous to

a (boson) mode

Note: We could use "mode" for both the fermion (single-particle) state and the boson mode, but by convention we do not usually do that.

Henceforth we use

single-particle state for fermions

mode for bosons

Exchange energy - 1

Suppose we have two electrons of identical spin.

They will certainly have a Coulomb repulsion,

and so we could write the Hamiltonian similarly to the hydrogen atom,

except here the two particles are identical

and the Coulomb potential is repulsive rather than attractive.

The Hamiltonian is therefore

$$\hat{H} = -\frac{\hbar^2}{2m_o}\left(\nabla^2_{\mathbf{r}_1} + \nabla^2_{\mathbf{r}_2}\right) + \frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \qquad (13.23)$$

Because they are fermions,

the state of the two particles is in general of the form

$$\psi_{tp}\left(\mathbf{r}_1, \mathbf{r}_2\right) = \frac{1}{\sqrt{2}}\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right) - \psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right] \qquad (13.24)$$

where the individual wavefunctions $\psi_a(\mathbf{r})$ ***and*** $\psi_b(\mathbf{r})$ ***are normalized,***

and the factor $1/\sqrt{2}$ **ensures the total wavefunction normalizes to unity also.**

We can also write this in bra-ket notation as

$$\left|\psi_{tp}\right\rangle = \frac{1}{\sqrt{2}}\left(|1,a\rangle|2,b\rangle - |2,a\rangle|1,b\rangle\right) \qquad (13.25)$$

where $|1,a\rangle \equiv \psi_a\left(\mathbf{r}_1\right)$ ***and so on.***

Note on order of wavefunction and bra or ket products

Note that the order of the products of the wavefunctions does not matter in expressions such as (13.24)

$$\psi_{tp}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\frac{1}{\sqrt{2}}\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)-\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right]$$

and (13.25)

$$\left|\psi_{tp}\right\rangle=\frac{1}{\sqrt{2}}\left(|1,a\rangle|2,b\rangle-|2,a\rangle|1,b\rangle\right).$$

Obviously

$$\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)=\psi_b\left(\mathbf{r}_2\right)\psi_a\left(\mathbf{r}_1\right) \tag{13.26}$$

since $\psi_a\left(\mathbf{r}_1\right)$ and $\psi_b\left(\mathbf{r}_2\right)$ are each simply a number for any given value of $\mathbf{r}_1$ or $\mathbf{r}_2$.

For the case of the bra-ket notation,

changing the order of the kets $|1,a\rangle$ and $|2,b\rangle$ could also result in a change in the order of integration in a bra-ket expression,

but that makes no difference for quantum mechanical wavefunctions,

so we also can state

$$|1,a\rangle|2,b\rangle=|2,b\rangle|1,a\rangle \tag{13.27}$$

Quite generally,

the order of the statement of the vectors corresponding to different degrees of freedom or dynamical variables does not matter in direct product spaces.

Exchange energy - 2

Now we evaluate the energy expectation value of this two-particle state.

$$\langle E\rangle = \left\langle \psi_{tp}\middle|\hat{H}\middle|\psi_{tp}\right\rangle \tag{13.28}$$

I.e.,

$$\langle E\rangle = \frac{1}{2}\left[\begin{array}{l}\langle 1,a|\langle 2,b|\hat{H}|1,a\rangle|2,b\rangle + \langle 2,a|\langle 1,b|\hat{H}|2,a\rangle|1,b\rangle \\ -\langle 1,a|\langle 2,b|\hat{H}|2,a\rangle|1,b\rangle - \langle 2,a|\langle 1,b|\hat{H}|1,a\rangle|2,b\rangle\end{array}\right] \tag{13.29}$$

The first two terms in Eq. (13.29) (which are actually equal) have a straightforward meaning.

Formally evaluating these, we have, for the first one,

$$\begin{aligned}\langle 1,a|\langle 2,b|\hat{H}|1,a\rangle|2,b\rangle &= \langle 1,a|\langle 2,b|\left(-\frac{\hbar^2}{2m_o}\left(\nabla^2_{\mathbf{r}_1}+\nabla^2_{\mathbf{r}_2}\right)+\frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_1-\mathbf{r}_2\right|}\right)|1,a\rangle|2,b\rangle \\ &= \langle 1,a|\langle 2,b|-\frac{\hbar^2}{2m_o}\nabla^2_{\mathbf{r}_1}|1,a\rangle|2,b\rangle + \langle 1,a|\langle 2,b|-\frac{\hbar^2}{2m_o}\nabla^2_{\mathbf{r}_2}|1,a\rangle|2,b\rangle \\ &\quad + \langle 1,a|\langle 2,b|\frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_1-\mathbf{r}_2\right|}|1,a\rangle|2,b\rangle \\ &= E_{KEa}+E_{KEb}+E_{PEab}\end{aligned} \tag{13.30}$$

Exchange energy - 3

Here, E_{KEa} is the kinetic energy of an electron in single-particle state a

$$E_{KEa} = \langle 1,a|\langle 2,b| -\frac{\hbar^2}{2m_o}\nabla^2_{\mathbf{r}_1} |1,a\rangle|2,b\rangle = \langle 1,a| -\frac{\hbar^2}{2m_o}\nabla^2_{\mathbf{r}_1} |1,a\rangle\langle 2,b||2,b\rangle$$
$$= -\frac{\hbar^2}{2m_o}\int \psi_a^*(\mathbf{r})\nabla^2\psi_a(\mathbf{r})\,d^3\mathbf{r} \tag{13.31}$$

(Note $\langle 2,b||2,b\rangle = 1$ because the single particle wavefunctions are normalized.)

Similarly,

$$E_{KEb} = -\frac{\hbar^2}{2m_o}\int \psi_b^*(\mathbf{r})\nabla^2\psi_b(\mathbf{r})\,d^3\mathbf{r} \tag{13.32}$$

is the kinetic energy of an electron in single-particle state b.

The final contribution, E_{PEab}, is the Coulomb potential energy from the interaction of the charge density from one electron in single-particle state a and the other in single-particle state b, i.e.,

$$E_{PEab} = \langle 1,a|\langle 2,b| \frac{e^2}{4\pi\varepsilon_o|\mathbf{r}_1 - \mathbf{r}_2|} |1,a\rangle|2,b\rangle = e^2\int \frac{|\psi_a(\mathbf{r})|^2 |\psi_b(\mathbf{r}')|^2}{4\pi\varepsilon_o|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}' \tag{13.33}$$

The second term, $\langle 2,a|\langle 1,b|\hat{H}|2,a\rangle|1,b\rangle$, in Eq. (13.29) gives the same answers

the naming of the variables $\mathbf{r}_1$ and $\mathbf{r}_2$ is interchanged, but the net result is identical mathematically.

Exchange energy - 4

Hence we have

$$\frac{1}{2}\left[\langle 1,a|\langle 2,b|\hat{H}|1,a\rangle|2,b\rangle+\langle 2,a|\langle 1,b|\hat{H}|2,a\rangle|1,b\rangle\right]=E_{KEa}+E_{KEb}+E_{PEab} \qquad (13.34)$$

This is the energy we expect semiclassically – the kinetic energies of the two particles and the potential energy from their interaction.

But there are more terms in Eq. (13.29).

$$\langle E\rangle=\frac{1}{2}\left[\begin{array}{l}\langle 1,a|\langle 2,b|\hat{H}|1,a\rangle|2,b\rangle+\langle 2,a|\langle 1,b|\hat{H}|2,a\rangle|1,b\rangle\\ -\langle 1,a|\langle 2,b|\hat{H}|2,a\rangle|1,b\rangle-\langle 2,a|\langle 1,b|\hat{H}|1,a\rangle|2,b\rangle\end{array}\right]$$

These additional terms constitute what is called the exchange energy, an energy term with no classical analog.

We note that, by the Hermiticity of the Hamiltonian,

$$\langle 2,a|\langle 1,b|\hat{H}|1,a\rangle|2,b\rangle=\left[\langle 1,a|\langle 2,b|\hat{H}|2,a\rangle|1,b\rangle\right]^{*} \qquad (13.35)$$

and so the exchange energy can be written

$$\begin{aligned}E_{EXab}&=-\frac{1}{2}\left(\langle 1,a|\langle 2,b|\hat{H}|2,a\rangle|1,b\rangle+\left[\langle 1,a|\langle 2,b|\hat{H}|2,a\rangle|1,b\rangle\right]^{*}\right)\\&=-2\,\mathrm{Re}\left[\int\psi_a^{*}(\mathbf{r}_1)\psi_b^{*}(\mathbf{r}_2)\hat{H}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\,d^3\mathbf{r}_1 d^3\mathbf{r}_2\right]\end{aligned} \qquad (13.36)$$

and finally

$$\langle E\rangle=E_{KEa}+E_{KEb}+E_{PEab}+E_{EXab} \qquad (13.37)$$

Exchange energy - 5

The requirement of antisymmetry with respect to particle exchange therefore

changes the energy of states involving two (or more) identical fermions.

This phenomenon of exchange energy is very important in, for example,

the states of the helium atom,

where different energy spectra result for the situations of the two electron spins being aligned (orthohelium) or antiparallel (parahelium).

It is important to understand that this change in energy

is not caused by the magnetic interaction between spins

though there might be a small correction from that.

It results from the exchange energy, not some additional term in the Hamiltonian itself.

It is also true that exchange energy phenomena are very important in magnetism.

Validity of single particle calculations - 1

If exchange energy is such a real phenomenon,

and electrons in general are in these kinds of states that involve other electrons and that are antisymmetric with respect to exchange,

why were the calculations we did on single electrons valid at all?

The answer is that,

if the two or more electrons are far apart from one another,

there is negligible correction from the exchange energy.

If the function $\psi_a(\mathbf{r})$ is only substantial in a region near some point $\mathbf{r}_a$,

then so also is the function $\nabla^2\psi_a(\mathbf{r})$.

Similarly, if the function $\psi_b(\mathbf{r})$ is only significant near to some point $\mathbf{r}_b$,

then so also is the function $\nabla^2\psi_b(\mathbf{r})$.

Hence, if the points $\mathbf{r}_a$ and $\mathbf{r}_b$ are far enough apart that there is negligible overlap of the functions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$,

$$\int \psi_a^*(\mathbf{r}_1)\nabla_{\mathbf{r}_1}^2\psi_b(\mathbf{r}_1)d^3\mathbf{r}_1 \simeq 0 \text{ and } \int \psi_b^*(\mathbf{r}_2)\nabla_{\mathbf{r}_2}^2\psi_a(\mathbf{r}_2)d^3\mathbf{r}_2 \simeq 0 \qquad (13.38)$$

Validity of single particle calculations - 2

Similarly, for such negligible overlap,

regardless of the form of the potential energy $V(\mathbf{r}_1,\mathbf{r}_2)$ *(*$= e^2/\left(4\pi\varepsilon_o\left|\mathbf{r}_1-\mathbf{r}_2\right|\right)$ *in the above example)*

$$\int \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)V(\mathbf{r}_1,\mathbf{r}_2)\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \simeq 0 \tag{13.39}$$

simply because the functions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ do not overlap.

Hence there is only a contribution to the exchange energy if the individual particle wavefunctions overlap.

This argument is unchanged if we add other potentials into the Hamiltonians for the individual particles,

such as a confining box,

or a proton to give an electrostatic potential to form a hydrogen atom.

In the practical absence of any significant exchange energy,

the problem essentially separates again into problems that are apparently for single electrons,

and our previous results,

such as for the hydrogen atom,

are completely valid for calculating energies and wavefunctions.

Extension to more than two non-identical particles

If we had N different (i.e., not identical) particles

that were approximately not interacting,

at least in some region of space and time

(e.g., substantially before or substantially after the scattering),

then we expect that we could construct the state $\left|\Psi_{different}\right\rangle$ for those

by multiplying the N single-particle states or modes, i.e.,

$$\left|\psi_{different}\right\rangle = |1,a\rangle|2,b\rangle|3,c\rangle\ldots|N,n\rangle \tag{13.40}$$

where the numbers and the letter N refer to the particles,

and the small letters refer to the single-particle state the individual particles are in.

Extension to more than two identical particles

Now suppose the particles are identical.

Even if we have many particles,

> ***it should still be true that swapping any two identical particles should make no difference to any observable.***

We can follow through the argument as before,

> ***and find that swapping the same particles a second time should get us back to where we started,***
>
> > **and again we would therefore find that swapping any two particles once either multiplies the by +1 (bosons) or –1 (fermions).**

More than two bosons - 1

If all the particles are identical bosons,

and we are interested in the state of the set of bosons where

one particle is in mode a,

another is in mode b,

another is in mode c, and so on,

then we can construct a state

the general symmetric state

that consists of a sum of all conceivable permutations of the particles among the states.

We can write the state as

$$\left|\psi_{identical\ bosons}\right\rangle \propto \sum_{\hat{P}} \hat{P} \left| |1,a\rangle |2,b\rangle |3,c\rangle \ldots |N,n\rangle \right\rangle \quad (13.41)$$

Here $\hat{P}$ is one of the permutation operators.

It is an operator that changes one function in the Hilbert space into another,

in this case by permuting the particles among the modes.

More than two bosons - 2

The meaning of the sum is that it is taken over all of those possible distinct permutation operators.

The notation Eq. (13.41) is just a mathematical way of saying we are summing over all permutations of the N particles among the chosen set of modes.

Incidentally, for this boson case,

it is quite allowable for two or more of the modes to be the same mode,

e.g., for mode b to be the same mode as mode a,

an important and general property of bosons.

Note that,

for any given set of modes a, b, c, $\ldots n$,

there is only one possible such boson state of N identical particles.

The state defined by Eq. (13.41) satisfies the symmetry requirement that

swapping any two particles does not change the sign of the state and leaves the state amplitude unchanged.

Swapping particles merely corresponds to changing the order of the terms in the sum, but leaves the sum itself unchanged.

More than two fermions

For the case of fermions, we can write the state for N identical fermions as

$$\left|\psi_{identical\ fermions}\right\rangle = \frac{1}{\sqrt{N!}} \sum_{\hat{P}=1}^{N!} \pm\hat{P}\left||1,a\rangle|2,b\rangle|3,c\rangle\ldots|N,n\rangle\right\rangle \tag{13.42}$$

where now by $\pm\hat{P}$ we mean that

- **we use the + sign when the permutation corresponds to an even number of pair-wise permutations of the individual particles,**
- **and the – sign when the permutation corresponds to an odd number of pair-wise permutations of the individual particles.**

Note in this case that if two of the single-particle states are identical,

e.g., if $b = a$,

then the fermion state is exactly zero because

for each permutation there is an identical one with opposite sign that exactly cancels it.

This is the extension of the Pauli exclusion principle to N particles.

Slater determinant

There is a particularly convenient way to write the N particle fermion state,

which is called the Slater determinant.

The determinant is simply another way of writing a sum of the form of Eq.(13.42),

i.e., we can write

$$\left|\psi_{identical\ fermions}\right\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} |1,a\rangle & |2,a\rangle & \cdots & |N,a\rangle \\ |1,b\rangle & |2,b\rangle & \cdots & |N,b\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |1,n\rangle & |2,n\rangle & \cdots & |N,n\rangle \end{vmatrix} \tag{13.43}$$

The reader may remember, from the theory of determinants, that

(i) the determinant is zero if two of the* columns *are identical, which here corresponds to the Pauli exclusion principle, and

(ii) the determinant changes sign if two of the* rows *are interchanged, which here corresponds to exchanging two particles.

Identical particles - 3

Reading – Section 13.6

Multiple particle basis functions

Multiple particle basis functions

So far, we have been considering states of the multiple particles

presuming the particles interact sufficiently weakly that

we can write the wavefunctions approximately as

products of the wavefunctions of the individual particles considered on their own.

Generally, we cannot factor multiple particle states this way.

How can we deal with strong interaction between the particles,

yet still handle the symmetries of the wavefunction with respect to exchange?

The answer is to construct basis functions for the direct product space

corresponding to the multiple particle system,

requiring them to have the required symmetry with respect to exchange.

If each basis function has the required symmetry with respect to exchange,

then any linear combination required to represent the state of the (possibly interacting) multiple particle system

will also have the same symmetry properties with respect to exchange.

Hence, we can, for example,

find some complete basis set to represent one of the particles, $\psi_i\left(\mathbf{r}_j\right) \equiv |j,i\rangle$***,***

and we can formally construct a basis function $\Psi_{ab\cdots n}\left(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N\right) \equiv \left|\Psi_{ab\cdots n}\right\rangle$ **for the** N **particle system.**

Basis functions for multiple particle systems

Depending on the symmetry of the particles with respect to exchange, there are different forms for this basis function.

(i) for non-identical particles

$$\psi_{ab\cdots n}\left(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N\right)=\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)\cdots\psi_n\left(\mathbf{r}_N\right) \tag{13.44}$$

or equivalently

$$\left|\Psi_{ab\cdots n}\right\rangle=|1,a\rangle|2,b\rangle\cdots|N,n\rangle \tag{13.45}$$

where each of the $\psi_a(\mathbf{r})$ *may be chosen to be any of the single particle basis functions* $\psi_i(\mathbf{r})$*.*

(ii) for identical bosons

$$\left|\Psi_{ab\cdots n}\right\rangle\propto\sum_{\hat{P}}\hat{P}|1,a\rangle|2,b\rangle\cdots|N,n\rangle \tag{13.46}$$

(iii) for identical fermions

$$\left|\Psi_{ab\cdots n}\right\rangle=\frac{1}{\sqrt{N!}}\sum_{\hat{P}=1}^{N!}\pm\hat{P}|1,a\rangle|2,b\rangle\cdots|N,n\rangle \tag{13.47}$$

Number of distinct basis functions – non-identical particles

In the case of non-identical particles,

there is one basis function for every choice of combination of single particle basis functions.

If we imagined there were M possible single particle basis functions,

and there are N particles,

then there are in general M^N such basis functions for the N particle system,

and specifying a state of that N particle system involves specifying M^N expansion coefficients,

and there are M^N distinct states of these N non-identical particles (even if we now allow them to interact), i.e.,

$$\begin{gathered}\text{Number of states of } N \text{ non-identical particles,}\\ \text{with } M \text{ available single-particle states or modes,}\\ = M^N\end{gathered} \tag{13.48}$$

Number of distinct basis functions – identical bosons - 1

In the case of identical bosons,

the N-particle basis states corresponding to different permutations of the same set of choices of basis modes are not distinct,

and so there are fewer basis states.

For example,

the state $\left|\Psi_{ab\cdots n}\right\rangle$ is not distinct from the state $\left|\Psi_{ba\cdots n}\right\rangle$ in Eq. (13.46)

$$\left|\Psi_{ab\cdots n}\right\rangle \propto \sum_{\hat{P}} \hat{P}\left|1,a\right\rangle\left|2,b\right\rangle\cdots\left|N,n\right\rangle$$

Since all permutations of the products of basis modes are already in the sum,

these two states are the same sum of products performed in a different order.

The counting of these states from first principles is complicated, but

it corresponds to a standard problem in permutations and combinations,

which is the problem of counting the number of combinations of M things

(here the single particle states)

taken N at a time

(since we always have N particles)

with repetitions,

for which the result is $(M+N-1)!/[N!(M-1)!]$.

Number of distinct basis functions – identical bosons - 2

For example,

the set of combinations of 2 particles among 3 modes, a, b, ***and*** c ***with repetitions is***

ab, ac, bc, aa, bb, cc

giving six in all,

which corresponds to $(3+2-1)!/[2!(3-1)!]=6$*.)*

Just as for the non-identical particle case,

this number of basis states is also the number of different possible states we can have for the system of particles even if we allow interactions.

$$\text{Number of states of } N \text{ identical bosons,} \\ \text{with } M \text{ available modes} = \frac{(M+N-1)!}{N!(M-1)!} \quad (13.49)$$

Number of distinct basis functions – identical fermions - 1

In the case of identical fermions,

just as in the identical boson case,

we avoid double counting permutations of the same choice of single-particle basis states.

Additionally many of these basis functions would not exist because they would involve more than one particle in the same single-particle state, so

there are even fewer possible basis states for multiple identical fermions.

Specifically,

if there are M ***choices for the first basis single-particle state*** a ***in*** $\left|\Psi_{ab\cdots n}\right\rangle$***,***

then there are $M-1$ **choices for the second single particle basis state** b**, and so on,**

down to $M-N+1$ *choices for the last single particle basis state* n.

Hence, instead of M^N **initial choices, we have only**

$$M(M-1)\cdots(M-N+1) = M!/(M-N)!.$$

We then also have to divide by $N!$

because there are $N!$ ***different orderings of*** N ***different entities***

(the different entities in this case are the different single-particle basis states).

Number of distinct basis functions – identical fermions - 2

Hence in the identical fermion case there are $M!/[(M-N)!N!]$ possible basis states,

and hence the same number of possible states altogether, even if we allow interactions between the particles. I.e.,

$$\begin{gathered}\text{Number of states of } N \text{ identical fermions,}\\ \text{with } M \text{ available single-particle states}\\ =\frac{M!}{(M-N)!N!}\end{gathered} \tag{13.50}$$

Example of number of states - 1

For example, suppose we have two particles,

- ***each of which can be in one of two different single-particle states or modes, a and b.***

Suppose these particles are in some potential such that there are two single-particle states or modes quite close in energy,

- ***and all other possible states are sufficiently far away in energy that, for other reasons,***
  - **we can approximately neglect them in our counting.**

We might be considering, for example, two particles in a weakly coupled pair of similar quantum boxes

- ***or a one dimensional problem, such as coupled potential wells.***
  - **Because we know for some other reason that the particles cannot have much energy**
    - *for example, the temperature may be low,*
      - we presume the particles can only be in one or other of the two lowest coupled single-particle states or modes of these two wells or boxes.

Example of number of states - 2

For each of the different situations we consider

(non-identical particles, identical bosons, and identical fermions)

these two single-particle states or modes might be somewhat different,

for example, because of exchange energy,

but that will not affect our argument here,

which is only one of counting of states.

For each situation (i.e., non-identical particles, bosons, fermions)

there will only be two single particle basis functions and, consequently,

only two single-particle basis functions or basis modes, a ***and*** b***, from which to make up the states of the pair of particles.***

Let us now write out the possible states in each case.

For all of these cases,

the number of possible single-particle states or modes of a particle is $M = 2$**, and the number of particles is** $N = 2$

(i) For non-identical particles,

such as two electrons with different spin,

the possible distinct states of this pair of particles are

$$|1,a\rangle|2,a\rangle,\ |1,b\rangle|2,b\rangle,\ |1,a\rangle|2,b\rangle,\ |1,b\rangle|2,a\rangle \qquad (13.51)$$

i.e., there are, from Eq. (13.48), $2^2 = 4$ *states of the pair of particles.*

Example of number of states – 3

(ii) For identical bosons,

such as two ^{4}He (helium-four) atoms,

which turn out to be bosons

because they are made from 6 particles each with spin ½ (two protons, two neutrons and two electrons, which therefore have an integer total spin)

the possible distinct states of this pair of a particles are,

$$|1,a\rangle|2,a\rangle,\ |1,b\rangle|2,b\rangle,\ \frac{1}{\sqrt{2}}\left(|1,a\rangle|2,b\rangle+|2,a\rangle|1,b\rangle\right) \qquad (13.52)$$

since $|1,a\rangle|2,a\rangle+|2,a\rangle|1,a\rangle$ *is describing the same state as* $|1,a\rangle|2,a\rangle$

and similarly for the state with both particles in the b mode.

(The $1/\sqrt{2}$ normalizes the symmetric combination state)

Here we have, from Eq. (13.49),

$(2+2-1)!/2!(2-1)!=3$ *possible states,*

in contrast to the four in the case of non-identical particles.

Example of number of states – 4

(iii) For identical fermions,

there is only one possible state of the pair of particles

since the two particles have to be in different single-particle states,

and there are only two single-particle states to choose from for each particle,

i.e., the state is

$$\frac{1}{\sqrt{2}}\left(|1,a\rangle|2,b\rangle-|2,a\rangle|1,b\rangle\right) \tag{13.53}$$

where again we have normalized this particular wavefunction for possible future use.

This count of only one state agrees with the formula Eq. (13.50),

which gives $2!/(2!0!)=1$ *state (where we remember that* $0!=1$*).*

Example of number of states - 5

The differences in the number of available states in the three cases of

non-identical particles,

identical bosons, and

identical fermions

leads to very different behavior once we consider the thermal occupation of states.

For example, if we presume that we are at some relatively high temperature,

such that the thermal energy, $k_B T$, is much larger than the energy separation of the two single-particle states or modes a and b,

then the thermal occupation probabilities of all the different two particle single-particle states or modes will all tend to be similar.

For the case of the non-identical particles,

which behave like classical particles as far as the counting of states is concerned,

with the four states $|1,a\rangle|2,a\rangle$, $|1,b\rangle|2,b\rangle$, $|1,a\rangle|2,b\rangle$, $|1,b\rangle|2,a\rangle$ of (13.51),

we therefore expect a probability of ~ ¼ of occupation of each of the states.

Therefore, the probability that the two particles are in the same state is ~ ½.

Example of number of states - 6

For the case of the identical bosons,

there are only three possible states,

so the probability of occupation of any one state is now ~ 1/3.

Two of the two-particle states have the particles in identical modes

$$|1,a\rangle|2,a\rangle,\ |1,b\rangle|2,b\rangle,$$

and only one two-particle state,

$$\frac{1}{\sqrt{2}}\left(|1,a\rangle|2,b\rangle+|2,a\rangle|1,b\rangle\right),$$

corresponds to the particles in different single particle states.

Hence the probability of finding the two identical bosons in the same single-particles state is now 2/3,

larger than the ½ for the non-identical particle case.

For the case of identical fermions,

there is only one possible state,

which therefore has probability ~1,

and it necessarily corresponds to the two particles being in different states.

Therefore identical bosons are more likely to be in the same states than are non-identical (or classical) particles,

and identical fermions are less likely to be in the same states than are non-identical (or classical) particles (in fact, they are never in the same states).

Example of number of states - 7

The most common description of the differences between bosons and fermions is that

we can have as many identical bosons in the same mode as we wish,

for identical fermions we can only have one in each single-particle state.

Identical bosons also differ from non-identical (or classical) particles,

which can have as many particles as we wish in a given mode also,

because there are fewer states in which identical bosons are in different modes, compared to the non-identical (or classical) case.

Bank account analogy for counting states - 1

Suppose you have

an antique jar (**a*****) in the kitchen with your spending money, and***

a box (**b*****) under the bed with your savings money.***

You put your dollar bills,

each labeled with a unique number,

into one or other of the antique jar (a) or the box (b).

This is like the quantum mechanical situation of

non-identical particles (the dollar bills) and

different single-particle states or modes (**a** or **b**)

into which they can be put (the jar or the box).

If I have two dollar bills,

then there are four possible situations (states of the entire system of two dollar bills in the antique jar and/or the box),

bill 1 in the box and bill 2 in the box

bill 1 in the box and bill 2 in the antique jar

bill 1 in the antique jar and bill 2 in the box

bill 1 in the antique jar and bill 2 in the antique jar

making four states altogether.

This reproduces the counting for non-identical particles.

Bank account analogy for counting states - 2

Consider next that you have two bank accounts

- ***a checking account (*****a*****), and***
- ***a savings account (*****b*****).***

Since these are bank accounts,

- ***I know how much money I have in each account,***
  - **but the dollars are themselves identical in the bank accounts,**
    - *so now there are only three possible states are*
      - Two dollars in the savings account
      - One dollar in the savings account and one in the checking account
      - Two dollars in the checking account

Note that there are

- ***two states in which both dollars are in the same account, but***
- ***only one in which they are in different accounts.***

This bank account argument above reproduces the counting we found above for boson states.

Bank account analogy for counting states - 3

Consider now that you have two bank accounts,

a checking account (a), and

a savings account (b),

but you are living in the Protectorate of Pauliana,

where you may only have one dollar in each bank account.

Then for your two dollars, there is only one possible state.

One dollar in the savings account, and one dollar in the checking account.

This reproduces the counting we found for fermion states above.

Identical particles – 4

Reading – 13.7 – 13.10

Thermal distribution functions

Important extreme examples of states of multiple identical particles

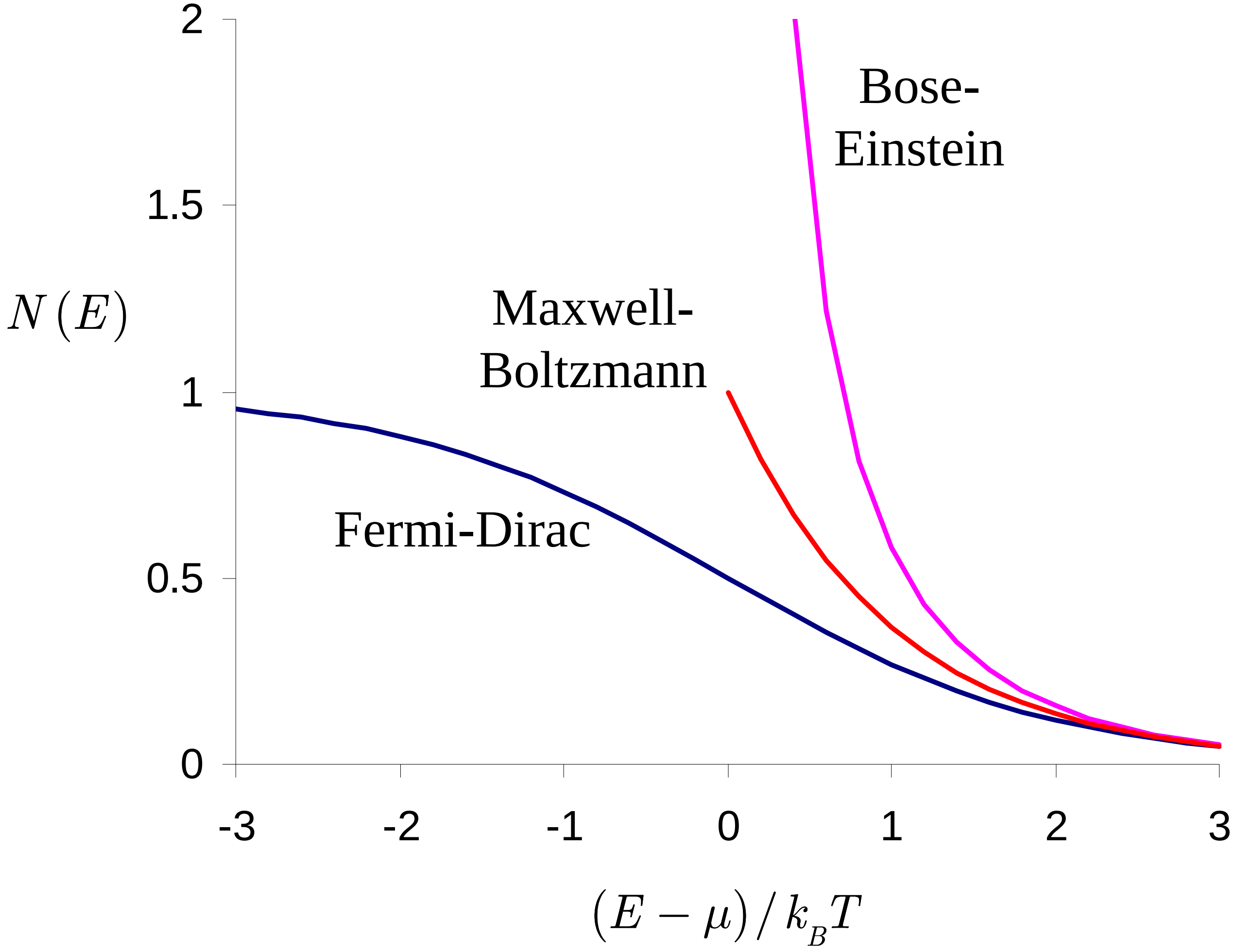
Particles and distinguishability

Thermal distribution functions - 1

Identical bosons obey the Bose-Einstein distribution, and

identical fermions obey the Fermi-Dirac distribution,

both of which are different from the classical Maxwell-Boltzmann distribution.



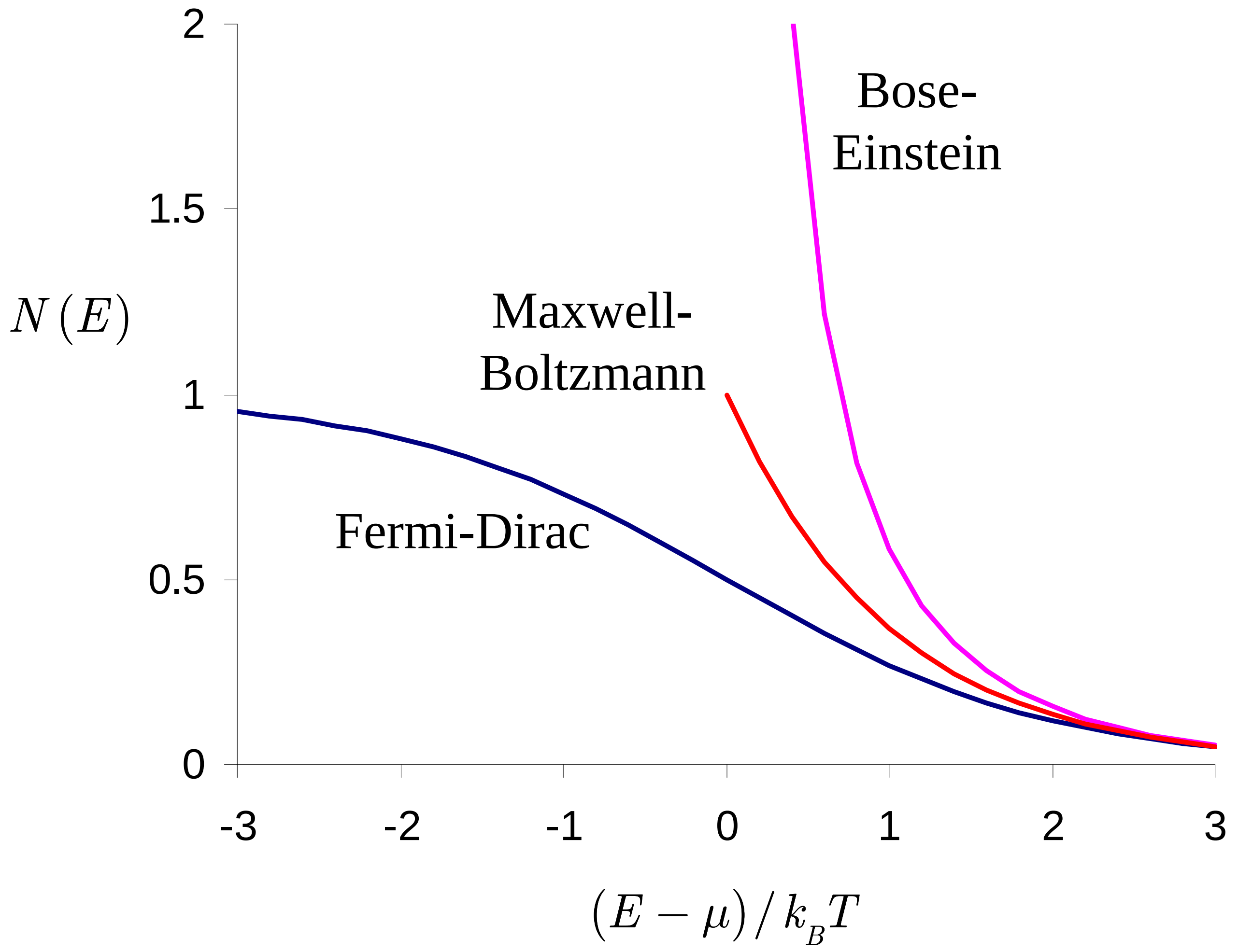
Thermal distribution functions - 2

Note that

identical bosons are **more** *likely to be in the same mode than are classical or non-identical particles*

- **the Bose-Einstein distribution lies above the Maxwell-Boltzmann distribution,**

identical fermions are **less** *likely to be in the same single-particle state than are classical or non-identical particles*



the Fermi-Dirac distribution lies below the Maxwell-Boltzmann distribution.

Thermal distribution functions - 3

The three distributions are,

for the average number of particles each in a single-particle state or mode of energy E at a temperature T with a chemical potential μ,

(i) Maxwell-Boltzmann

$$N(E) = \exp\left(\frac{\mu}{k_B T}\right)\exp\left(-\frac{E}{k_B T}\right) \tag{13.54}$$

(ii) Fermi-Dirac

$$N(E) = \frac{1}{1+\exp\left[\dfrac{E-\mu}{k_B T}\right]} \tag{13.55}$$

For the Fermi-Dirac case, the chemical potential μ is often called the Fermi energy, and is then written E_F.

(iii) Bose-Einstein

$$N(E) = \frac{1}{\exp\left[\dfrac{E-\mu}{k_B T}\right]-1} \tag{13.56}$$

Thermal distribution functions - 4

For the particular case of photons in a mode (or other similar bosons with only one possible state),

the chemical potential is zero.

The energy E of a particle is then $\hbar\omega$,

and so we have a special case of the Bose-Einstein distribution,

known as the Planck distribution,

which is

$$N(E) = \frac{1}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1} \tag{13.57}$$

Important extreme examples of states of multiple identical particles

In general, the states of multiple identical particles can be quite complicated.

> ***There are, however, some important states that turn out to be quite simple.***

Two examples are

> ***filled bands in semiconductors (or any crystalline solid) and***
>
> ***multiple photons in the same mode of the electromagnetic field.***

A filled semiconductor band

One important extreme example of a state for multiple identical fermions is a filled valence band in a semiconductor.

In the "single particle" approximation

where one electron is assumed to move in an average periodic potential,

and therefore is in a Bloch state of a particular $\mathbf{k}$ value.

The various possible Bloch states of a single electron (for a given spin)

correspond to all of the different possible $\mathbf{k}$ values in the band,

of which there are N_c if there are N_c unit cells in the crystal.

A full band therefore corresponds to N_c electrons of each spin in $2N_c$ different single-particle states

*(where the factor of 2 comes from the fact that there are two spin states associated with each **k** value).*

There is only one such state that obeys the antisymmetry with respect to exchange,

which is the Slater determinant of all of the single-particle states in the band.

N photons in a mode

Photons are bosons with a particularly simple behavior.

All the photons in a given mode of the electromagnetic field are, by definition, identical.

There is, however, only one state of any of these photons.

Photons in a mode do not have excited states of any kind,

and there is therefore no meaning to the identical photons in a given mode having more than one state they can choose from.

They are either there or they are not.

Therefore, $M = 1$**,**

and the number of possible states of the N *photons in the mode is simply*

$$(1+N-1)!/[N!(1-1)!] = 1.$$

That multiple particle state is simply all the photons in the same mode.

Quantum mechanical particles reconsidered - 1

Much of our confusion comes from the fact that we call the entities we have been discussing "particles"

- ***and is mostly an "ontological" problem.***

When we think of a particle,

- ***we attach attributes to it like***
  - **size, shape, charge, mass, position, velocity, and notions of discreteness, countability, and uniqueness.**
    - *These attributes are the "ontology" of a particle (the "nature of its being").*

When we think about a quantum mechanical particle,

- ***we have to delete or modify most of this ontology.***

We could save time if we just did not use the word "particle"

- ***avoiding having to selectively "unlearn" the previous ontology***
  - **from the above list, about all that remains for a quantum-mechanical particle is**
    - *charge, mass, an intertwined version of position and velocity (or momentum) from the uncertainty principle, some kind of discreteness, and heavily modified notions of counting.*
  - **We have also had to add other attributes of**
    - *wave-like interference and*
    - *spin*
  - **that are not possessed by classical particles.**

Quantum mechanical particles reconsidered - 2

There are fewer ontological problems if we consider levels of excitation of modes.

- ***Instead of saying there are three photons in mode* a *and 2 in mode* b*,***
  - **we say that mode a is in its third level of excitation, and mode b is in its second level of excitation.**
- ***The counting becomes simple***
  - **as we saw in the bank account analogy.**

It does not really matter if we never introduce the idea of particles

- ***– as long as we have the rules constructed by quantum mechanics for manipulating states, it does not matter what words we use***

Practically, "particles" are here to stay, though.

- ***We would find it disquieting to think of electrons as being excitation levels of modes rather than being particles.***

That is a psychological problem rather than a physical one,

- ***but the price we pay is a self-inflicted confusion about quantum mechanics!***

The good news is that,

- ***if we accept the rules of quantum mechanics and apply them faithfully,***
  - **all of these problems go away.**

Distinguishable and indistinguishable particles - 1

So far we used the word “identical”

and avoided the word “indistinguishable”

because there is a difference between these two concepts.

There are two different ideas here that we should not confuse.

We believe all electrons are identical.

They do not have separate identities or names

just as two dollars in a bank account do not have distinct identities or names.

We might, however, regard two specific electrons as being distinguishable from a practical point of view.

If they are so far apart that their interaction is negligible,

then we can regard them as distinct or “distinguishable”

because there is no physical process by which they could be swapped over.

This is like saying we have

one dollar in a bank account in, say, California, and

another in a bank account in Hawaii,

but for some reason there are no communications between the two banks.

Distinguishable and indistinguishable particles - 2

When there is no possibility of exchange,

- ***it makes no difference to any calculation whether we "symmetrize" the two-particle wavefunction into its correct two-identical particle form.***
  - **We saw this when we discussing exchange energy for two electrons whose wavefunctions do not overlap.**
    - *In this case, we can get away with treating these two "distinguishable" electrons as if they were non-identical particles.*
      - It is also true that, because it will make no difference to this calculation, we can still symmetrize the wavefunction properly if we want to.

So, even if two particles are identical,

- **if there is no reasonable physical process by which they could be swapped**
  - *such "distinguishable" particles can be treated as if they were non-identical.*

Distinguishable and indistinguishable particles - 3

It is also true that all photons are identical.

This leads to the conclusion that a microwave photon and a gamma ray photon are identical.

Photons in different modes

e.g., different frequencies or different directions

mostly do not interact with one another

we can pass two light beams right through one another, for example.

We can therefore often regard photons in different modes as being distinguishable,

treating them as if they were non-identical particles,

and hence dropping the symmetrization of the state in such cases.

We cannot, however, always do that,

if in doubt we should symmetrize the state because that is always correct.

Distinguishable and indistinguishable particles - 4

How can a microwave photon and the gamma ray be identical?

Suppose they are in a medium in which two-photon absorption is possible.

- ***Even if the photon energies do not add up to correspond to that absorbing transition,***
  - **there is still a nonlinear refractive effect (i.e., intensity-dependent refractive index)**
    - *or, more generally, what is known as a* four-wave mixing effect *that results.*
  - **We can, loosely, view that effect as corresponding to**
    - *“virtual” two-photon absorption*
      - followed almost immediately by two-photon emission
        - in that process,
        - we have lost track of which photon is which
- ***So, in general,***
  - **we would not calculate quite the right answer if we did not symmetrize the initial state of the two photons correctly.**
    - *In that case, the two photons are certainly not distinguishable.*

Distinguishable and indistinguishable particles - 5

So, we can say as an approximation that

two identical particles are distinguishable if the exchange interaction between them is negligibly small

then the "distinguishability" lets us treat them as nonidentical particles for practical purposes.

Conversely, if we say that two particles are indistinguishable

because of the possibility of exchange of them

then we are saying that we have to symmetrize the state properly with respect to exchange.

The density matrix – 1

Reading – Sections 14.1 – 14.4

Pure and mixed states

Density operator

Density matrix and ensemble average values

Time evolution of the density matrix

The density matrix

The density operator, or density matrix

- ***helps connect quantum mechanics with statistical mechanics***
  - **Just as we need statistical ideas in complicated classical systems**
    - *e.g., large collections of atoms or molecules*
  - **we need the same ideas in complicated quantum mechanical systems.**

One example application

- ***turn the infinitely sharp “δ-function” optical transitions into absorption lines with finite width***

Pure and mixed states

So far the only randomness considered is from quantum-mechanical measurement.

Consider, e.g., state of polarization of a photon.

So far, we could write a general state of polarization as

$$|\psi\rangle = a_H |H\rangle + a_V |V\rangle \tag{14.1}$$

where $|H\rangle$ *means a horizontally polarized photon state*

and $|V\rangle$ *means a vertically polarized one*

If we measure,

using e.g., a polarizing beamsplitter oriented to separate horizontal and vertical polarizations to different outputs with different detectors

we expect probabilities

$|a_H|^2$ ***of measuring horizontal polarization***

$|a_V|^2$ ***of measuring vertical polarization.***

More complete description of optical polarization

Since we must have $\left|a_H\right|^2+\left|a_V\right|^2=1$ by normalization

we could also choose to write

$$a_H=\cos\theta \quad a_V=\exp(i\delta)\sin\theta \tag{14.2}$$

$\delta=0$ **corresponds to linear polarization**

θ **is the angle of the optical electric vector relative to the horizontal axis**

When $\delta\neq 0$, the field is in general "elliptically polarized",

which is the most general possible state of polarization of a propagating photon

$\delta=\pm\pi/2$ **with θ = 45º give the two different kinds of circularly polarized photons (right and left circularly polarized).**

we can always build a polarizing filter that will pass a photon in of any specific polarization, 100% of the time.

even for elliptically polarization

we could arrange to delay only the horizontal polarization by a compensating amount $-\delta$ to make the photon linearly polarized

then orient a linear polarizer at an angle θ so that the photon was always passed through.

Pure states

When we can make a polarization filter so that we will get 100% transmission of the photons,

we say that the photons are in a "pure" state (here, Eq. (14.1)).

All states considered so far have been pure states

we can at least imagine that an appropriate filter could be made to pass any particles that are in any one such specific quantum mechanical state with 100% efficiency.

Mixed states

Suppose, though, that we have a beam that is a mixture from two different, and quite independent, lasers, "1" and "2".

- ***Presume laser 1 contributes a fraction P_1 of the photons,***
- ***and laser 2 contributes a fraction P_2.***
  - **Then the probability that a given photon is from laser 1 is P_1**
  - **and similarly there is probability P_2 it is from laser 2.**
- ***Presume also that these two lasers give photons of two possibly different polarization states, $|\psi_1\rangle$ and $|\psi_2\rangle$ respectively***

We can describe this as a "mixed state", and it is measurably different

- ***no setting of our polarizing filter will in general pass 100% of the photons***
  - **If we set the polarization filter to pass all the photons in state $|\psi_1\rangle$**
  - **it will in general not pass all the photons in state $|\psi_2\rangle$, and *vice versa*.**
  - **If we set the polarizing filter in any other state, it will not pass 100% of either set of photons.**

Mixed states

Hence,

- ***we cannot simply write this mixed state as some linear combination of the two different polarization states***
  - **as we have previously done for linear combinations of quantum mechanical states.**

- ***If we were able to do that,***
  - **e.g., in some linear combination of the form** $b_1|\psi_1\rangle + b_2|\psi_2\rangle$**,**
    - *we would be able to construct a polarizing filter that would pass 100% of the photons in this new, pure polarization state.*

Pure states for potential wells

Suppose, for some particle with mass, we have a potential well,

such as the simple "infinite" one-dimensional potential well

If we put the particle in a pure state that is an equal linear superposition of the lowest two states of this well,

$$|\psi\rangle = (1/\sqrt{2})(|\psi_1\rangle + |\psi_2\rangle),$$

the position of this particle,

given formally by the expectation value $\langle z \rangle$ of the $\hat{z}$ position operator,

will oscillate back and forwards

because of the different time-evolution factors $\exp(-iE_1 t/\hbar)$ and $\exp(-iE_2 t/\hbar)$ for the two energy eigenstates (with energies E_1 and E_2 respectively).

Mixed states for potential wells

Suppose instead we take an ensemble of identical potential wells

and randomly prepare

half of them with the particle in the lowest state and

half of them with the particle in the second state.

Statistically, since we do not know which wells are which,

at least before performing any measurements,

each of these wells is in a mixed state,

with 50% probability of being in either the first or second state.

Now we evaluate the expectation value $\langle z \rangle$ of the $\hat{z}$ position operator for each potential well.

In each well, $\langle z \rangle$ *evaluates to the position of the center of the well*

since both these wavefunctions are equally balanced about the center

The “ensemble average”, $\overline{\langle z \rangle}$, of expectation values from the different wells

is also zero,

and there is no oscillation in time.

Again it would not be correct simply to write the mixed state as a linear combination of the form $b_1 |\psi_1\rangle + b_2 |\psi_2\rangle$.

Mixed state in skewed wells

Suppose each well is skewed

by applying electric field perpendicular to the wells for the case of a charged particle like an electron in the well.

Then $\langle z \rangle$ is different for the first and second states of the well

with $\langle z \rangle = z_1$ for the first state and $\langle z \rangle = z_2$ for the second state.

For the pure state, we still expect oscillation.

For a mixed state

with probabilities P_1 and P_2 respectively that we had prepared a given well in the first or second state

we would still have no oscillation,

and our ensemble average value of the measured position would now be

$$\overline{\langle z \rangle} = P_1 z_1 + P_2 z_2 \equiv \sum_{j=1}^{2} P_j \langle \psi_j | \hat{z} | \psi_j \rangle \qquad (14.3)$$

Mixed state ensemble average expectation value

We expect that the ensemble average expectation value for some operator $\hat{A}$ corresponding to an observable quantity can be written

$$\overline{\langle A \rangle} = \sum_j P_j \langle \psi_j | \hat{A} | \psi_j \rangle \qquad (14.4)$$

for some set of different quantum mechanical state preparations $|\psi_j\rangle$ made with respective probabilities P_j.

Note that the different $|\psi_j\rangle$ need not be orthogonal.

We could be considering several different polarization states that are quite close to one another in angle.

For example, there might be some fluctuation in time in the precise output polarization of some laser

giving a mixed state of many different possible similar but not identical polarizations.

Representing mixed states

Can we find a convenient mathematical way of handling mixed states?

We have already concluded that the linear superposition form $b_1|\psi_1\rangle + b_2|\psi_2\rangle$ *will not work for mixed states*

We would also like a representation that works in the limit when the mixed state becomes pure (i.e., only one pure state in the "mixture")

The answer to this question is to introduce the density operator.

Density operator

However we are going to represent the mixed state,

it must obviously contain the probabilities P_j and the pure states $|\psi_j\rangle$,

but it must not simply be a linear combination of the states.

The structure we propose instead is the density operator

$$\rho = \sum_j P_j |\psi_j\rangle\langle\psi_j| \quad (14.5)$$

This is an operator

because it contains the outer products of state vectors (i.e., $|\psi_j\rangle\langle\psi_j|$).

We deliberately leave the "hat" off of the top of this operator

to emphasize that its physical meaning and use are quite different from other operators we have considered.

ρ **is *not* an operator representing some physical observable.**

Rather, ρ is representing the state *(in general, a mixed state) of the system.*

Density operator

If ρ is a useful way of representing the mixed state,

it must allow us to calculate quantities like

the ensemble average measured value $\overline{\langle A \rangle}$ for any physical observable with corresponding operator $\hat{A}$.

In fact, if we can evaluate $\overline{\langle A \rangle}$ for any physically observable quantity,

then ρ will be the most complete way we can have of describing this mixed quantum mechanical state

because it will tell us the value we will get of any measurable quantity, to within our underlying statistical uncertainties.

Density matrix and ensemble average values

Write the density operator in terms of a complete orthonormal basis set, $|\phi_m\rangle$.

First we expand each of the pure states $|\psi_j\rangle$ in this set, obtaining

$$|\psi_j\rangle = \sum_u c_u^{(j)} |\phi_u\rangle \qquad (14.6)$$

Then we use Eq. (14.6) and its adjoint in Eq. (14.5) $\rho = \sum_j P_j |\psi_j\rangle\langle\psi_j|$ to obtain

$$\begin{aligned}\rho &= \sum_j P_j \left(\sum_u c_u^{(j)} |\phi_u\rangle \right)\left(\sum_v \left(c_v^{(j)}\right)^* \langle\phi_v| \right) \\ &= \sum_{u,v} \left(\sum_j P_j c_u^{(j)} \left(c_v^{(j)}\right)^* \right) |\phi_u\rangle\langle\phi_v|\end{aligned} \qquad (14.7)$$

Written this way, the matrix representation of ρ is now clear.

We have for a matrix element in this basis

$$\rho_{uv} \equiv \langle\phi_u|\rho|\phi_v\rangle = \sum_j P_j c_u^{(j)} \left(c_v^{(j)}\right)^* \equiv \overline{c_u c_v^*} \qquad (14.8)$$

Here we have also introduced and defined the idea of the ensemble average of the coefficient product $\overline{c_u c_v^*}$.

Given the form Eq. (14.8), we now usually talk of ρ as the density matrix,

with matrix elements given as in Eq. (14.8).

Properties of the density matrix - 1

We can deduce from Eq. (14.8) that

(i) The density matrix is Hermitian, i.e., explicitly

$$\rho_{vu} \equiv \sum_j P_j c_v^{(j)} \left(c_u^{(j)}\right)^* = \left(\sum_j P_j c_u^{(j)} \left(c_v^{(j)}\right)^*\right)^* = \rho_{uv}^* \tag{14.9}$$

Because the density matrix is Hermitian,

so also is the density operator since the density matrix is just a representation of the density operator.

(ii) The diagonal elements ρ_{mm} ***give us the probabilities of finding the system in a specific one of the states*** $|\phi_m\rangle$***.***

$c_m^{(j)}(c_m^{(j)})^* \equiv |c_m^{(j)}|^2$ **is the probability for any specific pure state *j* that we will find the system in state *m*.**

Hence adding these up with probabilities P_j *gives us the overall probability of finding the system in state* m *in the mixed state.*

(The off-diagonal elements are a measure of the “coherence” between different states in the system, and we will return to discuss this later.)

Properties of the density matrix - 2

(iii) The sum of the diagonal elements of the density matrix is unity,

i.e., remembering that we can formally write the sum of the diagonal elements of some matrix or operator as the trace (Tr) of the matrix or operator,

$$Tr(\rho) = \sum_m \rho_{mm} = \sum_m \sum_j P_j \left| c_m^{(j)} \right|^2 = \sum_j P_j \sum_m \left| c_m^{(j)} \right|^2 = \sum_j P_j = 1 \qquad (14.10)$$

because

(a) the state $\left|\psi_j\right\rangle$ is normalized (so $\sum_m | c_m^{(j)} |^2 = 1$), and

(b) the sum of all the probabilities P_j of the various states $\left|\psi_j\right\rangle$ in the mixed state must be 1.

Ensemble average value from the density matrix

Consider an operator $\hat{A}$ corresponding to some physical observable,

and specifically consider the product $\rho\hat{A}$, i.e.,

$$\rho\hat{A} = \sum_{u.v}\left(\sum_j P_j c_u^{(j)}\left(c_v^{(j)}\right)^*\right)|\phi_u\rangle\langle\phi_v|\hat{A} \tag{14.11}$$

We can therefore write some diagonal element of the resulting matrix as

$$\begin{aligned}\langle\phi_q|\rho\hat{A}|\phi_q\rangle &= \sum_{u.v}\left(\sum_j P_j c_u^{(j)}\left(c_v^{(j)}\right)^*\right)\langle\phi_q|\phi_u\rangle\langle\phi_v|\hat{A}|\phi_q\rangle = \sum_{u.v}\left(\sum_j P_j c_u^{(j)}\left(c_v^{(j)}\right)^*\right)\delta_{qu}\langle\phi_v|\hat{A}|\phi_q\rangle \\ &= \sum_v\sum_j P_j c_q^{(j)}\left(c_v^{(j)}\right)^*\langle\phi_v|\hat{A}|\phi_q\rangle\end{aligned} \tag{14.12}$$

Then the sum of the all of these diagonal elements is

$$\begin{aligned}\sum_q\langle\phi_q|\rho\hat{A}|\phi_q\rangle &= \sum_j P_j\left(\sum_v\left(c_v^{(j)}\right)^*\langle\phi_v|\right)\hat{A}\left(\sum_q c_q^{(j)}|\phi_q\rangle\right) \\ &= \sum_j P_j\langle\psi_j|\hat{A}|\psi_j\rangle\end{aligned} \tag{14.13}$$

Note this is the same as the ensemble average value $\overline{\langle A\rangle}$ of the expectation value of the operator $\hat{A}$ for this mixed state as given in Eq. (14.4) ($\overline{\langle A\rangle} = \sum_j P_j\langle\psi_j|\hat{A}|\psi_j\rangle$)above.

Ensemble average value from the density matrix

Hence we have a key result of density matrix theory

$$\overline{\langle A \rangle} = Tr\left(\rho \hat{A}\right) \tag{14.14}$$

The density matrix, through Eq. (14.14), therefore describes any measurable ensemble average property of a mixed state.

Hence the density matrix gives a full description of a mixed state.

Note that this result, Eq. (14.14),

is completely independent of the basis used to calculate the trace

the basis $|\phi_m\rangle$ could be any set that is complete for the problem of interest.

Note also that, if we have the system in a pure state $|\psi\rangle$,

in which case $P = 1$ ***for that state (and zero for any other state),***

then we recover the usual result for the expectation value,

i.e., $Tr\left(\rho \hat{A}\right) = \langle \psi | \hat{A} | \psi \rangle = \langle A \rangle$**,**

so the density matrix description gives the correct answers for pure or mixed states.

Time-evolution of the density matrix - 1

When we want to understand how a pure state $\left|\psi_j\right\rangle$ evolves,

we can use the Schrödinger equation

$$\hat{H}\left|\psi_j\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\psi_j\right\rangle \qquad (14.15)$$

How can we describe the evolution of a mixed state?

In principle, we can consider each pure state in the mixture,

and appropriately average the result

We can directly calculate the time-evolution of the density matrix.

We start with the Schrödinger equation (14.15),

and substitute using the expansion, Eq. (14.6) $\left|\psi_j\right\rangle = \sum_u c_u^{(j)}\left|\phi_u\right\rangle$ **to obtain**

$$i\hbar\sum_n \frac{\partial c_n^{(j)}(t)}{\partial t}\left|\phi_n\right\rangle = \sum_n c_n^{(j)}(t)\hat{H}\left|\phi_n\right\rangle \qquad (14.16)$$

where we have put all of the time dependence of the state into the $c_n^{(j)}(t)$.

Now operating from the left of Eq. (14.16) with $\left\langle\phi_m\right|$***, we have***

$$i\hbar\frac{\partial c_m^{(j)}(t)}{\partial t} = \sum_n c_n^{(j)}(t)H_{mn} \qquad (14.17)$$

where $H_{mn} = \left\langle\phi_m\right|\hat{H}\left|\phi_n\right\rangle$ **is a matrix element of the Hamiltonian.**

Time-evolution of the density matrix - 2

Also, we can take the complex conjugate of both sides of Eq. (14.17).

Noting that $\hat{H}$ is Hermitian, i.e., $H_{mn}^{*}=H_{nm}$, we have

$$-i\hbar\frac{\partial\left(c_m^{(j)}(t)\right)^*}{\partial t}=\sum_n\left(c_n^{(j)}(t)\right)^*H_{nm} \tag{14.18}$$

or, trivially, changing indices

$$-i\hbar\frac{\partial\left(c_n^{(j)}(t)\right)^*}{\partial t}=\sum_s\left(c_s^{(j)}(t)\right)^*H_{sn} \tag{14.19}$$

But, from (14.8), $\rho_{uv}=\sum_j P_j c_u^{(j)}\left(c_v^{(j)}\right)^*$

$$\frac{\partial\rho_{mn}}{\partial t}=\sum_j P_j\left(c_m^{(j)}\frac{\partial\left(c_n^{(j)}\right)^*}{\partial t}+\left(c_n^{(j)}\right)^*\frac{\partial c_m^{(j)}}{\partial t}\right) \tag{14.20}$$

Time-evolution of the density matrix - 3

From Eqs. (14.17) $i\hbar\frac{\partial c_m^{(j)}(t)}{\partial t}=\sum_n c_n^{(j)}(t)H_{mn}$ **and (14.19)** $-i\hbar\frac{\partial\left(c_n^{(j)}(t)\right)^*}{\partial t}=\sum_s\left(c_s^{(j)}(t)\right)^* H_{sn}$

and changing the summation index in Eq. (14.17) from n to q),

Eq. (14.20) $\frac{\partial\rho_{mn}}{\partial t}=\sum_j P_j\left(c_m^{(j)}\frac{\partial\left(c_n^{(j)}\right)^*}{\partial t}+\left(c_n^{(j)}\right)^*\frac{\partial c_m^{(j)}}{\partial t}\right)$ becomes

$$\frac{\partial\rho_{mn}}{\partial t}=\sum_j P_j\left(\frac{i}{\hbar}c_m^{(j)}\sum_q\left(c_q^{(j)}\right)^* H_{qn}-\frac{i}{\hbar}\left(c_n^{(j)}\right)^*\sum_s c_s^{(j)}H_{ms}\right)$$
$$=\frac{i}{\hbar}\left(\sum_q\left(\sum_j P_j c_m^{(j)}\left(c_q^{(j)}\right)^*\right)H_{qn}-\sum_s H_{ms}\left(\sum_j P_j c_s^{(j)}\left(c_n^{(j)}\right)^*\right)\right) \quad (14.21)$$

Using the definition Eq. (14.8) ($\rho_{uv}\equiv\sum_j P_j c_u^{(j)}\left(c_v^{(j)}\right)^*$**) we have**

$$\frac{\partial\rho_{mn}}{\partial t}=\frac{i}{\hbar}\left(\sum_q\rho_{mq}H_{qn}-\sum_s H_{ms}\rho_{sn}\right)=\frac{i}{\hbar}\left(\left(\rho\hat{H}\right)_{mn}-\left(\hat{H}\rho\right)_{mn}\right)=\frac{i}{\hbar}\left[\rho,\hat{H}\right]_{mn} \quad (14.22)$$

or equivalently,

$$\frac{\partial\rho}{\partial t}=\frac{i}{\hbar}\left[\rho,\hat{H}\right] \quad (14.23)$$

The density matrix – 2

Reading – Sections 14.5 – 14.6

Interaction of light with a two-level "atomic" system

Density matrix and perturbation theory

Interaction of light with a two-level "atomic" system - 1

Take a two-level system with energies E_1, E_2, and eigenfunctions $|\psi_1\rangle$, $|\psi_2\rangle$.

Presume the system is much smaller than an optical wavelength,

so an incident optical field E will simply be uniform across the system

and take E to be polarized in the z direction.

We take an "electric dipole" interaction between the light and the electron,

so that the energy change on displacing by an amount z is $e\mathsf{E}z$.

Hence we can take the (semiclassical) perturbing Hamiltonian is

$$\hat{H}_p = e\mathsf{E}z = -\mathsf{E}\hat{\mu} \tag{14.24}$$

where $\hat{\mu}$ is the electric dipole operator, with matrix elements

$$\mu_{mn} = -e\langle\psi_m|z|\psi_n\rangle \tag{14.25}$$

so that

$$\left(\hat{H}_p\right)_{mn} \equiv H_{pmn} = -\mathsf{E}\mu_{mn} \tag{14.26}$$

We choose the states $|\psi_1\rangle$ and $|\psi_2\rangle$ to have definite parity, so

$$\mu_{11} = \mu_{22} = 0 \text{ and hence } H_{p11} = H_{p22} = 0 \tag{14.27}$$

and we are free to choose the relative phase of the two wavefunctions such that μ_{12} is real so that we have

$$\mu_{12} = \mu_{21} \equiv \mu_d \tag{14.28}$$

Interaction of light with a two-level "atomic" system - 2

Hence the dipole operator of this system can be written as

$$\hat{\mu} = \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix} \tag{14.29}$$

and the perturbing Hamiltonian is

$$\hat{H}_p = \begin{bmatrix} 0 & \text{-E}\mu_d \\ \text{-E}\mu_d & 0 \end{bmatrix} \tag{14.30}$$

The unperturbed Hamiltonian $\hat{H}_o$ is just a 2 x 2 diagonal matrix on this basis,

with E_1 and E_2 as the diagonal elements,

so the total Hamiltonian is

$$\hat{H} = \hat{H}_o + \hat{H}_p = \begin{bmatrix} E_1 & \text{-E}\mu_d \\ \text{-E}\mu_d & E_2 \end{bmatrix} \tag{14.31}$$

The density matrix is also a 2 x 2 matrix

because there are only two basis states under consideration here,

and in general we can write it as

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \tag{14.32}$$

The dipole of the system

The dipole induced in this system is important for two different reasons.

First, as above,

we see that it is closely related to the perturbing Hamiltonian.

Second,

it represents the response of the system (the polarization) to the electric field.

and the relation between polarization and electric field gives the electric susceptibilities or dielectric constants

that we typically use to describe the optical properties of materials.

So we want the expectation value or ensemble average value of the dipole.

We have not yet defined the system's state, but we can use (14.14) ($\overline{\langle A \rangle} = Tr\left(\rho \hat{A}\right)$) to write

$$\overline{\langle \mu \rangle} = Tr\left(\rho \hat{\mu}\right) \tag{14.33}$$

Using Eqs. (14.29) ($\hat{\mu} = \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix}$) and (14.32) ($\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}$), we have

$$\rho\hat{\mu} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix} = \begin{bmatrix} \rho_{12}\mu_d & \rho_{11}\mu_d \\ \rho_{22}\mu_d & \rho_{21}\mu_d \end{bmatrix} \tag{14.34}$$

Hence

$$\overline{\langle \mu \rangle} = \mu_d \left(\rho_{12} + \rho_{21}\right) \tag{14.35}$$

Behavior of the density matrix in time - 1

We have, from Eq. (14.23) ($\frac{\partial\rho}{\partial t}=\frac{i}{\hbar}\left[\rho,\hat{H}\right]$) with the definitions of ρ from Eq. (14.32) ($\rho=\begin{bmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{bmatrix}$) and $\hat{H}$ ($\hat{H}=\hat{H}_o+\hat{H}_p=\begin{bmatrix}E_1 & \text{-E}\mu_d\\ \text{-E}\mu_d & E_2\end{bmatrix}$) from Eq. (14.31)

$$\begin{aligned}\frac{d\rho}{dt}&=\frac{i}{\hbar}\left(\rho\hat{H}-\hat{H}\rho\right)\\ &=\frac{i}{\hbar}\left(\begin{bmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{bmatrix}\begin{bmatrix}E_1 & \text{-E}\mu_d\\ \text{-E}\mu_d & E_2\end{bmatrix}-\begin{bmatrix}E_1 & \text{-E}\mu_d\\ \text{-E}\mu_d & E_2\end{bmatrix}\begin{bmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{bmatrix}\right)\\ &=\frac{i}{\hbar}\begin{bmatrix}-\text{E}\mu_d\left(\rho_{12}-\rho_{21}\right) & -\text{E}\mu_d\left(\rho_{11}-\rho_{22}\right)+\left(E_2-E_1\right)\rho_{12}\\ -\text{E}\mu_d\left(\rho_{22}-\rho_{11}\right)+\left(E_1-E_2\right)\rho_{21} & -\text{E}\mu_d\left(\rho_{21}-\rho_{12}\right)\end{bmatrix}\end{aligned} \qquad (14.36)$$

Taking the “2 – 1” element of both sides, with $\hbar\omega_{21}=E_2-E_1$.

$$\begin{aligned}\frac{d\rho_{21}}{dt}&=\frac{i}{\hbar}\left(\left(\rho_{11}-\rho_{22}\right)\text{E}\mu_d-\left(E_2-E_1\right)\rho_{21}\right)\\ &=-i\omega_{21}\rho_{21}+i\frac{\mu_d}{\hbar}\text{E}\left(\rho_{11}-\rho_{22}\right)\end{aligned} \qquad (14.37)$$

For the fractional population difference $\rho_{11}-\rho_{22}$ between the lower and upper states, using the Hermiticity of ρ (which tells us that $\rho_{12}=\rho_{21}^*$).

$$\frac{d}{dt}\left(\rho_{11}-\rho_{22}\right)=2i\frac{\mu_d}{\hbar}\text{E}\left(\rho_{21}-\rho_{21}^*\right) \qquad (14.38)$$

Behavior of the density matrix in time - 2

Note: this is not a perturbation theory analysis.

Solving

(14.37) $\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right)$ and (14.38) $\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21} - \rho_{21}^*\right)$

covers any possible behavior of this idealized system.

So far, there is nothing in these equations so far that was not in the original time dependent Schrödinger equation

solving that separately for each of the possible pure starting states $\left|\psi_j\right\rangle$***of interest***

then averaging the resulting expectation values for some quantity of interest

such as the dipole moment

gives the same results as we get from our density matrix analysis so far.

A key benefit of the density matrix approach is, however, that

it enables us to model additional random processes that lie outside the idealized problem,

and about which we may know relatively little.

Density matrix and relaxation times - 1

Consider the fractional population difference $\rho_{11} - \rho_{22}$ between the "lower" and "upper" states.

We might know that, in equilibrium, with no applied fields

this difference settles to a value, $(\rho_{11} - \rho_{22})_o$.

Suppose we have some different specific fractional population difference $\rho_{11} - \rho_{22}$.

Then experience might tell us that

such systems often settle back down again to $(\rho_{11} - \rho_{22})_o$

with an exponential decay,

with a characteristic time constant T_1.

e.g., because of random collisions of an atom,

with the walls of the box containing the atom,

or possibly with other atoms,

or possibly just due to spontaneous emission.

Then we could hypothesize that we could add a term to Eq. (14.38)

$$\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21} - \rho_{21}^*\right) - \frac{\left(\rho_{11} - \rho_{22}\right) - \left(\rho_{11} - \rho_{22}\right)_o}{T_1} \tag{14.39}$$

Density matrix and relaxation times - 2

We have to consider a similar process also for the off-diagonal elements of the density matrix, as in Eq. (14.37) ($\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right)$).

To understand this, we need to understand the meaning of the off-diagonal elements.

Within any given pure state *j*,

the product $c_u^{(j)}\left(c_v^{(j)}\right)^*$ is something that is in general oscillating.

There is a time dependence $\exp\left(-iE_u t/\hbar\right)$ built into $c_u^{(j)}$.

Similarly $\left(c_v^{(j)}\right)^*$ has a time dependence $\exp\left(iE_v t/\hbar\right)$,

so the product has an oscillation of the form $\exp(-i(E_u - E_v)t/\hbar)$.

As time evolves, the system can get scattered into another pure state k with some probability,

possibly even a state in which ρ_{11} and ρ_{22} are unchanged,

but in which the phases of the coefficients $c_1^{(k)}$ and $c_2^{(k)}$ are different.

At any given time, therefore, we may have an ensemble of different possibilities for the quantum mechanical state,

and in general these different possibilities will have different phases of oscillation.

Density matrix and relaxation times - 3

If we have sufficiently many such random phases that are sufficiently different in our mixed state,

then the ensemble average of a product $c_u c_v^*$ ***for different*** u ***and*** v***, i.e.,*** $\overline{c_u c_v^*}$***, will average out to zero.***

But this ensemble average is simply the off-diagonal density matrix element ρ_{uv} **, as defined in Eq. (14.8).**

Hence, these off-diagonal elements contain information about the coherence of the populations in different states.

The processes that scatter into states with different phases can be called “dephasing” processes.

The simplest model is that dephasing processes cause an exponential settling of any off-diagonal element to zero,

with some time constant T_2**.**

Hence we postulate adding a term $-\rho_{21}/T_2$ *to Eq. (14.37) to obtain*

$$\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right) - \frac{\rho_{21}}{T_2} \tag{14.40}$$

In the absence of an optical field E,

ρ_{21} ***would execute an oscillation at approximately frequency*** ω_{21}***,***

decaying to zero approximately exponentially with a time constant T_2**.**

Behavior with oscillating field - 1

We want to solve for the case of an oscillating electric field

$$\mathsf{E}(t) = \mathsf{E}_o \cos \omega t = \frac{\mathsf{E}_o}{2}\left(\exp(i\omega t) + \exp(-i\omega t)\right) \qquad (14.41)$$

We define a new "slowly varying" quantity

$$\beta_{21}(t) = \rho_{21}(t)\exp(i\omega t) \qquad (14.42)$$

and substitute using this to obtain, instead of Eqs. (14.39) and (14.40),

$$\frac{d}{dt}(\rho_{11} - \rho_{22}) = i\frac{\mu_d}{\hbar}\mathsf{E}_o\left(\beta_{21} - \beta_{21}^*\right) - \frac{(\rho_{11} - \rho_{22}) - (\rho_{11} - \rho_{22})_o}{T_1} \qquad (14.43)$$

$$\frac{d\beta_{21}}{dt} = i(\omega - \omega_{21})\beta_{21} + i\frac{\mu_d}{2\hbar}\mathsf{E}_o(\rho_{11} - \rho_{22}) - \frac{\beta_{21}}{T_2} \qquad (14.44)$$

where we have also made the approximation of dropping all terms proportional to $\exp(\pm 2i\omega t)$***.***

Such terms will average out to zero over timescales of cycles, and hence will make relatively little contribution to the resulting values of $\rho_{11} - \rho_{22}$ **and** β_{21}

These equations (14.43) and (14.44) are often known as the Bloch equations,

equations that were first derived in the field of magnetic resonance.

Behavior with oscillating field - 2

In terms of β_{21} we now have for the ensemble average of the dipole moment of our system, from Eq. (14.35) ($\overline{\langle\mu\rangle} = \mu_d\left(\rho_{12} + \rho_{21}\right)$),

$$\begin{aligned}\overline{\langle\mu\rangle} &= \mu_d\left(\beta_{12}\exp(i\omega t) + \beta_{21}\exp(-i\omega t)\right) \\ &= 2\mu_d\left[\operatorname{Re}(\beta_{21})\cos\omega t + \operatorname{Im}(\beta_{21})\sin\omega t\right]\end{aligned} \tag{14.45}$$

where we have used the fact that $\beta_{21} = \beta_{12}^*$***,***

which follows from the definition, Eq. (14.42)

and the fact that the density matrix itself is Hermitian.

Now let us solve in the “steady state”

for a monochromatic field and when the system has settled down.

In steady state $\rho_{11} - \rho_{22}$, will no longer be changing,

so $d(\rho_{11} - \rho_{22})/dt = 0$**.**

Behavior with oscillating field - 3

Any coherent responses will have settled down to following the appropriate driving field terms.

We therefore expect that $d\beta_{21}/dt = 0$ ***in the steady state.***

Therefore, setting the left-hand sides of both (14.43)

$$\frac{d}{dt}\left(\rho_{11}-\rho_{22}\right) = i\frac{\mu_d}{\hbar}\mathsf{E}_o\left(\beta_{21}-\beta_{21}^{*}\right) - \frac{\left(\rho_{11}-\rho_{22}\right)-\left(\rho_{11}-\rho_{22}\right)_o}{T_1}$$

and (14.44)

$$\frac{d\beta_{21}}{dt} = i\left(\omega-\omega_{21}\right)\beta_{21} + i\frac{\mu_d}{2\hbar}\mathsf{E}_o\left(\rho_{11}-\rho_{22}\right) - \frac{\beta_{21}}{T_2}$$

to zero, we can solve these equations.

leading to

$$\rho_{11}-\rho_{22} = \left(\rho_{11}-\rho_{22}\right)_o \frac{1+\left(\omega-\omega_{21}\right)^2 T_2^2}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.46)$$

$$\mathrm{Im}\left(\beta_{21}\right) = \frac{\Omega T_2\left(\rho_{11}-\rho_{22}\right)_o}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.47)$$

$$\mathrm{Re}\left(\beta_{21}\right) = \frac{\left(\omega_{21}-\omega\right)\Omega T_2^2\left(\rho_{11}-\rho_{22}\right)_o}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.48)$$

where $\Omega = \mu_d \mathsf{E}_o / 2\hbar$.

Behavior with oscillating field - 4

Presume that we have some large number N of such systems ("atoms") per unit volume.

The population difference between the number in the lower state and the number in the higher state (per unit volume) is therefore $\Delta N = N\left(\rho_{11} - \rho_{22}\right)$,

and the population difference in the absence of the optical field is $\Delta N_o = N\left(\rho_{11} - \rho_{22}\right)_o$.

Then instead of Eq. (14.46) we can write

$$\Delta N = \Delta N_o \frac{1+\left(\omega - \omega_{21}\right)^2 T_2^2}{1+\left(\omega - \omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.49)$$

Behavior with oscillating field - 5

In general in electromagnetism, the (static) polarization P is defined as

$$\mathrm{P} = \varepsilon_o \chi \mathrm{E} \qquad (14.50)$$

where χ is the susceptibility.

When we have an oscillating field,

the response of the medium,

and hence the polarization,

can be out of phase with the electric field,

and then it is convenient to generalize the idea of susceptibility.

We can formally think of it as a complex quantity with real and imaginary parts χ' *and* χ'' *respectively,*

or equivalently we can explicitly write the response to a real field $\mathrm{E}_o \cos \omega t$ as

$$\mathrm{P} = \varepsilon_o \mathrm{E}_o \left(\chi' \cos \omega t + \chi'' \sin \omega t \right) \qquad (14.51)$$

It is also generally true in electromagnetism that the polarization is the dipole moment per unit volume.

Hence here we can also write

$$\mathrm{P} = N \overline{\langle \mu \rangle} \qquad (14.52)$$

Behavior with oscillating field - 6

Hence, putting Eqs. **(14.45)** $\overline{\langle\mu\rangle} = 2\mu_d\left[\mathrm{Re}\left(\beta_{21}\right)\cos\omega t + \mathrm{Im}\left(\beta_{21}\right)\sin\omega t\right]$**,**

(14.47) $\mathrm{Im}\left(\beta_{21}\right) = \dfrac{\Omega T_2\left(\rho_{11}-\rho_{22}\right)_o}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$**,**

(14.48) $\mathrm{Re}\left(\beta_{21}\right) = \dfrac{\left(\omega_{21}-\omega\right)\Omega T_2^2\left(\rho_{11}-\rho_{22}\right)_o}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$**,**

(14.51) $\mathsf{P} = \varepsilon_o \mathsf{E}_o\left(\chi'\cos\omega t + \chi''\sin\omega t\right)$**, and**

(14.52) $\mathsf{P} = N\overline{\langle\mu\rangle}$ **together,**

$$\chi'(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar}\,\frac{\left(\omega_{21}-\omega\right)T_2}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.53)$$

$$\chi''(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar}\,\frac{1}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1} \qquad (14.54)$$

In electromagnetism,

the in-phase component of the polarization

and hence χ' – the real part of χ – is responsible for refractive index,

and the quadrature (i.e., 90 degrees shifted) component

and hence χ'' – the imaginary part of χ – is responsible for optical absorption.

Behavior with oscillating field - 7

If we consider the case where the electric field amplitude is small,

then $\Omega \simeq 0$**,**

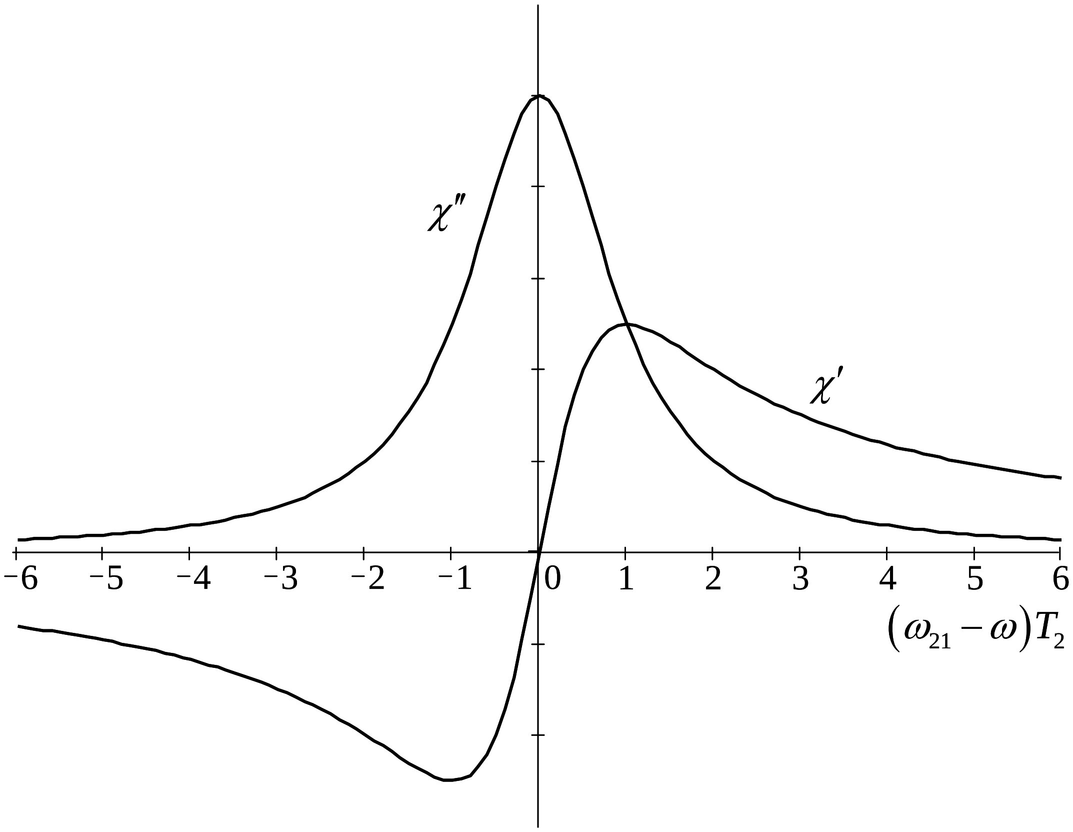
and we have the normal "linear" refraction variation

$$\chi'(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{(\omega_{21} - \omega) T_2}{1 + (\omega - \omega_{21})^2 T_2^2} \quad (14.55)$$

and Lorentzian absorption line

$$\chi''(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{1}{1 + (\omega - \omega_{21})^2 T_2^2} \quad (14.56)$$

associated with an "atomic" or "two-level" transition.



Lorentzian absorption line and corresponding refractive effects

Note that, finally, we have eliminated the δ-function behavior of absorbing transitions that we got from simple time-dependent perturbation theory.

Now we have an absorbing line with a much more reasonable shape,

with a width ~ $1/T_2$,

i.e., the more dephasing "collisions" there are with the "atom",

the wider the absorption line.

Incidentally,

any process that leads to the recovery of the atom from its excited state back to its lower state

will also cause a decay of the off-diagonal elements,

and so even if there are no additional dephasing processes,

the absorbing line will still have a width.

When the only recovery process is spontaneous emission,

the resulting line-width is called the natural line-width.

We can view the line-width of the absorbing transition as being consistent with the energy-time uncertainty principle

if the state (or the coherence of the state) only persists for a finite time,

then the state cannot have a well-defined energy,

hence the line-width.

Absorption saturation

The approach we have taken so far is exact for all fields.

In particular, these results model absorption saturation

If we keep trying to absorb more photons into an ensemble of these "atoms"

there will be fewer and fewer atoms in their lower states

and also more and more in their upper states

which removes these atoms from absorption

It also allows them to show stimulated emission from the upper to the lower state

which is a process that is exactly the opposite of absorption

Hence the absorption should disappear as we go to higher intensities.

The quantity Ω^2 ***is proportional to the electric field squared,***

which in turn is proportional to the intensity *I* of the light field

Hence we can write $4\Omega^2 T_2 T_1 \equiv I / I_S$ *where* I_S *is called the saturation intensity.*

Hence, for example, on resonance ($\omega_{21} = \omega$**), we have**

$$\chi''(\omega) \propto \frac{1}{1 + I / I_S} \quad (14.57)$$

This equation describes the process of "absorption saturation" that is often seen with the high intensities available from lasers.

Density matrix and perturbation theory

So far we showed an exact solution of a simple problem,

including both linear response and the non-linear response of absorption saturation.

Just as in solutions of Schrödinger's equation,

for more complicated systems, exact solutions are usually not possible.

Just as for Schrödinger's equation, we can use perturbation theory,

but now with Eq. (14.22) $\frac{\partial \rho_{mn}}{\partial t} = \frac{i}{\hbar}\left[\rho, \hat{H}\right]_{mn}$ *for the time evolution of the density matrix instead of Schrödinger's equation.*

One approach generalizes the relaxation time approximations, writing instead of Eq. (14.22)

$$\frac{\partial \rho_{mn}}{\partial t} = \frac{i}{\hbar}\left[\rho, \hat{H}\right]_{mn} - \gamma_{mn}\left(\rho_{mn} - \rho_{mno}\right) \tag{14.58}$$

ρ_{mno} *is the equilibrium value for* ρ_{mn} *and* γ_{mn} *is its "relaxation rate"*

One then starts with equations like (14.58) instead of the time-dependent Schrödinger equation and constructs a perturbation theory just as before.

This density matrix version is the one commonly used for calculating non-linear optical coefficients

eliminating the singularities when the transition energy and the photon energy coincide.

Harmonic oscillators and photons – 1

Reading – Sections 15.1 – 15.2

Harmonic oscillator and raising and lowering operators

Hamilton’s equations and generalized position and momentum

Harmonic oscillators, annihilation and creation operators, and photons

We treat the harmonic oscillator using “raising” and “lowering” operators

- ***that take us from one harmonic oscillator state to another.***
  - **allowing us to rewrite the harmonic oscillator mathematics.**

We then show that the electromagnetic field for a given mode can also be described in a manner exactly analogous to a harmonic oscillator.

- ***We describe the states in terms of the number of photons per mode, with***
  - **the photon number corresponding to the harmonic oscillator state number**
- ***The raising and lowering operators are now called***
  - **“creation” and “annihilation” operators for photons,**
    - *and are key operators for describing electromagnetic fields.*

Hence, we can describe the electromagnetic field quantum mechanically

- **rather than the semiclassical use of classical electric and magnetic fields.**

We say we have “quantized” the electromagnetic field.

- ***This quantization is then the basis for all of quantum optics***
  - **properly explaining phenomena such as**
    - *spontaneous emission*
    - *noise in lasers and optical amplifiers*
    - *and a large number of other optical behaviors that have no classical analog.*

Harmonic oscillator and raising and lowering operators - 1

The Schrödinger equation for the harmonic oscillator was, as in Eq. (2.75)

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + \frac{1}{2}m\omega^2 z^2\right]\psi = E\psi \qquad (15.1)$$

where ω is the angular frequency of oscillation of the classical oscillator.

We introduce a dimensionless distance, as in Eq. (2.76)

$$\xi = \sqrt{\frac{m\omega}{\hbar}}z \qquad (15.2)$$

which enables us to rewrite the Schrödinger equation, as in Eq. (2.77), as

$$\frac{1}{2}\left[-\frac{d^2}{d\xi^2} + \xi^2\right]\psi = \frac{E}{\hbar\omega}\psi \qquad (15.3)$$

The term $-d^2/d\xi^2 + \xi^2$ reminds us of the difference of two squares of numbers

$$-a^2 + b^2 = b^2 - a^2 = (-a+b)(a+b) \qquad (15.4)$$

though here we have the difference that $d^2/d\xi^2$ is an operator.

Harmonic oscillator and raising and lowering operators - 2

If we examine a product of this form for our present case, we have

$$\frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi}+\xi\right)\times\frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right)=\frac{1}{2}\left(-\frac{d^2}{d\xi^2}+\xi^2\right)-\frac{1}{2}\left(\frac{d}{d\xi}\xi-\xi\frac{d}{d\xi}\right) \quad (15.5)$$

As before, when we were considering the commutator of momentum and position, we note that, for any function $f(\xi)$

$$\begin{aligned}\left(\frac{d}{d\xi}\xi-\xi\frac{d}{d\xi}\right)f(\xi)&=\frac{d}{d\xi}\left(\xi f(\xi)\right)-\xi\frac{d}{d\xi}f(\xi)\\&=f(\xi)\frac{d\xi}{d\xi}+\xi\frac{d}{d\xi}f(\xi)-\xi\frac{d}{d\xi}f(\xi)=f(\xi)\end{aligned} \quad (15.6)$$

so we can write the commutation relation

$$\left(\frac{d}{d\xi}\xi-\xi\frac{d}{d\xi}\right)=1 \quad (15.7)$$

Hence, from Eq. (15.5), we have

$$\frac{1}{2}\left(-\frac{d^2}{d\xi^2}+\xi^2\right)=\frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi}+\xi\right)\times\frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right)+\frac{1}{2} \quad (15.8)$$

Harmonic oscillator and raising and lowering operators - 3

We can choose to write the "raising" or "creation" operator

$$\hat{a}^\dagger \equiv \frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi}+\xi\right) \tag{15.9}$$

(pronounced "a dagger")

and the "lowering" or "annihilation" operator,

$$\hat{a} \equiv \frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right) \tag{15.10}$$

Note each of these operators is the Hermitian adjoint of the other.

The operator $d/d\xi$ is anti-Hermitian, as demonstrated earlier for d/dz,

i.e., $\langle\phi|d/d\xi|\psi\rangle = -\left[\langle\psi|d/d\xi|\phi\rangle\right]^*$ *for two arbitrary states* $|\phi\rangle$ *and* $|\psi\rangle$*.*

though ξ is Hermitian (it represents the position operator)

Therefore

$$\langle\phi|\hat{a}|\psi\rangle = \langle\phi|\frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right)|\psi\rangle = \left[\langle\psi|\frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi}+\xi\right)|\phi\rangle\right]^* = \left[\langle\psi|\hat{a}^\dagger|\phi\rangle\right]^* \tag{15.11}$$

showing that the operators $\hat{a}$ and $\hat{a}^\dagger$ are Hermitian adjoints.

Note these operators are not Hermitian

i.e., it is not true that $\hat{a} = \hat{a}^\dagger$

Hamiltonian written using raising and lowering operators

Now using the definitions for these operators,

Eqs. (15.9) $\hat{a}^\dagger \equiv \frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi}+\xi\right)$ **and (15.10)** $\hat{a} \equiv \frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right)$

we can write,

from Eq. (15.3) $\frac{1}{2}\left[-\frac{d^2}{d\xi^2}+\xi^2\right]\psi = \frac{E}{\hbar\omega}\psi$

$$\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)\psi = \frac{E}{\hbar\omega}\psi \qquad (15.12)$$

In other words, we can rewrite the Hamiltonian as

$$\hat{H} \equiv \hbar\omega\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right) \qquad (15.13)$$

Number operator

We know from the previous solution of the harmonic oscillator that the eigenenergy associated with eigenstate $|\psi_n\rangle$ is

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right),$$

and so, given Eq. (15.13) $\hat{H} \equiv \hbar\omega\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)$

we know that

$$\hat{a}^\dagger\hat{a}|\psi_n\rangle = n|\psi_n\rangle \tag{15.14}$$

This operator $\hat{a}^\dagger\hat{a}$ obviously has the harmonic oscillator states as its eigenstates,

and the number of the state as its eigenvalue,

and is sometimes called the number operator, $\hat{N}$, i.e.,

$$\hat{N} \equiv \hat{a}^\dagger\hat{a} \tag{15.15}$$

with the eigenequation

$$\hat{N}|\psi_n\rangle = n|\psi_n\rangle \tag{15.16}$$

Properties of raising and lowering operators

The operators $\hat{a}$ and $\hat{a}^\dagger$ have a very important property, which is their commutator.

Specifically, we find

$$\left[\hat{a},\hat{a}^\dagger\right]=\hat{a}\hat{a}^\dagger-\hat{a}^\dagger\hat{a}=1 \tag{15.17}$$

We can use this property, together with the property in Eq. (15.14),

$$\hat{a}^\dagger\hat{a}\left|\psi_n\right\rangle=n\left|\psi_n\right\rangle$$

to show the reason why these operators are called

raising and lowering operators, or

creation and annihilation operators.

Effect of raising and lowering operators on eigenstates - 1

Suppose first we operate on both sides of Eq. (15.14) ($\hat{a}^\dagger \hat{a}|\psi_n\rangle = n|\psi_n\rangle$) with $\hat{a}$. Then we have

$$\hat{a}\left(\hat{a}^\dagger \hat{a}\right)|\psi_n\rangle = n\hat{a}|\psi_n\rangle \tag{15.18}$$

i.e., regrouping on the left, and substituting from Eq. (15.17) ($\left[\hat{a},\hat{a}^\dagger\right] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$) we have

$$\left(\hat{a}\hat{a}^\dagger\right)\left(\hat{a}|\psi_n\rangle\right) = \left(1 + \hat{a}^\dagger\hat{a}\right)\left(\hat{a}|\psi_n\rangle\right) = n\left(\hat{a}|\psi_n\rangle\right) \tag{15.19}$$

i.e.,

$$\hat{a}^\dagger\hat{a}\left(\hat{a}|\psi_n\rangle\right) = (n-1)\left(\hat{a}|\psi_n\rangle\right) \tag{15.20}$$

But this means, from Eq. (15.14), that

$\hat{a}|\psi_n\rangle$ ***is simply*** $|\psi_{n-1}\rangle$***,***

at least within some normalizing constant A_n, i.e.,

$$\hat{a}|\psi_n\rangle = A_n|\psi_{n-1}\rangle \tag{15.21}$$

Hence we see why the operator $\hat{a}$ is called the lowering operator,

because it changes the state $|\psi_n\rangle$ into the state $|\psi_{n-1}\rangle$.

Effect of raising and lowering operators on eigenstates - 2

We can perform a similar analysis, operating on both sides of Eq. (15.14) ($\hat{a}^\dagger \hat{a}|\psi_n\rangle = n|\psi_n\rangle$) with $\hat{a}^\dagger$.

The details of this are left as an exercise.

The result is, similarly to Eq. (15.20),

$$\hat{a}^\dagger \hat{a}\left(\hat{a}^\dagger|\psi_n\rangle\right) = (n+1)\left(\hat{a}^\dagger|\psi_n\rangle\right) \tag{15.22}$$

Again, we conclude from Eq. (15.14) that

$\hat{a}^\dagger|\psi_n\rangle$ ***must simply be*** $|\psi_{n+1}\rangle$***,***

at least within some normalizing constant B_{n+1}

$$\hat{a}^\dagger|\psi_n\rangle = B_{n+1}|\psi_{n+1}\rangle \tag{15.23}$$

and we similarly see why the operator $\hat{a}^\dagger$ is called the raising operator,

because it changes the state $|\psi_n\rangle$ ***into the state*** $|\psi_{n+1}\rangle$***.***

Incidentally, one way to remember which operator is which is to

think of the superscript dagger "†" as a "+" sign corresponding to raising the state.

Indeed, it is quite a common notation to use a superscript "+" sign.

Deducing the normalizing coefficients

We can now proceed one step further, which is to deduce what A_n and B_n are.

Premultiplying Eq. (15.21) ($\hat{a}|\psi_n\rangle = A_n|\psi_{n-1}\rangle$) by $\langle\psi_{n-1}|$ gives

$$\langle\psi_{n-1}|\hat{a}|\psi_n\rangle = A_n \qquad (15.24)$$

But, using

the normal properties of operators and state vectors, and the conjugate of Eq. (15.23) ($\hat{a}^\dagger|\psi_n\rangle = B_{n+1}|\psi_{n+1}\rangle$) rewritten for initial state $|\psi_{n-1}\rangle$ rather than $|\psi_n\rangle$,

$$\langle\psi_{n-1}|\hat{a} = \left[\hat{a}^\dagger|\psi_{n-1}\rangle\right]^\dagger = \left[B_n|\psi_n\rangle\right]^\dagger = B_n^*\langle\psi_n| \qquad (15.25)$$

so

$$\langle\psi_{n-1}|\hat{a}|\psi_n\rangle = A_n = B_n^*\langle\psi_n|\psi_n\rangle = B_n^* \qquad (15.26)$$

Hence

$$\hat{a}^\dagger\hat{a}|\psi_n\rangle = A_n\hat{a}^\dagger|\psi_{n-1}\rangle = A_nB_n|\psi_n\rangle = |A_n|^2|\psi_n\rangle = n|\psi_n\rangle \qquad (15.27)$$

and so

$$A_n = \sqrt{n} \qquad (15.28)$$

at least within a unit complex constant, which we choose to be +1.

Hence, we have instead of Eq. (15.21) ($\hat{a}|\psi_n\rangle = A_n|\psi_{n-1}\rangle$), $$\hat{a}|\psi_n\rangle = \sqrt{n}|\psi_{n-1}\rangle \qquad (15.29)$$

and instead of Eq. (15.23) ($\hat{a}^\dagger|\psi_n\rangle = B_{n+1}|\psi_{n+1}\rangle$) $$\hat{a}^\dagger|\psi_n\rangle = \sqrt{n+1}|\psi_{n+1}\rangle \qquad (15.30)$$

Harmonic oscillator eigenfunctions stated using raising and lowering operators – lowest state

We know that the harmonic oscillator has a lowest state,

which corresponds to $n=0$**.**

Hence, from Eq. (15.29), $\hat{a}|\psi_n\rangle = \sqrt{n}|\psi_{n-1}\rangle$**,**

we must have

$$\hat{a}|\psi_0\rangle = 0 \tag{15.31}$$

We can use this as an alternative method of deducing $|\psi_0\rangle \equiv \psi_0(\xi)$**.**

Using the differential operator definition of $\hat{a}$ ***from Eq. (15.10), we have***

$$\frac{1}{\sqrt{2}}\left(\frac{d}{d\xi}+\xi\right)\psi_0(\xi)=0 \tag{15.32}$$

from which we can immediately verify that the solution is

$$\psi_0(\xi)=\frac{1}{(\pi)^{1/4}}\exp\left(-\frac{\xi^2}{2}\right) \tag{15.33}$$

where we have also normalized the solution,

in agreement with our previous method of direct solution of the second order differential Schrödinger equation.

Harmonic oscillator eigenfunctions stated using raising and lowering operators – higher states

Now, we can proceed using the raising operator to construct all the other solutions for different n.

Successive application of $\hat{a}^{\dagger}$ to $|\psi_0\rangle$ gives

$$\left(\hat{a}^{\dagger}\right)^n |\psi_0\rangle = \sqrt{n!}\,|\psi_n\rangle \tag{15.34}$$

and so the normalized eigenstates can be written as

$$|\psi_n\rangle = \frac{1}{\sqrt{n!}}\left(\hat{a}^{\dagger}\right)^n |\psi_0\rangle \tag{15.35}$$

We see by this approach that each eigenfunction can be progressively deduced from the preceding ones.

We would reconstruct the previously derived solutions with Hermite polynomials and Gaussians if we proceeded this way.

We may either use this result actually to construct the eigenfunctions,

or as a substitution to allow convenient manipulations of the states by operators.

Why introduce raising and lowering operators

Raising and lowering operators give us a compact and elegant way of stating the properties of the harmonic oscillator,

a way in which the properties can largely be stated without using the actual wavefunction in space.

This latter aspect is particularly useful as we generalize the harmonic oscillator to other results

where the concept of a wavefunction in space is possibly not meaningful,

such as the electromagnetic field.

Harmonic oscillator states and identical bosons

Note, incidentally, that saying that

the harmonic oscillator is in state n

is mathematically identical to considering that

the harmonic oscillator "mode" contains a number n of identical particles.

Each particle has energy $\hbar\omega$.

It is of course meaningless to say what order the particles are in

we can only say that we have n identical particles in the oscillator mode.

This is exactly the kind of behavior we expect for

identical bosons that can only each have one possible state.

As we deduced above,

there is only one state in which we have n identical bosons,

and there is only one state here associated with the quantum number n.

This becomes a useful concept as we talk about the electromagnetic field.

Quantization of the electromagnetic fields

We previously turned classical problems into quantum mechanical ones

by writing a classical equation in terms of momentum and position,

and then substituting the operator $-i\hbar\partial/\partial x$ for the momentum p_x

Here we find quantities for the electromagnetic field that are mathematically analogous to momentum and position for a particle.

We do this by examining the classical Hamiltonian

for quantities that behave for the electromagnetic field Hamiltonian like the momentum and position in the mechanical particle Hamiltonian

Hamilton’s equations and generalized position & momentum - 1

In classical mechanics,

the Hamiltonian, H, represents the total energy and,

in the simple case of one particle in one dimension, is a function of

the momentum, p,

and the position, q.

p and q are considered to be independent variables.

Hence, in classical mechanics,

$$H = \frac{p^2}{2m} + V(q) \tag{15.36}$$

where $V(q)$ is the potential energy.

Hamilton's equations and generalized position & momentum - 2

The force on the particle is the negative of the gradient of the potential (a particle accelerates when going down hill), i.e., with $H = \frac{p^2}{2m} + V(q)$, the force is

$$F = -\frac{dV}{dq} \equiv -\frac{\partial H}{\partial q} \tag{15.37}$$

As usual, from Newton's second law, (force = rate of change of momentum) we know therefore that

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q} \tag{15.38}$$

We note that

$$\frac{\partial H}{\partial p} = \frac{p}{m} \tag{15.39}$$

Since $p = mv$ where v is the particle velocity,

and, by definition, $v \equiv dq/dt$***,***

we therefore have

$$\frac{dq}{dt} = \frac{\partial H}{\partial p} \tag{15.40}$$

The two equations (15.38) and (15.40) are known as Hamilton's equations.

Hamilton's equations and generalized position & momentum - 3

If the Hamiltonian depends on two quantities p and q,

> ***and these quantities and the Hamiltonian obey the Hamiltonian equations (15.38) and (15.40),***
>
> > **then we have found the quantities analogous to momentum and position**

It has been very successful in quantum mechanics to use these quantities as the basis for quantization by

> ***substituting a differential operator*** $-i\hbar\, d/dq$ ***for*** p ***in the corresponding Hamiltonian.***

Note that in this general case both p and q may bear little relation to the momentum or position of anything;

> ***all that matters is that they and the Hamiltonian obey the Hamiltonian equations (15.38) and (15.40).***

Harmonic oscillators and photons – 2

Reading – Sections 15.3 – 15.5

Quantization of the electromagnetic field

Nature of the quantum mechanical states of an electromagnetic mode

Field operators

Description of a mode of the electromagnetic field - 1

We imagine a box of length L in the x direction.

- ***We presume it is arbitrarily large in the other dimensions,***
  - **and consequently the mode can be described as a standing plane wave in the x direction, of some wavevector k.**

We expect that the electric field $\mathbf{E}$ is perpendicular to the x direction,

- ***as both the $\mathbf{E}$ field and the magnetic field $\mathbf{B}$ are transverse to the direction of propagation for a simple plane electromagnetic wave.***

We will choose the mode to be polarized in the z direction,

- ***with an appropriate amplitude, E_z.***
  - **The $\mathbf{E}$ field in the other two directions is taken to be zero.**

We also expect that the magnetic field $\mathbf{B}$ is perpendicular to the $\mathbf{E}$ field,

- ***so we choose it polarized in the y direction,***
  - **with amplitude B_y,**
    - *with zero $\mathbf{B}$ field in the other two directions.*

Description of a mode of the electromagnetic field - 2

Hence we postulate that

$$E_z = p(t) D \sin kx \tag{15.41}$$

and

$$B_y = q(t) \frac{D}{c} \cos kx \tag{15.42}$$

where c is the velocity of light, introduced here for subsequent convenience,

D is a constant still to be determined, and

$p(t)$ and $q(t)$ are at the moment simply functions of time yet to be determined.

We now check that these fields satisfy the appropriate Maxwell's equations,

which will justify all our postulations about these classical fields,

and will tell us some other required relations between our postulated quantities.

For this we now presume that we are in a vacuum,

so there is no charge density and no magnetic materials,

and the permittivity and permeability are their vacuum values of ε_o and μ_o respectively.

Description of a mode of the electromagnetic field - 3

Using the Maxwell equation

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad (15.43)$$

and noting that $\partial E_z / \partial y = 0$ ***because we have an infinite plane wave with no variation in the*** y ***direction,***

$$\frac{\partial E_z}{\partial x} = \frac{\partial B_y}{\partial t} \qquad (15.44)$$

i.e., with our choices $E_z = p(t) D \sin kx$ **(Eq. (15.41)),** $B_y = q(t) \frac{D}{c} \cos kx$ **(Eq. (15.42))**

$$kpD \cos kx = \frac{D}{c} \frac{\partial q}{\partial t} \cos kx \qquad (15.45)$$

so

$$\frac{dq}{dt} = \omega p \qquad (15.46)$$

where $\omega = kc$.

Description of a mode of the electromagnetic field - 4

Similarly, using the Maxwell equation

$$\nabla \times \mathbf{B} = \varepsilon_o \mu_o \frac{\partial \mathbf{E}}{\partial t} \tag{15.47}$$

and noting that $\partial B_y / \partial z = 0$ ***because the plane wave has no variation in the*** z ***direction,***

$$\frac{\partial B_y}{\partial x} = \varepsilon_o \mu_o \frac{\partial E_z}{\partial t} \tag{15.48}$$

i.e., with our choices $E_z = p(t) D \sin kx$ **(Eq. (15.41)),** $B_y = q(t) \frac{D}{c} \cos kx$ **(Eq. (15.42))**

$$-kq \frac{D}{c} \sin kx = \varepsilon_o \mu_o \frac{dp}{dt} D \sin kx \tag{15.49}$$

i.e., using the relation from electromagnetism

$$\varepsilon_o \mu_o = \frac{1}{c^2} \tag{15.50}$$

we have

$$\frac{dp}{dt} = -\omega q \tag{15.51}$$

Description of a mode of the electromagnetic field - 5

So we have found that our postulated form for the mode of the radiation field

does indeed satisfy the two Maxwell equations,

$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$ ***(15.43) and*** $\nabla \times \mathbf{B} = \varepsilon_o \mu_o \frac{\partial \mathbf{E}}{\partial t}$ ***(15.47),***

and gives us the relations

$\frac{dq}{dt} = \omega p$ **(15.46) and** $\frac{dp}{dt} = -\omega q$ **(15.51)**

between our time-varying amplitudes p **and** q**.**

Differentiating Eq. (15.46) with respect to time t**, and substituting from Eq. (15.51), we find**

$$\frac{d^2 q}{dt^2} = -\omega^2 q \qquad (15.52)$$

which means that the electromagnetic mode does indeed behave exactly like a harmonic oscillator, with oscillation (angular) frequency ω***.***

Hamiltonian for the electromagnetic mode - 1

Now we want to construct the Hamiltonian for the mode,

so that we find quantities that behave analogously to momentum and position by obeying Hamilton's equations, (15.38) and (15.40).

Formally in an electromagnetic field in a vacuum, the energy density is

$$W = \frac{1}{2}\left(\varepsilon_o \mathbf{E}^2 + \frac{1}{\mu_o}\mathbf{B}^2\right) \tag{15.53}$$

In a box of length L, then, per unit cross-sectional area, the total energy is the Hamiltonian

$$\begin{aligned} H &= \int_0^L W dx \\ &= \frac{D^2}{2}\int_0^L \left(\varepsilon_o p^2 \sin^2 kx + \frac{1}{\mu_o c^2} q^2 \cos^2 kx\right) dx \\ &= \frac{D^2 \varepsilon_o}{2}\int_0^L \left(p^2 \sin^2 kx + q^2 \cos^2 kx\right) dx \\ &= \frac{D^2 L \varepsilon_o}{4}\left[p^2 + q^2\right] \end{aligned} \tag{15.54}$$

Hamiltonian for the electromagnetic mode - 2

We now try to choose D so as to get p and q to correspond to the analogs of momentum and position with the Hamiltonian H of Eq. (15.54)

by having H, p, and q obey Hamilton's equations, (15.38) and (15.40).

We note that we already have the relation (15.46) between dq/dt and p, and the relation (15.51) between dp/dt and q.

Inspection shows that, if we choose

$$H = \frac{\omega}{2}\left(p^2 + q^2\right) \tag{15.55}$$

i.e.,

$$D = \sqrt{\frac{2\omega}{L\varepsilon_o}} \tag{15.56}$$

then H, p, and q do indeed satisfy Hamilton's equations (15.38) and (15.40),

making p and q the analogs of momentum and position. Using (15.46)

$$\frac{\partial H}{\partial p} = \omega p = \frac{dq}{dt} \tag{15.57}$$

and using (15.51)

$$\frac{\partial H}{\partial q} = \omega q = -\frac{dp}{dt} \tag{15.58}$$

Quantization of the electromagnetic field - 1

Having derived a classical Hamiltonian for an electromagnetic mode, we now proceed to quantize it. We postulate that we can substitute the operator

$$\hat{p} = -i\hbar \frac{d}{dq} \qquad (15.59)$$

for the scalar quantity p of the classical Hamiltonian, obtaining

$$\hat{H} = \frac{\omega}{2}\left[-\hbar^2 \frac{d^2}{dq^2} + q^2\right] \qquad (15.60)$$

It is more convenient to use the dimensionless unit

$$\xi = q/\sqrt{\hbar} \qquad (15.61)$$

For future use, we also can define a dimensionless momentum operator

$$\hat{\pi} = \hat{p}/\sqrt{\hbar} \equiv -i\frac{d}{d\xi} \qquad (15.62)$$

Use of the dimensionless unit ξ gives the Hamiltonian in the form

$$\hat{H} = \frac{\hbar\omega}{2}\left[-\frac{d^2}{d\xi^2} + \xi^2\right] \qquad (15.63)$$

identical to the Hamiltonian for the harmonic oscillator (e.g., in Eq. (15.3)).

Incidentally, we can also write $\hat{H} = \frac{\hbar\omega}{2}\left(\hat{\pi}^2 + \xi^2\right)$ (15.64)

Quantization of the electromagnetic field - 2

This completes the postulation of the mathematical analogy between a mode of the electromagnetic field and a quantum harmonic oscillator.

Obviously,

if our basic postulation of the quantization by substitution of the operator of (15.59) $\hat{p} = -i\hbar \frac{d}{dq}$ is correct for describing an electromagnetic mode quantum mechanically

and it appears in practice that it is

we can now re-use all of the formalism for the harmonic oscillator to describe the electromagnetic mode,

including the raising and lowering operators (creation and annihilation operators).

Mode notation - 1

Because there are many possible modes of the electromagnetic field, as we think about a future generalization to considering all of those modes,

we need to distinguish which mode the operators refer to.

It is common to use the index λ to index the different modes.

With that new notation, we have for a given mode,

a frequency ω_λ,

a Hamiltonian $\hat{H}_\lambda$,

creation and annihilation operators $\hat{a}_\lambda^\dagger$ and $\hat{a}_\lambda$,

and a number operator $\hat{N}_\lambda$.

We can also label the eigenstates similarly as $|\psi_{\lambda n}\rangle$ as being the *n*th eigenstate associated with the mode λ.

We should also change to using the coordinate ξ_λ,

since each different mode will have its own corresponding coordinate.

Mode notation - 2

With this notation, we can rewrite some of our results before to summarize the key relations for the electromagnetic mode case.

Analogous to Eq. (15.13)

$$\hat{H}_\lambda \equiv \hbar\omega_\lambda \left(\hat{a}_\lambda^\dagger \hat{a}_\lambda + \frac{1}{2} \right) \tag{15.65}$$

The number operator for this mode is defined, analogously to Eq.(15.15), as

$$\hat{N}_\lambda \equiv \hat{a}_\lambda^\dagger \hat{a}_\lambda \tag{15.66}$$

so, analogously to Eqs. (15.14) and (15.16)

$$\hat{N}_\lambda \left| \psi_{\lambda n} \right\rangle = \hat{a}_\lambda^\dagger \hat{a}_\lambda \left| \psi_{\lambda n} \right\rangle = n_\lambda \left| \psi_{\lambda n} \right\rangle \tag{15.67}$$

Now we make the association of n_λ with the number of photons in the mode,

with an energy that grows in proportion to the number of photons by an amount $n_\lambda \hbar\omega$.

Mode notation - 3

We also have the commutation relation, analogous to Eq.(15.17),

$$\left[\hat{a}_\lambda, \hat{a}_\lambda^\dagger\right] = \hat{a}_\lambda \hat{a}_\lambda^\dagger - \hat{a}_\lambda^\dagger \hat{a}_\lambda = 1 \tag{15.68}$$

We have the lowering relation, analogous to Eq. (15.29)

$$\hat{a}_\lambda \left|\psi_{\lambda n}\right\rangle = \sqrt{n_\lambda}\left|\psi_{\lambda n-1}\right\rangle \tag{15.69}$$

which now takes the state with n_λ ***photons in mode*** λ ***and changes it into the state with*** $n_\lambda - 1$ ***photons***

hence we call $\hat{a}_\lambda$ **the annihilation operator for than mode.**

Similarly, we have the raising relation, analogous to Eq. (15.31)

$$\hat{a}_\lambda^\dagger \left|\psi_{\lambda n}\right\rangle = \sqrt{n_\lambda + 1}\left|\psi_{\lambda n+1}\right\rangle \tag{15.70}$$

which is taking the state with n_λ ***photons in mode*** λ ***and changing it into the state with*** $n_\lambda + 1$ ***photons,***

so we call $\hat{a}_\lambda^\dagger$ **the creation operator for that mode.**

We also expect we have, by analogy with Eq.(15.31),

$$\hat{a}_\lambda \left|\psi_{\lambda 0}\right\rangle = 0 \tag{15.71}$$

and, as in Eq. (15.35)

$$\left|\psi_{\lambda n}\right\rangle = \frac{1}{\sqrt{n_\lambda !}}\left(\hat{a}_\lambda^\dagger\right)^{n_\lambda}\left|\psi_{\lambda 0}\right\rangle \tag{15.72}$$

Nature of the quantum mechanical states of an electromagnetic mode - 1

We have quantized the electromagnetic field mode by analogy,

leading to an abstract set of results.

Do we have to be this abstract?

Can't we use the wavefunction as before?

The wavefunction does have some meaning,

though it is quite different from that of the electron spatial wavefunction, for example.

Just as before in Eq.(15.33),

we have for the state with no photons in the mode,

$$\psi_{\lambda 0}\left(\xi_\lambda\right)=\frac{1}{\left(\pi\right)^{1/4}}\exp\left(-\frac{\xi_\lambda^2}{2}\right) \qquad (15.73)$$

but if we now work backwards to find the physical interpretation of the coordinate ξ_λ, we find, from Eqs. (15.50), (15.56), and (15.42),

$$B_y=\xi_\lambda\sqrt{\frac{2\mu_o\hbar\omega_\lambda}{L}}\cos kx \qquad (15.74)$$

Nature of the quantum mechanical states of an electromagnetic mode - 2

In other words,

ξ_λ ***is, in a dimensionless form, the amplitude of the mode of the magnetic field.***

It is not a spatial coordinate.

For example, we can interpret

$\left|\psi_{\lambda 0}\left(\xi_\lambda\right)\right|^2$ ***as being the probability that,***

for the lowest state of this electromagnetic field mode,

the field mode will be found to have (dimensionless) amplitude ξ_λ***.***

That probability is therefore the Gaussian $\left(1/\sqrt{\pi}\right)\exp\left(-\xi_\lambda{}^2\right)$**.**

We would find related results for the states of the mode with more photons.

Some non-classical behaviors

Note two behaviors very different from classical electromagnetic fields, namely

(i) that, in a state with a given number of photons,

the magnetic field amplitude is not a fixed quantity,

but is rather described by a distribution, and

(ii) even with no photons in the mode,

the magnetic field amplitude is not zero.

Similar results can be stated for the electric field mode amplitude.

The presence of such amplitudes of the electric and magnetic fields even with no photons is called

vacuum fluctuations.

In general, the states with specific numbers of photons,

which correspond to the eigenstates of the Hamiltonian or the number operator,

do *not* have precisely defined electric or magnetic field amplitudes.

Wavefunctions in quantized electromagnetic field modes

Though we may sometimes be interested in these distributions of magnetic or electric field amplitude,

we are generally much less interested in these than we were in the probabilities of finding particles at points in space.

As a result, in the quantized electromagnetic field,

we make relatively little use of the wavefunctions themselves.

Most of the results we are interested in,

such as processes where we are adding or subtracting photons

can more conveniently be described through the use of operators and state vectors.

Typically, the basis set and the resulting state we will use for electromagnetic fields

will not be written as functions, $\psi(\xi_\lambda)$, of the amplitudes, ξ_λ, of the fields in the modes,

but as basis vectors corresponding to specific numbers of photons in a mode,

i.e., basis vectors corresponding to energy or number eigenstates of the mode

$$\left|\psi_{\lambda n}\right\rangle \equiv \left|n_\lambda\right\rangle \qquad (15.75)$$

ξ_λ as an operator - 1

Remembering the original definitions of them in terms of ξ and $d/d\xi$, we have, analogously to Eq. (15.9)

$$\hat{a}_\lambda^\dagger \equiv \frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi_\lambda}+\xi_\lambda\right) \tag{15.76}$$

and, analogously to Eq. (15.10)

$$\hat{a}_\lambda \equiv \frac{1}{\sqrt{2}}\left(\frac{d}{d\xi_\lambda}+\xi_\lambda\right) \tag{15.77}$$

Now we note that we can write

$$\hat{\xi}_\lambda \equiv \frac{1}{\sqrt{2}}\left(\hat{a}_\lambda+\hat{a}_\lambda^\dagger\right) \tag{15.78}$$

ξ_λ as an operator - 2

Note that ξ_λ (which we can now write as $\hat{\xi}_\lambda$) is really an operator, not just a coordinate,

just like the position $\mathbf{r}$ in the spatial representation of electron wavefunctions

There we used the quantity $\mathbf{r}$ when we wanted to evaluate the expectation value of position in some state $\phi(\mathbf{r})$,

writing $\langle \mathbf{r} \rangle \equiv \langle \phi | \mathbf{r} | \phi \rangle = \int \phi^* (\mathbf{r}) \mathbf{r} \phi(\mathbf{r}) d^3\mathbf{r}$.

The ability to use the quantity as its own operator is a consequence of being in the representation based on that quantity.

In this $\mathbf{r}$ representation,

where we write $f(\mathbf{r})$ as a vector of its values at each of the points $\mathbf{r}$,

the operator corresponding to $\mathbf{r}$ is simply a diagonal matrix,

with elements of value $\mathbf{r}$ along the diagonal.

If we change representations, we must explicitly recognize that $\mathbf{r}$ is an operator, which should be written as $\hat{\mathbf{r}}$, and the corresponding matrix in any other basis is not diagonal.

Similarly ξ_λ is actually an operator, which we must recognize now that we will use this operator with the photon number basis states

Dimensionless generalized momentum operator

We can also write the dimensionless form of the generalized momentum operator, defined as in Eq. (15.62) as

$$\hat{\pi}_\lambda = -i d / d\xi_\lambda \equiv \hat{p}_\lambda / \sqrt{\hbar}\,, \tag{15.79}$$

in the form

$$\hat{\pi}_\lambda = \frac{i}{\sqrt{2}}\left(\hat{a}_\lambda^\dagger - \hat{a}_\lambda\right) \tag{15.80}$$

Field operators

With the definitions of the dimensionless operators ξ_λ and $\hat{\pi}_\lambda$,

we now substitute back into the relations (15.41) ($E_z = p(t)D\sin kx$) and (15.42) ($B_y = q(t)\frac{D}{c}\cos kx$) that defined the electric and magnetic fields in our mode.

Instead of scalar quantities for the electric and magnetic fields for this mode, we now have operators

$$\hat{E}_{\lambda z} = i\left(\hat{a}_\lambda^\dagger - \hat{a}_\lambda\right)\sqrt{\frac{\hbar\omega_\lambda}{\varepsilon_o L}}\sin kx \qquad (15.81)$$

and

$$\hat{B}_{\lambda y} = \left(\hat{a}_\lambda^\dagger + \hat{a}_\lambda\right)\sqrt{\frac{\mu_o\hbar\omega_\lambda}{L}}\cos kx \qquad (15.82)$$

Meaning of field operators

Just as before,

if we want to know the average value of a measurable quantity,

we take the expected value of its operator, and the same is true here.

For a state $|\phi\rangle$ of this mode, we would have

$$\langle E_{\lambda z} \rangle = \langle \phi | \hat{E}_{\lambda z} | \phi \rangle \tag{15.83}$$

$$\langle B_{\lambda y} \rangle = \langle \phi | \hat{B}_{\lambda y} | \phi \rangle \tag{15.84}$$

Quantum field theory

This postulation of operators for the electric and magnetic fields is an example of a

quantum field theory.

We started out in our discussion of quantum mechanics quantizing the states of a particle.

We have now come to a description in which we are quantizing a field,

and we can view the particles,

in this case photons,

as emerging from the quantization of the field.

It is also possible and useful to construct quantum field theories for electrons in a solid, for example,

which gives a particularly elegant way of writing solid state physics.

Much of modern quantum mechanics that is concerned with elementary particles is also in the form of quantum field theories.

Uncertainty principle of electric & magnetic fields in a mode - 1

Note that the electric and magnetic field operators do not commute

we cannot in general simultaneously know both the electric and magnetic field exactly!

Explicitly, from Eqs. (15.81) and (15.82), we have

$$\left[\hat{E}_{\lambda z},\hat{B}_{\lambda y}\right]=i\frac{\hbar\omega_\lambda}{L}\sqrt{\frac{\mu_o}{\varepsilon_o}}\sin kx\cos kx\left[\hat{a}_\lambda^\dagger-\hat{a}_\lambda,\hat{a}_\lambda+\hat{a}_\lambda^\dagger\right] \tag{15.85}$$

i.e.,

$$\left[\hat{E}_{\lambda z},\hat{B}_{\lambda y}\right]=$$

$$i\frac{\hbar\omega_\lambda}{L}\sqrt{\frac{\mu_o}{\varepsilon_o}}\sin kx\cos kx\left(\hat{a}_\lambda^\dagger\hat{a}_\lambda+\hat{a}_\lambda^\dagger\hat{a}_\lambda^\dagger-\hat{a}_\lambda\hat{a}_\lambda-\hat{a}_\lambda\hat{a}_\lambda^\dagger-\hat{a}_\lambda\hat{a}_\lambda^\dagger+\hat{a}_\lambda\hat{a}_\lambda-\hat{a}_\lambda^\dagger\hat{a}_\lambda^\dagger+\hat{a}_\lambda^\dagger\hat{a}_\lambda\right)$$

$$=2i\frac{\hbar\omega_\lambda}{L}\sqrt{\frac{\mu_o}{\varepsilon_o}}\sin kx\cos kx\left[\hat{a}_\lambda^\dagger\hat{a}_\lambda-\hat{a}_\lambda\hat{a}_\lambda^\dagger\right] \tag{15.86}$$

So, using the known commutator of the creation and annihilation operators, Eq. (15.68), we have

$$\left[\hat{E}_{\lambda z},\hat{B}_{\lambda y}\right]=2i\frac{\hbar\omega_\lambda}{L}\sqrt{\frac{\mu_o}{\varepsilon_o}}\sin kx\cos kx \tag{15.87}$$

Uncertainty principle of electric & magnetic fields in a mode - 2

We remember that the general form of the commutation relation,

$$\left[\hat{A},\hat{B}\right]=i\hat{C} \qquad \text{(Eq. (5.4))}$$

leads to the uncertainty principle

$$\Delta A \Delta B \geq \left|C\right|/2 \qquad \text{(from Eq. (5.23)),}$$

and so we have for the standard deviations of the expected values of the electric and magnetic fields in this mode

$$\Delta E_{\lambda z} \Delta B_{\lambda y} \geq \frac{\hbar\omega_\lambda}{L}\sqrt{\frac{\mu_o}{\varepsilon_o}}\sin kx \cos kx \qquad (15.88)$$

Harmonic oscillators and photons – 3

Reading – Sections 15.6 – 15.8

Quantum mechanical states of an electromagnetic field mode

Generalization to sets of modes

Vibrational modes

Quantum mechanical states of an electromagnetic field mode

Many states are possible quantum mechanically for the electromagnetic mode.

- ***Nearly all of these are quite different from the fields we are used to classically.***
  - **Examples include**
    - *the number states*
    - *the coherent state*
    - *and others, not discussed here, including*
      - squeezed states
      - photon antibunched states.

Only the coherent state has much relation to the fields we expect in a mode from a classical analysis.

- ***It is essentially the kind of field generated by a laser,***
  - **and corresponds quite closely to our classical notion of an electromagnetic field in a mode.**

The other states are in practice quite difficult to generate controllably,

- ***generally requiring sophisticated nonlinear optical techniques,***
  - **and have all only been demonstrated to a limited degree in the laboratory.**

Number state - 1

The eigenstates $|n_\lambda\rangle$ of the Hamiltonian and the number operator correspond to a specific number n_λ photons in the mode, and are known as the number states or Fock states.

In these states, the probability of measuring any particular amplitude $B_{\lambda y}$ in the mode

is distributed according to the square of the Hermite-Gaussian harmonic oscillator solutions with quantum number n_λ.

The $E_{\lambda z}$ amplitudes are similarly distributed.

The expectation values of the electric and magnetic field amplitudes are both zero for any number state.

For example, for the electric field mode amplitude, we have

$$\begin{aligned}\langle n_\lambda|\hat{E}_{\lambda z}|n_\lambda\rangle &= i\sqrt{\frac{\hbar\omega_\lambda}{L\varepsilon_o}}\sin kx\langle n_\lambda|\hat{a}_\lambda^\dagger - \hat{a}_\lambda|n_\lambda\rangle \\ &= i\sqrt{\frac{\hbar\omega_\lambda}{L\varepsilon_o}}\sin kx\left(\sqrt{n+1}\langle n_\lambda||n_\lambda+1\rangle - \sqrt{n}\langle n_\lambda||n_\lambda-1\rangle\right) = 0\end{aligned} \qquad (15.89)$$

because the states $|n_\lambda\rangle$, $|n_\lambda - 1\rangle$, and $|n_\lambda + 1\rangle$ are all orthogonal,

being different eigenstates of the same Hermitian operator.

A similar proof can be performed for the magnetic field mode amplitude.

Number state - 2

We might think it very odd that there may be energy in this mode,

but yet there appears to be no field.

It is not correct that there is no field in the mode,

it is just that the average value of the amplitude is zero.

This can be explained if we presume that the phase of the field is quite undetermined in such a number state.

Any given measurement is quite likely to result in a finite amplitude for the electric or magnetic field in the mode,

but,

because of the possibility of the amplitude being positive or negative,

the average is zero.

We do see, though, that the number states, while simple mathematically, bear little relation to classical fields.

Representation of time dependence – Schrödinger and Heisenberg representations - 1

So far, from a quantum mechanical point of view

we have used solutions to the time-independent Schrödinger equation for the electromagnetic mode.

Note here that we use the term "Schrödinger equation" in the generalized sense where we mean that

$$\hat{H}|\phi\rangle = E|\phi\rangle \tag{15.90}$$

is a (time-independent) Schrödinger equation for a system

in an eigenstate $|\phi\rangle$ with eigenenergy E.

Explicitly, for the eigenstates of our electromagnetic mode, we have

$$\hat{H}|n_\lambda\rangle = (n_\lambda + 1/2)\hbar\omega_\lambda |n_\lambda\rangle \tag{15.91}$$

In our generalization of our earlier postulations about quantum mechanics,

we also postulate here that the time-dependent generalized Schrödinger equation is valid, i.e.,

$$\hat{H}|\phi\rangle = i\hbar \frac{\partial}{\partial t}|\phi\rangle \tag{15.92}$$

This postulation does appear to work.

Representation of time dependence – Schrödinger and Heisenberg representations - 2

We implicitly assume the time-dependence of the system is described by

time-dependence of the state, not of the operators.

It is a matter of taste whether we put the time dependence into the states or the operators.

When we evaluate the expectation value of the operator, we obtain identical results.

The time-dependent state picture is described as the Schrödinger representation,

and the time-dependent operator picture is described as the Heisenberg representation.

Either one is valid,

though in the Heisenberg representation we cannot use the time-dependent Schrödinger equation,

and must use a somewhat different, but equivalent, formalism.

Here we will explicitly operate in the Schrödinger picture,

adding the time dependence to the states,

and choosing the operators (specifically the creation and annihilation operators) to be time-independent.

Time-dependence of states in the electromagnetic mode

With this approach to describing time-dependence,

as before, to get the time variation of a given state,

we multiply the time-independent energy eigenstate descriptions by $\exp\left[-i\left(n_\lambda+1/2\right)\hbar\omega_\lambda t/\hbar\right]=\exp\left[-i\left(n_\lambda+1/2\right)\omega_\lambda t\right]$

to make Eq.(15.91)

$$\hat{H}\left|n_\lambda\right\rangle=\left(n_\lambda+1/2\right)\hbar\omega_\lambda\left|n_\lambda\right\rangle$$

consistent with Eq. (15.92).

$$\hat{H}\left|\phi\right\rangle=i\hbar\frac{\partial}{\partial t}\left|\phi\right\rangle$$

Including the time dependence in this way, our number states become

$$\exp\left[-i\left(n_\lambda+1/2\right)\omega_\lambda t\right]\left|n_\lambda\right\rangle \qquad (15.93)$$

Coherent state

The state that corresponds most closely to the classical field in an electromagnetic mode is the coherent state

introduced previously as an example with the harmonic oscillator.

Now, using our current notation,

we can rewrite the coherent state originally proposed in Eq. (3.23) as

$$\left|\Psi_{\lambda\bar{n}}\right\rangle = \sum_{n_\lambda=0}^{\infty} c_{\lambda\bar{n}n} \exp\left[-i\left(n_\lambda + \frac{1}{2}\right)\omega_\lambda t\right]\left|n_\lambda\right\rangle \tag{15.94}$$

where

$$c_{\lambda\bar{n}n} = \sqrt{\frac{\bar{n}^{n_\lambda}\exp(-\bar{n})}{n_\lambda!}} \tag{15.95}$$

Here the quantity $\bar{n}$ will turn out to be the expected value of the number of photons in the mode.

As before, we note that

$$\left|c_{\lambda\bar{n}n}\right|^2 = \frac{\bar{n}^{n_\lambda}\exp(-\bar{n})}{n_\lambda!} \tag{15.96}$$

is the Poisson distribution with mean $\bar{n}$ and standard deviation $\sqrt{\bar{n}}$.

Statistics of photons in coherent states

Note that, in the coherent state, the number of photons in the mode is not determined.

The coefficients $\left|c_{\lambda\bar{n}n}\right|^2$ tell us the probability that

we will find n_λ photons in the mode if we make a measurement.

This number is now found to be distributed according to a Poisson distribution.

It is in fact the case that the statistics of the number of photons in an oscillating "classical" electromagnetic field are Poissonian.

For example,

if one puts a photodetector in a laser beam,

one will measure a Poissonian distribution of the arrival rates of the photons,

an effect known as shot noise.

Coherent state as an eigenstate of a non-Hermitian operator

Note that the coherent state is not an eigenstate of any operator representing a physically observable quantity.

In fact the coherent states are the eigenstates of the annihilation operator, $\hat{a}$***, the proof of which is left as an exercise.***

The annihilation operator is not a Hermitian operator, and does not represent an observable physical quantity.

Oscillation in coherent states

We have shown by explicit illustration before that

- ***this state oscillates at frequency ω_λ,***
  - **and that remains true here.**

In this state, the electric and magnetic fields do not have precise values,

- ***just as the position did not have precise values before in the mechanical harmonic oscillator.***

As the average number of photons $\bar{n}$ increases,

- ***the relative variation in the values of the electric and magnetic fields decreases,***
  - **and the behavior resembles a classical pair of oscillating electric and magnetic fields ever more closely.**

Oscillation in coherent states

Example animations (click on the desired $\bar{n}$ expression)

$\bar{n} = 1$ oscillations

$\bar{n} = 10$ oscillations

$\bar{n} = 100$ oscillations

Generalization to sets of modes

Thus far, we have considered only one specific plane wave mode of the electromagnetic field.

Now we extend to complete sets of modes for describing classical solutions of Maxwell's equations.

e.g., propagating or standing waves in free space

Laguerre-Gaussian modes of a typical laser cavity

Each such mode is a harmonic oscillator with annihilation and creation operators.

Sets of classical modes - 1

Now we postulate a set of classical modes, each of which has the following form

$$\mathbf{E}_\lambda(\mathbf{r},t) = -p_\lambda(t) D_\lambda \mathbf{u}_\lambda(\mathbf{r}) \qquad (15.97)$$

$$\mathbf{B}_\lambda(\mathbf{r},t) = q_\lambda(t) \frac{D_\lambda}{c} \mathbf{v}_\lambda(\mathbf{r}) \qquad (15.98)$$

Here $\mathbf{E}_\lambda$, $\mathbf{B}_\lambda$, $\mathbf{u}_\lambda$, and $\mathbf{v}_\lambda$ are all in general vectors, and D_λ is a constant.

The forms of Eqs. (15.41) and (15.42) correspond to these with $\mathbf{u}_\lambda(\mathbf{r}) = -\hat{\mathbf{z}}\sin(kx)$ and $\mathbf{v}_\lambda(\mathbf{r}) = \hat{\mathbf{y}}\cos(kx)$.)

These satisfy Maxwell's equations and the wave equation in free space if we require that

$$\nabla \times \mathbf{u}_\lambda(\mathbf{r}) = \frac{\omega_\lambda}{c} \mathbf{v}_\lambda(\mathbf{r}) \qquad (15.99) \qquad \nabla \times \mathbf{v}_\lambda(\mathbf{r}) = \frac{\omega_\lambda}{c} \mathbf{u}_\lambda(\mathbf{r}) \qquad (15.100)$$

$$\frac{dq_\lambda}{dt} = \omega_\lambda p_\lambda \qquad (15.101) \qquad \frac{dp_\lambda}{dt} = -\omega_\lambda q_\lambda \qquad (15.102)$$

We presume the classical electromagnetic problem has been solved with the boundary conditions of the system to yield these electromagnetic modes for the problem.

Sets of classical modes - 2

We will also presume that

the spatial functions $\mathbf{u}_\lambda(\mathbf{r})$ *and* $\mathbf{v}_\lambda(\mathbf{r})$ *are normalized over the entire volume*

they are all orthogonal, i.e.,

$$\int \mathbf{u}_{\lambda 1}(\mathbf{r}).\mathbf{u}_{\lambda 2}(\mathbf{r})d^3\mathbf{r}=\delta_{\lambda 1,\lambda 2} \tag{15.103}$$

and

$$\int \mathbf{v}_{\lambda 1}(\mathbf{r}).\mathbf{v}_{\lambda 2}(\mathbf{r})d^3\mathbf{r}=\delta_{\lambda 1,\lambda 2} \tag{15.104}$$

Classical superpositions and energy

Now suppose the system is in a classical superposition of such electromagnetic modes, i.e.,

$$\mathbf{E}(\mathbf{r},t)=\sum_{\lambda}-p_{\lambda}(t)D_{\lambda}\mathbf{u}_{\lambda}(\mathbf{r}) \quad (15.105)$$

$$\mathbf{B}(\mathbf{r},t)=\sum_{\lambda}q_{\lambda}(t)\frac{D_{\lambda}}{c}\mathbf{v}_{\lambda}(\mathbf{r}) \quad (15.106)$$

We can write for the total energy of such a field

$$\begin{aligned}H&=\int\frac{1}{2}\left(\varepsilon_o\mathbf{E}^2+\frac{1}{\mu_o}\mathbf{B}^2\right)d^3\mathbf{r}\\&=\frac{1}{2}\varepsilon_o\sum_{\lambda 1,\lambda 2}D_{\lambda 1}D_{\lambda 2}\int\left[p_{\lambda 1}p_{\lambda 2}\mathbf{u}_{\lambda 1}(\mathbf{r}).\mathbf{u}_{\lambda 2}(\mathbf{r})+q_{\lambda 1}q_{\lambda 2}\mathbf{v}_{\lambda 1}(\mathbf{r}).\mathbf{v}_{\lambda 2}(\mathbf{r})\right]d^3\mathbf{r} \quad (15.107)\\&=\frac{1}{2}\varepsilon_o\sum_{\lambda}D_{\lambda}^2\left(p_{\lambda}^2+q_{\lambda}^2\right)\end{aligned}$$

where we have used the orthogonality of the spatial electromagnetic modes to eliminate all cross-terms in the integral,

and have used $1/c^2=\varepsilon_o\mu_o$**.**

Separation into classical Hamiltonians for each mode - 1

We can write this total energy (or classical Hamiltonian function) as

the sum of separate energies (or classical Hamiltonian functions) for each separate mode, i.e.,

$$H = \sum_{\lambda} H_{\lambda} \tag{15.108}$$

where

$$H_{\lambda} = \frac{1}{2}\varepsilon_o D_{\lambda}^2 \left(p_{\lambda}^2 + q_{\lambda}^2 \right) \tag{15.109}$$

We cast this classical mode Hamiltonian into the correct form so that we get Hamilton's equations as in (15.38) and (15.40),

i.e., in the present notation we want to obtain

$$\frac{dp_{\lambda}}{dt} = -\frac{\partial H_{\lambda}}{\partial q_{\lambda}} \tag{15.110}$$

and

$$\frac{dq_{\lambda}}{dt} = \frac{\partial H_{\lambda}}{\partial p_{\lambda}} \tag{15.111}$$

Separation into classical Hamiltonians for each mode - 2

If we choose

$$D_\lambda = \sqrt{\frac{\omega_\lambda}{\varepsilon_o}} \tag{15.112}$$

then we now have

$$H_\lambda = \frac{\omega_\lambda}{2}\left(p_\lambda^2 + q_\lambda^2\right) \tag{15.113}$$

Explicitly considering Eq. (15.111) ($\frac{dq_\lambda}{dt} = \frac{\partial H_\lambda}{\partial p_\lambda}$), for example, we have, using Eq. (15.101) ($\frac{dq_\lambda}{dt} = \omega_\lambda p_\lambda$)

$$\frac{\partial H_\lambda}{\partial p_\lambda} = \omega_\lambda p_\lambda = \frac{dq_\lambda}{dt} \tag{15.114}$$

as required.

Quantization of individual modes

We can proceed for each mode exactly as we did before,

quantizing each mode with its own annihilation and creation operators.

We postulate a "momentum" operator for each mode, as in Eq. (15.59)

$$\hat{p}_\lambda = -i\hbar \frac{d}{dq_\lambda} \tag{15.115}$$

and thereby propose the quantum mechanical Hamiltonian for the mode as in Eq.(15.60), from Eq. (15.113) above

$$\hat{H}_\lambda = \frac{\omega_\lambda}{2}\left[-\hbar^2 \frac{d^2}{dq_\lambda{}^2} + q_\lambda^2\right] \tag{15.116}$$

We next rewrite this Hamiltonian as in Eqs. (15.63) and (15.65) as

$$\hat{H}_\lambda = \frac{\hbar\omega_\lambda}{2}\left[-\frac{d^2}{d\xi_\lambda{}^2} + \xi_\lambda{}^2\right] = \hbar\omega_\lambda\left(\hat{a}_\lambda^\dagger \hat{a}_\lambda + \frac{1}{2}\right) \tag{15.117}$$

where we have defined dimensionless units $\xi_\lambda = q_\lambda / \sqrt{\hbar}$***, and have creation and annihilation operators defined as in Eq. (15.9)***

$$\hat{a}_\lambda^\dagger \equiv \frac{1}{\sqrt{2}}\left(-\frac{d}{d\xi_\lambda} + \xi_\lambda\right) \tag{15.118}$$

$$\hat{a}_\lambda \equiv \frac{1}{\sqrt{2}}\left(\frac{d}{d\xi_\lambda} + \xi_\lambda\right) \tag{15.119}$$

with the total Hamiltonian for the set of modes $\hat{H} = \sum_\lambda \hbar\omega_\lambda\left(\hat{a}_\lambda^\dagger \hat{a}_\lambda + \frac{1}{2}\right)$ (15.120)

Multimode photon states

When we are considering multiple different photon modes,

it is convenient to write the state of such a system in what we can call the

occupation number representation.

In such a representation,

for each basis state we merely write down a list of the number of photons in each particular mode.

For example, the state with

one photon in mode k*, three in mode* m *and none in any other mode*

could be written as

$$\left|0_a, \ldots, 0_j, 1_k, 0_l, 3_m, 0_n, \ldots\right\rangle$$

where we have labeled the modes progressively with the lower case letters.

Single mode creation and annihilation operators with multimode states

Just as before, the creation and annihilation operators will have the properties, now specific to the given mode, analogous to Eq.(15.69),

$$\hat{a}_\lambda \left| \ldots, n_\lambda, \ldots \right\rangle = \sqrt{n_\lambda} \left| \ldots, (n_\lambda - 1)_\lambda, \ldots \right\rangle \tag{15.121}$$

with

$$\hat{a}_\lambda \left| \ldots, 0_\lambda, \ldots \right\rangle = 0 \tag{15.122}$$

Similarly, analogous to Eq.(15.70), we have

$$\hat{a}_\lambda^\dagger \left| \ldots, n_\lambda, \ldots \right\rangle = \sqrt{n_\lambda + 1} \left| \ldots, (n_\lambda + 1)_\lambda, \ldots \right\rangle \tag{15.123}$$

As in Eq.(15.66), the number operator for a specific mode in the multimode case is

$$\hat{N}_\lambda \equiv \hat{a}_\lambda^\dagger \hat{a}_\lambda \tag{15.124}$$

Writing multimode states using operators

We can create a multimode state by progressively operating with the appropriate creation operators starting mathematically with the

"zero" state or completely "empty" state,

often written simply as $|0\rangle$***.***

For the above example state, we could write

$$\left|0_a,\ldots,0_j,1_k,0_l,3_m,0_n,\ldots\right\rangle = \frac{1}{\sqrt{1!3!}}\hat{a}_k^\dagger\hat{a}_m^\dagger\hat{a}_m^\dagger\hat{a}_m^\dagger\left|0\right\rangle \tag{15.125}$$

where we had to introduce the square root factor with factorials so that we could keep the state normalized,

compensating for the square root factors introduced by the creation operators.

In general, we can write a state with n_1 **particles in mode 1,** n_2 **particles in mode 2, and so on, as**

$$\left|n_1,n_2,\ldots,n_\lambda,\ldots\right\rangle = \frac{1}{\sqrt{n_1!n_2!\ldots n_\lambda!\ldots}}\left(\hat{a}_1^\dagger\right)^{n_1}\left(\hat{a}_2^\dagger\right)^{n_2}\ldots\left(\hat{a}_\lambda^\dagger\right)^{n_\lambda}\ldots\left|0\right\rangle \tag{15.126}$$

Commutation relations for boson operators - 1

With bosons, it makes no difference to the final state in what order we create particles in a mode.

The result of a different order of creation could be viewed as permuting

the particles (the photons)

among the single particle states (here the modes),

but any permutation of bosons among the single particle states makes no difference to the resulting multi-boson state.

Hence the creation operators commute with one another,

i.e., for operators operating on any state,

$$\hat{a}_j^\dagger \hat{a}_k^\dagger = \hat{a}_k^\dagger \hat{a}_j^\dagger ,$$

or, in the form of a commutation relation

$$\hat{a}_j^\dagger \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_j^\dagger = 0 \qquad (15.127)$$

A similar argument can be made for annihilation operators that it does not matter what order we destroy particles, and so we similarly have

$$\hat{a}_j \hat{a}_k - \hat{a}_k \hat{a}_j = 0 \qquad (15.128)$$

Commutation relations for boson operators - 2

For the case of mixtures of annihilation and creation operators,

if we are annihilating a boson in one mode and creating one in another,

it does not matter what order we do that either.

Only if we are creating and annihilating in the same mode does it matter what order we do this,

with a commutation relation we have previously deduced (Eq.(15.68)).

Hence in general we can write

$$\hat{a}_j \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_j = \delta_{jk} \qquad (15.129)$$

This completes the commutation relations we need for the boson operators,

and the relations we need for working with photons themselves in a quantum mechanical manner.

Multimode field operators - 1

It is now straightforward to construct the full multimode electric and magnetic field operators.

Working from the classical definition of the multimode electric field, Eq. (15.105) ($\mathbf{E}(\mathbf{r},t)=\sum_{\lambda}-p_{\lambda}(t)D_{\lambda}\mathbf{u}_{\lambda}(\mathbf{r})$), as an expansion in classical field modes,

we substitute the operator $\hat{p}_{\lambda}$ for the quantity $p_{\lambda}(t)$ in each mode,

using also the value of D_{λ} from (15.112)($D_{\lambda}=\sqrt{\frac{\omega_{\lambda}}{\varepsilon_o}}$),

obtaining

$$\hat{\mathbf{E}}=\sum_{\lambda}-\hat{p}_{\lambda}(t)\sqrt{\frac{\omega_{\lambda}}{\varepsilon_o}}\mathbf{u}_{\lambda}(\mathbf{r}) \tag{15.130}$$

Noting that, from Eqs. (15.79) and (15.80),

$$\hat{p}_{\lambda}=i\sqrt{\frac{\hbar}{2}}\left(\hat{a}_{\lambda}^{\dagger}-\hat{a}_{\lambda}\right) \tag{15.131}$$

we therefore have

$$\hat{\mathbf{E}}(\mathbf{r},t)=i\sum_{\lambda}\left(\hat{a}_{\lambda}-\hat{a}_{\lambda}^{\dagger}\right)\sqrt{\frac{\hbar\omega_{\lambda}}{2\varepsilon_o}}\mathbf{u}_{\lambda}(\mathbf{r}) \tag{15.132}$$

Multimode field operators - 2

By a similar argument,

we can start with the classical expression for a multimode magnetic field, Eq. (15.106) ($\mathbf{B}(\mathbf{r},t)=\sum_{\lambda} q_{\lambda}(t)\frac{D_{\lambda}}{c}\mathbf{v}_{\lambda}(\mathbf{r})$),

substituting the operator $\hat{q}_{\lambda}$ for the quantity $q_{\lambda}(t)$ in each mode, to obtain

$$\mathbf{B}(\mathbf{r},t)=\sum_{\lambda}\hat{q}_{\lambda}\frac{D_{\lambda}}{c}\mathbf{v}_{\lambda}(\mathbf{r}) \tag{15.133}$$

Using Eqs. (15.61) and (15.78), we can write

$$\hat{q}_{\lambda} \equiv \sqrt{\frac{\hbar}{2}}\left(\hat{a}_{\lambda}+\hat{a}_{\lambda}^{\dagger}\right) \tag{15.134}$$

so we obtain

$$\hat{\mathbf{B}}(\mathbf{r},t)=\sum_{\lambda}\left(\hat{a}_{\lambda}+\hat{a}_{\lambda}^{\dagger}\right)\sqrt{\frac{\hbar\omega_{\lambda}\mu_{o}}{2}}\mathbf{v}_{\lambda}(\mathbf{r}) \tag{15.135}$$

Vibrational modes - 1

At the start of this chapter, we dealt with an abstract harmonic oscillator.

Any mechanical vibrating mode can also be analyzed in this way.

Such modes occur in particular in molecules and in crystalline solids.

In a classical view, we can think of systems of atoms as being masses connected by springs.

In principle, there is a spring connecting each mass to each other mass.

For any finite number N of such masses

we can write down $3N$ coupled differential equations

(one for each mass and each of the three spatial coordinate directions)

in which the forces from the springs connecting to each other mass act on a given mass to accelerate it according to Newton's second law.

One then looks for solutions in which every mass in the crystal is oscillating at the same frequency.

This leads to a matrix equation that can be solved for the eigenvectors,

with the frequency (or its square) essentially as the eigenvalues.

The resulting eigenvectors correspond to the modes of the system,

and are known as the normal modes.

Vibrational modes - 2

If we change to these eigenvectors as the mathematical basis,

- ***we again obtain a set of uncoupled harmonic oscillator equations.***
  - **The overall amplitude of the mode's displacement from its equilibrium position behaves like the position coordinate of a harmonic oscillator,**
  - **and a corresponding coordinate based on the time rate of change of the position coordinate and a mass parameter serves as the momentum coordinate.**

We then rigorously obtain equations for each mode that can be quantized using harmonic oscillator model above.

- ***Each mode then has its own creation and annihilation operators.***
  - **This analysis leads to a formalism that,**
    - *when expressed in terms of boson creation and annihilation operators,*
  - **is identical to that from Eq. (15.108) to Eq. (15.129) of the multimode photon case above.**
- ***Instead of photon modes, we have the normal modes of vibration of the system.***

We can also think of quasi-particles occupying these modes just as we think of photons occupying the photon modes.

- ***In solid state physics for crystalline materials, the resulting particles are called phonons.***

Fermion operators – 1

Reading – Section 16.1 up to the start of "Mixtures of creation and annihilation operators"

Postulation of fermion annihilation and creation operators

Fermion annihilation and creation operators

Annihilation and creation operators for boson modes led to the quantization of the electromagnetic field into photons

Here we introduce annihilation and creation operators for fermions.

These operators will lead to the natural quantization of the number of fermions possible in a fermion "mode",

limiting us to zero or one as required,

and,

analogously to the boson operator description of the electromagnetic wave with field operators,

will allow us to describe the quantum mechanical wave associated with electrons and similar particles in terms of the fermion operators

Once we work in systems with many fermions,

the use of fermion creation and annihilation operators is almost essential from a practical point of view.

Even with a single fermion,

the creation and annihilation operators give a particularly simple notation that we can use to describe other operators, such as the Hamiltonian.

Postulation of fermion annihilation and creation operators

Here we postulate annihilation and creation operators for fermions, giving them the required properties.

- ***The key property these operators require, in comparison to the boson operators, is that***
  - **they will correctly change the sign of the wavefunction upon exchange of particles.**
- ***This will lead us to a formalism similar in character to the boson operators,***
  - **though we will find so-called anticommutation relations instead of the commutation relations of the boson operators.**

With such fermion operators we never again have to worry about the details of the antisymmetry with respect to exchange of fermions;

- ***the anticommutation relations will take care of these details quite conveniently.***

Description and ordering of multiple fermion states - 1

Remember that we can write a basis state for multiple identical fermions as

$$\left|\psi_{N;\,a,b,\ldots n}\right\rangle = \frac{1}{\sqrt{N!}}\sum_{\hat{P}=1}^{N!}\pm\hat{P}\left|\,|1,a\rangle|2,b\rangle|3,c\rangle\ldots|N,n\rangle\right\rangle$$
$$\equiv \frac{1}{\sqrt{N!}}\begin{vmatrix} |1,a\rangle & |2,a\rangle & \cdots & |N,a\rangle \\ |1,b\rangle & |2,b\rangle & \cdots & |N,b\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |1,n\rangle & |2,n\rangle & \cdots & |N,n\rangle \end{vmatrix} \tag{16.1}$$

Here, there are N identical fermions, and they occupy single-particle basis states $a, b, \ldots, n$.

Single-particle basis states are individual states a fermion can occupy, and here each has a lower case letter associated with it.

For example,

each possible electron state in a potential well or atom corresponds to a different single-particle basis state here.

If we had a system with multiple potential wells or atoms, each possible single electron state associated with each potential well or atom would have its own unique label.

Description and ordering of multiple fermion states - 2

Though the notation above might seem to imply that each of the possible states is occupied, that is not in general the case.

- ***In fact, very few of the possible single-particle states will be occupied in any given multiple fermion basis state.***
  - **We might, for example have**
    - *three electrons in a system with five potential wells,*
      - and be considering a (multiple particle) basis state in which there is
        - one electron in the ground state of well 1,
        - one in the second state of well 3, and
        - one in the 17th state of well 4.
      - All of the other single-particle basis states would be unoccupied in this multiple particle basis state.
- ***The formalism also allows a mathematical basis state that might have two electrons in one well,***
  - **one on the lowest state and**
  - **one on the sixth state**
- ***Such a state is a viable two-particle basis state,***
  - **though it is not necessarily an eigenstate of the Hamiltonian**
    - *(the first electron would give rise to a repulsive potential for the second electron, and so the second electron would not see a simple square potential any more).*

Comparison of the boson and fermion cases

Each of the single-particle fermion basis states can be considered as a "mode" of the fermion field,

just as the boson basis states were modes of the electromagnetic field.

The boson modes could have any integer number of particles in them,

though the fermion modes can only have zero or one.

Just as the boson annihilation and creation operators for a given mode allowed

any positive or zero integer number of bosons in the mode,

so also the fermion annihilation and creation operators will allow

only zero or one fermion in the mode

if we set them up correctly.

Choice of an order for labeling single-particle fermion states

It is important in our manipulations in the fermion case that,

in the determinants for the multiple fermion basis functions,

we define one standard order of labeling of the single-particle basis states.

For example, if we had a system with five potential wells,

we might label sequentially all of the states in well 1,

then next all of the states in well 2, and so on.

We could choose some other labeling sequence,

labeling all of the first states in wells 1 through 5,

then all of the second states in wells 1 through 5,

and so on,

or we could even choose some more complicated labeling sequence.

It does not matter what sequence we choose,

but we have to have one standard labeling sequence.

Here, we label the single-particle basis states (or fermion modes) using the lower case letters,

and our standard order will be the one in which those lower case letters are in alphabetical order.

Example 3 fermion state and occupation number notation

We might, for example, have a basis state corresponding to three identical fermions,

one in state b, one in state k, and one in state m.

In standard order, we would write that state as

$$\left|\psi_{3;\,b,k,m}\right\rangle = \frac{1}{\sqrt{3!}}\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \equiv \left|0_a,1_b,0_c,\ldots,1_k,0_{l,}\ldots,1_m,0_n\ldots\right\rangle \tag{16.2}$$

Here we have also introduced another notation to describe this basis state,

which we can describe as the occupation number notation.

This notation is similar to the boson occupation number notation

In this notation,

0_a ***in the ket means that the single-particle fermion state (or fermion mode) a is empty, and***

1_b ***means state b is occupied***

Because this is a fermion state, the determinant combination of the different fermions to the occupied states is understood.

States not in standard order

We could also write a state that was not in standard order for the rows, e.g.,

$$\left|\psi_{3;\,k,b,m}\right\rangle = \frac{1}{\sqrt{3!}}\begin{vmatrix} |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \tag{16.3}$$

To get that state into standard order for the rows,

we would have to swap the first and second rows in the determinant.

We know that if we swap two adjacent rows in a determinant

we have to multiple the determinant by -1***,***

and so, swapping the top two rows, we have

$$\left|\psi_{3;\,k,b,m}\right\rangle = -\frac{1}{\sqrt{3!}}\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \tag{16.4}$$

$$= -\left|0_a,1_b,0_c,\ldots,1_k,0_l,\ldots,1_m,0_n\ldots\right\rangle = -\left|\psi_{3;\,b,k,m}\right\rangle$$

Fermion creation operators

Now we postulate a fermion creation operator for fermion “mode” or single-particle basis state k,

and write it as $\hat{b}_k^\dagger$.

It must take any state in which single-particle basis state k is empty and

turn it into one in which this state k is occupied.

We also need it to have a very particular behavior with regard to the sign of the wavefunction it creates,

so that operations that are equivalent to swapping two particles will change the sign of the wavefunction.

This sign behavior means we have to construct the operator with some care over signs, though in the end this is quite straightforward.

These sign requirements lead to a very particular kind of commutation relation for the fermion annihilation and creation operators (an anticommutation relation).

Here we will progressively build up the properties of these operators, starting with the creation operator.

Construction of creation operator - 1

Suppose we start with the state where

single-particle states b and m are occupied,

but state k and all other states are not.

In the permutation notation, we therefore propose that $\hat{b}_k^\dagger$ has the following effect on that state:

$$\hat{b}_k^\dagger \frac{1}{\sqrt{2!}} \sum_{\hat{P}=1}^{2!} \pm \hat{P} \left| |1,b\rangle |2,m\rangle \right\rangle = \frac{1}{\sqrt{3!}} \sum_{\hat{P}=1}^{3!} \pm \hat{P} \left| |1,b\rangle |2,m\rangle |3,k\rangle \right\rangle \tag{16.5}$$

In other words, the action of $\hat{b}_k^\dagger$ is to add a third particle into the system,

and we propose that it adds it to the end of the list in the permutation notation.

Adding to the end of the list is equivalent to adding a row to the bottom of the determinant (and a column to the right), i.e., (16.5) is also

(now dropping the normalization factors just for convenience since we are primarily interested in the sign behavior here)

$$\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix} \tag{16.6}$$

(Note that the sequence in the permutation notation is the same as the sequence down the leading diagonal of the determinant notation.)

Construction of creation operator - 2

For this case,

$$\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix}$$

the determinant is not written in standard order.

To get this particular determinant into standard order,

we need to swap the bottom two rows,

and in performing this one swap,

we must therefore multiply the determinant by -1.

Hence, in this case

$$\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = -\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \tag{16.7}$$

Construction of creation operator - 3

Suppose now that we add another particle,

this time in state j,

using the operator $\hat{b}_j^\dagger$.

Then we have

$$\hat{b}_j^\dagger \hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = -\hat{b}_j^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix}$$
$$= -\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \end{vmatrix} \qquad (16.8)$$

To get to standard order,

we have to swap the bottom j row with the adjacent m row,

multiplying by -1,

and then swap the j row, now second from the bottom, with the adjacent k row,

multiplying again by -1,

Construction of creation operator - 4

i.e.,

$$\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \end{vmatrix} \rightarrow -1 \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix}$$

$$\rightarrow (-1)^2 \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix} \qquad (16.9)$$

and so

$$\hat{b}_j^\dagger \hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = -\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix} \qquad (16.10)$$

Construction of creation operator - 5

Now suppose we do this two-particle creation operation in the opposite order.

First, just as for Eq. (16.7)

$$\hat{b}_j^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = -\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \qquad (16.11)$$

Next, if we operate with $\hat{b}_k^\dagger$ we obtain

$$\hat{b}_k^\dagger \hat{b}_j^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = -\begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \end{vmatrix} \qquad (16.12)$$

Construction of creation operator - 6

Now, however,

we only have to swap adjacent rows once,

not twice as in (16.9),

to get the determinant into standard order,

i.e., swapping the bottom two rows and multiplying by -1, we obtain

$$\hat{b}_k^\dagger \hat{b}_j^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} = \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix} \qquad (16.13)$$

This result is -1 times the result from that of the operators in the order $\hat{b}_j^\dagger \hat{b}_k^\dagger$ in (16.10).

Note that this behavior corresponds exactly to what we want for fermion creation operators.

Swapping two particles must give a change in sign for the overall fermion wavefunction.

Creating two particles in one order rather than the other must give a result that is equivalent to swapping the two particles in the resulting state.

Generality of sign behavior for creation operator pairs - 1

This behavior of obtaining opposite signs for the result if the particles are created in opposite order is a general one.

It does not matter what the initial state is or what specific states the particles are being created in.

For example, we would get the same difference in sign in the result if we had considered the pairs of operators $\hat{b}_a^\dagger \hat{b}_k^\dagger$ and $\hat{b}_k^\dagger \hat{b}_a^\dagger$, or the pairs $\hat{b}_j^\dagger \hat{b}_n^\dagger$ and $\hat{b}_n^\dagger \hat{b}_j^\dagger$.

Note one of the pairs of operators always results in one more swap of adjacent rows than the other,

because it encounters one more row to be swapped.

In the pair $\hat{b}_j^\dagger \hat{b}_k^\dagger$,

the row added by $\hat{b}_j^\dagger$ is swapped past the row for a particle in state k,

whereas the row added by $\hat{b}_k^\dagger$ in the pair $\hat{b}_k^\dagger \hat{b}_j^\dagger$ does not have to be swapped past the row added by the $\hat{b}_j^\dagger$.

This asymmetry is because one of the two states in the pair has to be ahead of the other in the standard order.

Generality of sign behavior for creation operator pairs - 2

Hence we have the result,

valid for any state with single-particle states j and k initially empty

$$\hat{b}_j^\dagger \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j^\dagger = 0 \qquad (16.14)$$

In fact, this relation (16.14) is universally true for any state.

Note first that, for any state in which state k is initially occupied,

the fermion creation operator for that state must have the property that

$$\hat{b}_k^\dagger \left| \ldots, 1_k, \ldots \right\rangle = 0 \qquad (16.15)$$

because we cannot create two fermions in one single-particle state.

Hence when the single-particle state k is occupied, trivially we have

$$\hat{b}_j^\dagger \hat{b}_k^\dagger \left| \ldots, 1_k, \ldots \right\rangle = 0 \text{ and } \hat{b}_k^\dagger \hat{b}_j^\dagger \left| \ldots, 1_k, \ldots \right\rangle = 0 \qquad (16.16)$$

Hence Eq. (16.14) still works here because each individual term is zero.

We get an exactly similar result if the initial state is such that the single-particle state j is occupied.

We also trivially get the same result for any initial state if $j = k$

because we are trying to create at least two fermions in the single-particle state (three if it is already occupied),

and so we also get zero for both terms.

Hence we conclude that (16.14) is valid for any starting state.

Anticommutation relation

A relation of the form of (16.14) ($\hat{b}_j^\dagger \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j^\dagger = 0$) is called an anticommutation relation.

It is like a commutation relation between operators,

but with a plus sign in the middle rather than the minus sign of a commutation relation.

A notation sometimes used for an anticommutator of two operators, taking the expression of (16.14) as an example, is

$$\hat{b}_j^\dagger \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j^\dagger \equiv \left\{ \hat{b}_j^\dagger, \hat{b}_k^\dagger \right\} \tag{16.17}$$

Here we will progressively develop a family of anticommutation relations for the fermion operators.

They will turn out to be the principal relations we use for simplifying expressions using fermion operators,

and they are often quite convenient and useful.

Formalization of sign behavior of creation operator

To proceed further, let us generalize and formalize the definition of the creation operator and the resulting signs.

- ***We see, with our choice that we add the particle in state k initially to the end of the list,***
  - **or, equivalently, to the bottom of the determinant,**
- ***and then swap it into place,***
  - **that the number of swaps we have to perform is**
    - *the number, S_k, of occupied states that are above the state k of interest in the standard order.*

With this definition, we can write formally

$$\hat{b}_k^\dagger \left| \ldots, 0_k, \ldots \right\rangle = (-1)^{S_k} \left| \ldots, 1_k, \ldots \right\rangle \qquad (16.18)$$

Fermion annihilation operators

Now we can proceed to define annihilation operators.

From (16.18) ($\hat{b}_k^\dagger \left|\dots,0_k,\dots\right\rangle = (-1)^{S_k} \left|\dots,1_k,\dots\right\rangle$), we can see that

$$\left\langle\dots,1_k,\dots\right|\hat{b}_k^\dagger\left|\dots,0_k,\dots\right\rangle = (-1)^{S_k}\left\langle\dots,1_k,\dots|\dots,1_k,\dots\right\rangle = (-1)^{S_k} \tag{16.19}$$

Let us now take the complex conjugate

or, actually, the Hermitian adjoint,

of both sides of (16.19), i.e.,

$$\begin{aligned}\left\langle\dots,1_k,\dots\right|\hat{b}_k^\dagger\left|\dots,0_k,\dots\right\rangle^\dagger &= \left(\hat{b}_k^\dagger\left|\dots,0_k,\dots\right\rangle\right)^\dagger\left(\left\langle\dots,1_k,\dots\right|\right)^\dagger \\ &= \left\langle\dots,0_k,\dots\right|\hat{b}_k\left|\dots,1_k,\dots\right\rangle \\ &= (-1)^{S_k}\end{aligned} \tag{16.20}$$

From (16.20) we deduce therefore that

$$\hat{b}_k\left|\dots,1_k,\dots\right\rangle = (-1)^{S_k}\left|\dots,0_k,\dots\right\rangle \tag{16.21}$$

Hence, whereas $\hat{b}_k^\dagger$ creates a fermion in single-particle state k (provided that state was empty),

$\hat{b}_k$ annihilates a fermion in single-particle state k provided that state was full, and is called the fermion annihilation operator for state k.

Fermion annihilation operator anticommutation relation

We can think of the action of the annihilation operator on the Slater determinant as progressively

swapping the row corresponding to state k in the determinant with the one below it

until that row gets to the bottom of the determinant,

in which case we remove it (and the last column) of the determinant,

in an inverse fashion to the process with the creation operator we discussed above.

By a similar set of arguments, we arrive at the anticommutation relation for the annihilation operator, valid for all states and for $j = k$,

$$\hat{b}_j \hat{b}_k + \hat{b}_k \hat{b}_j = 0 \tag{16.22}$$

where we will also have used the relation, analogous to (16.15), ($\hat{b}_k^\dagger |\ldots, 1_k, \ldots\rangle = 0$)

$$\hat{b}_k |\ldots, 0_k, \ldots\rangle = 0 \tag{16.23}$$

which merely states that, if the single-particle state k is empty to start with, we cannot annihilate another particle from that state.

Fermion operators – 2

Reading – Section 16.1 from "Mixtures of creation and annihilation operators" – Section 16.3 up to the start of "Single-particle fermion Hamiltonians with multiple particle states"

Mixtures of annihilation and creation operators

Wavefunction operator

Fermion Hamiltonians

Mixtures of creation and annihilation operators - 1

Suppose single-particle states b, j, and m are initially occupied,

and we operate on this state first with the annihilation operator $\hat{b}_j$.

Then we have

$$\hat{b}_j \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} = -\begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} \tag{16.24}$$

where we had to swap the j and m rows to get the j row to the bottom.

Now we operate with $\hat{b}_k^\dagger$, obtaining

$$\begin{aligned} \hat{b}_k^\dagger \hat{b}_j \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} &= -\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |2,m\rangle \end{vmatrix} \\ &= \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \end{aligned} \tag{16.25}$$

where the minus sign is cancelled because we had to swap the k row from the bottom with the m row.

Mixtures of creation and annihilation operators - 2

Next let us consider applying these operators in the opposite order.

$$\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} = - \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix} \quad (16.26)$$

where we had to swap the k row from the bottom with the m row.

Applying the $\hat{b}_j$ operator now gives

$$\hat{b}_j\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} = -\hat{b}_j \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle & |4,b\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{vmatrix}$$

$$= - \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \quad (16.27)$$

In operating with $\hat{b}_j$, two swaps are required because we have to swap past both the m and k rows.

Mixtures of creation and annihilation operators - 3

As before,

- ***we find an additional row swap required with one order of operators rather than the other.***
  - **The result (16.27) is minus the result (16.25).**

Hence we see that,

- ***at least when operating on states when single-particle state j is initially full and single-particle state k is initially empty,***

$$\hat{b}_j \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j = 0 \tag{16.28}$$

Again, if state j is initially empty, then both pairs of operators will lead to a zero result, and similarly if state k is initially full.

- ***Hence, as long as states j and k are different states, (16.28) is universally true.***

Mixtures of creation and annihilation operators - 4

The only special case we have to consider more carefully here is for $j = k$.

Suppose single-particle state k is initially full. Then we have

$$\hat{b}_k \hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} = 0 \tag{16.29}$$

because $\hat{b}_k^\dagger$ operating on this state gives zero.

For the other order of operators, we have

$$\begin{aligned} \hat{b}_k^\dagger \hat{b}_k \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} &= -\hat{b}_k^\dagger \begin{vmatrix} |1,b\rangle & |2,b\rangle \\ |1,m\rangle & |1,m\rangle \end{vmatrix} \\ &= \begin{vmatrix} |1,b\rangle & |2,b\rangle & |3,b\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \\ |1,m\rangle & |2,m\rangle & |3,m\rangle \end{vmatrix} \end{aligned} \tag{16.30}$$

It is left as an exercise for the reader to repeat this derivation for the situation where state k is initially empty.

In both cases, the result is the same; one or other of the pairs returns the original state and the other pair returns zero.

Anticommutation relation for mixed annihilation and creation operators

Hence we can say that

$$\hat{b}_k \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_k = 1 \tag{16.31}$$

Putting (16.31) together with (16.28) ($\hat{b}_j \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j = 0$), we can write the anticommutation relation

$$\hat{b}_j \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j = \delta_{jk} \tag{16.32}$$

Fermion number operator

Finally, we note that $\hat{b}_k^\dagger \hat{b}_k$ is the fermion number operator for the state k,

i.e., it will tell us the number of fermions occupying state k.

If the state is initially empty,

it will return the value zero,

and if the state is initially full

it will return the value 1.

We can write this as

$$\hat{N}_k = \hat{b}_k^\dagger \hat{b}_k \tag{16.33}$$

Wave function operator - 1

It is very convenient to have an operator, in occupation number form, that represents the quantum mechanical wavefunction itself.

It can give a simple way to transform operators, such as Hamiltonians, from a spatial form into the occupation number representation.

Consider first a wavefunction operator when we have a single particle.

We propose an operator

$$\hat{\psi}(\mathbf{r}) = \sum_j \hat{b}_j \phi_j(\mathbf{r}) \tag{16.34}$$

where the $\phi_k(\mathbf{r})$ are some complete set for describing functions of space.

Suppose a single particle was in state m, i.e., with wavefunction $\phi_m(\mathbf{r})$.

We can also write that state as

$$|\ldots 0_l, 1_m, 0_n, \ldots\rangle \equiv \hat{b}_m^\dagger |0\rangle \tag{16.35}$$

where $|0\rangle$ is the state with no fermions present in any single-particle state.

Then we find that

$$\begin{aligned} \hat{\psi}(\mathbf{r})|\ldots 0_l, 1_m, 0_n, \ldots\rangle &= \hat{\psi}(\mathbf{r})\hat{b}_m^\dagger |0\rangle \\ &= \sum_j \phi_j(\mathbf{r}) \hat{b}_j \hat{b}_m^\dagger |0\rangle \end{aligned} \tag{16.36}$$

Wave function operator - 2

Now in Eq. (16.36)

$$\hat{\psi}(\mathbf{r})\left|\ldots 0_l, 1_m, 0_n, \ldots\right\rangle = \sum_j \phi_j(\mathbf{r})\hat{b}_j\hat{b}_m^\dagger|0\rangle$$

we use the anticommutation relation Eq. (16.32)

$$\hat{b}_j\hat{b}_k^\dagger + \hat{b}_k^\dagger\hat{b}_j = \delta_{jk},$$

obtaining

$$\hat{\psi}(\mathbf{r})\left|\ldots 0_l, 1_m, 0_n, \ldots\right\rangle = \sum_j \phi_j(\mathbf{r})\left(\delta_{jm} - \hat{b}_m^\dagger\hat{b}_j\right)|0\rangle \qquad (16.37)$$

But

$$\hat{b}_j|0\rangle = 0 \qquad (16.38)$$

because an attempt to annihilate a particle that is not there results in a null result.

Hence we have

$$\hat{\psi}(\mathbf{r})\left|\ldots 0_l, 1_m, 0_n, \ldots\right\rangle = \phi_m(\mathbf{r})|0\rangle \qquad (16.39)$$

We can see then that this operator has successfully extracted the amplitude $\phi_m(\mathbf{r})$.

We have also acquired the ket $|0\rangle$ in the result, which might seem odd,

but remember that we should have a state vector here because the result of operating on a state vector should be a state vector.

Wave function operator - 3

We can also see by a simple extension of the above algebra that,

if the particle is initially not in a specific single-particle state,

but in a linear superposition, i.e.,

$$\left|\psi_S\right\rangle = \sum_k c_k \left|\ldots,1_k,\ldots\right\rangle \tag{16.40}$$

where by $\left|\ldots,1_k,\ldots\right\rangle$ *we mean the state with one particle in state* k *and no other single-particle states occupied,*

then

$$\hat{\psi}(\mathbf{r})\left|\psi_S\right\rangle = \left(\sum_k c_k \phi_k(\mathbf{r})\right)\left|0\right\rangle \tag{16.41}$$

which has now extracted the linear superposition of wavefunctions we would have desired.

Two-particle wavefunction operator

The next more complex case is to propose a wavefunction operator for a two-fermion state.

We propose

$$\hat{\psi}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\sum_{j,n}\hat{b}_n\hat{b}_j\phi_j(\mathbf{r}_1)\phi_n(\mathbf{r}_2) \qquad (16.42)$$

(The $1/\sqrt{2}$ term is to ensure normalization of the final result.)

It is left as an exercise to demonstrate that

such an operator,

operating on a state with two different single-particle states occupied,

leads to a linear combination of products of wavefunctions that is correctly antisymmetric with respect to exchange of these two particles,

i.e., if this operator acts on a state s that has

one fermion in single-particle state k and an identical fermion in single-particle state m, i.e., the state $|\ldots,1_k,\ldots,1_m,\ldots\rangle \equiv \hat{b}_k^\dagger\hat{b}_m^\dagger|0\rangle$,

then

$$\hat{\psi}(\mathbf{r}_1,\mathbf{r}_2)|\ldots,1_k,\ldots,1_m,\ldots\rangle=\frac{1}{\sqrt{2}}\left[\phi_k(\mathbf{r}_1)\phi_m(\mathbf{r}_2)-\phi_k(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\right]|0\rangle \qquad (16.43)$$

Multiple fermion wavefunction operator

We can propose to extend such wavefunction operators to larger numbers of particles, postulating

$$\hat{\psi}(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=\frac{1}{\sqrt{N!}}\sum_{a,b,\ldots,n}\hat{b}_n\ldots\hat{b}_b\hat{b}_a\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)\ldots\phi_n(\mathbf{r}_N) \tag{16.44}$$

with the expectation that these operators will also extract the correct sum of permutations.

Operators represented using fermion annihilation and creation operators

Above we constructed the fermion annihilation and creation operators.

Here we use the fermion operators to represent other operators, especially Hamiltonians

It leads to a simple way of representing fermion operators

valid for both single and multiple particle systems.

We will consider progressively more sophisticated cases of fermion operators,

showing how these can be written using creation and annihilation operators.

Single-particle fermion Hamiltonian with a single fermion

First, consider the simplest case of a Hamiltonian for a single fermion.

Previously, we had a simple Hamiltonian such as the simplest Schrödinger equation for a single particle

$$\hat{H}_{\mathbf{r}} = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \qquad (16.45)$$

The expected value for energy was then,

for any given state $|\psi\rangle$

(presuming for simplicity here that the state can also be described by a spatial wavefunction $\psi(\mathbf{r})$*),*

$$\langle E\rangle = \langle\psi|\hat{H}_{\mathbf{r}}|\psi\rangle = \int \psi^*(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]\psi(\mathbf{r})\,d^3\mathbf{r} \qquad (16.46)$$

Postulation of new Hamiltonian with fermion character - 1

Now we postulate a new Hamiltonian operator, with fermion particle character.

Our postulated method for constructing such an operator

substitute for the wavefunction in an equation such as (16.46)

$$\langle E\rangle = \langle\psi|\hat{H}_{\mathbf{r}}|\psi\rangle = \int \psi^*(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]\psi(\mathbf{r})\,d^3\mathbf{r}$$

with the wavefunction operator,

generating our desired new fermion operator instead of the expectation value.

Hence we obtain for our single particle Hamiltonian operator

$$\hat{H} \equiv \int \hat{\psi}^\dagger(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]\hat{\psi}(\mathbf{r})\,d^3\mathbf{r} \qquad (16.47)$$

Presume for simplicity that

the single particle basis states with spatial wavefunctions $\phi_m(\mathbf{r})$

are the eigenstates of this single particle Hamiltonian,

with corresponding eigenenergies E_m*;*

this is the most common choice of basis,

at least using the eigenstates for some unperturbed Hamiltonian operator

Postulation of new Hamiltonian with fermion character - 2

Now using the definition of the wavefunction operator from Eq. (16.34)**,**

$$\hat{\psi}(\mathbf{r}) = \sum_j \hat{b}_j \phi_j(\mathbf{r})$$

we obtain

$$\begin{aligned}\hat{H} &= \int \sum_{j,k} \hat{b}_j^\dagger \hat{b}_k \phi_j^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \phi_k(\mathbf{r})\, d^3\mathbf{r} \\ &= \sum_{j,k} \hat{b}_j^\dagger \hat{b}_k E_k \int \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r})\, d^3\mathbf{r} \\ &= \sum_{j,k} \hat{b}_j^\dagger \hat{b}_k E_k \delta_{jk}\end{aligned} \qquad (16.48)$$

i.e.,

$$\hat{H} = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j \equiv \sum_j E_j \hat{N}_j \qquad (16.49)$$

Expectation value of energy with this new Hamiltonian operator

Suppose that the system was in some state $|\psi\rangle$ that was

a linear superposition of the basis states,

then we could write,

in the $\mathbf{r}$ representation

$$|\psi\rangle = \sum_m c_m \phi_m(\mathbf{r}) \tag{16.50}$$

or equivalently in the number state notation

$$|\psi\rangle = \sum_m c_m \hat{b}_m^\dagger |0\rangle \tag{16.51}$$

where we have used the notation $\hat{b}_m^\dagger |0\rangle$ as a convenient way of writing the basis state in which only the single particle state m is occupied.

Note we can take the Hermitian conjugate of both sides to obtain

$$\langle\psi| = \sum_m c_m^* \langle 0|\hat{b}_m \tag{16.52}$$

Now let us formally evaluate the expectation value of the energy in this state using the Hamiltonian (16.49).

$$\langle E\rangle = \langle\psi|\hat{H}|\psi\rangle = \sum_{m,n,j} c_m^* c_n E_j \langle 0|\hat{b}_m \hat{b}_j^\dagger \hat{b}_j \hat{b}_n^\dagger |0\rangle \tag{16.53}$$

Simplifying expressions using anticommutation relations

Now we simplify $\hat{b}_m \hat{b}_j^\dagger \hat{b}_j \hat{b}_n^\dagger |0\rangle$ using anticommutation relations.

A standard algebraic approach is to

use the anticommutation relations to push annihilation operators to the right;

that will lead to disappearance of terms because

an annihilation operator acting on the empty state $|0\rangle$ gives a zero result.

We will therefore keep making substitutions of the form

$$\hat{b}_m \hat{b}_j^\dagger = \delta_{mj} - \hat{b}_j^\dagger \hat{b}_m \tag{16.54}$$

which is just the anticommutation relation for operators $\hat{b}_m$ and $\hat{b}_j^\dagger$.

Hence, we have

$$\begin{aligned} \hat{b}_m \hat{b}_j^\dagger \hat{b}_j \hat{b}_n^\dagger |0\rangle &= \left(\delta_{mj} - \hat{b}_j^\dagger \hat{b}_m\right)\left(\delta_{nj} - \hat{b}_n^\dagger \hat{b}_j\right)|0\rangle \\ &= \left(\delta_{mj} - \hat{b}_j^\dagger \hat{b}_m\right)\delta_{nj}|0\rangle \\ &= \delta_{mj}\delta_{nj}|0\rangle \end{aligned} \tag{16.55}$$

Incidentally, this operation with this anticommutation relation is a very powerful and frequently used algebraic manipulation with fermion operators.

Expectation value of energy with this new Hamiltonian operator

Hence, substituting back into (16.53)

$$\langle E\rangle = \langle\psi|\hat{H}|\psi\rangle = \sum_{m,n,j} c_m^* c_n E_j \langle 0|\hat{b}_m \hat{b}_j^\dagger \hat{b}_j \hat{b}_n^\dagger |0\rangle$$

we have

$$\begin{aligned}\langle E\rangle &= \sum_{m,n,j} c_m^* c_n E_j \delta_{mj} \delta_{nj} \langle 0|0\rangle \\ &= \sum_j \left|c_j\right|^2 E_j\end{aligned} \tag{16.56}$$

which is exactly the result we would have expected based on our previous approach.

Hence this new approach to Hamiltonians does appear to work, at least for this simple example.

Fermion operators – 3

Reading – Section 16.3 from the start of "Single particle fermion operators with multiple particle states"

Single particle fermion operators with multiple particle states

Representation of general single-particle fermion operators

Two particle fermion operators

Single-particle Hamiltonians with multiple particle states - 1

Now we take a more complicated example

single-particle fermion Hamiltonians with multiple fermions.

What we mean by a single-particle Hamiltonian is that

the Hamiltonian of any one fermion can be written entirely in terms of that fermion's properties and coordinates,

i.e., that fermion's energy does not depend on the other fermions in the system,

or equivalently the fermions are non-interacting.

This is a good starting point for multiple uncharged fermions,

such as a set of neutrons, so dilute that there are negligible collisions.

A very important example is the single-electron model in a crystalline solid.

Approximately, each electron moves in the average periodic potential, $V(\mathbf{r})$, *created by all other electrons and nuclei,*

This decouples the Hamiltonians for the different electrons,

giving a total Hamiltonian that is the sum of the single-electron Hamiltonians.

Single-particle Hamiltonians with multiple particle states - 2

Suppose then that we have N identical fermions.

Fermion i is presumed to have a single-particle Hamiltonian in the original $\mathbf{r}$ form such as

$$\hat{H}_{\mathbf{r}i} = -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_i} + V\left(\mathbf{r}_i\right) \qquad (16.57)$$

with the total Hamiltonian for the set of N fermions consequently being in the original $\mathbf{r}$ form

$$\hat{H}_{\mathbf{r}} = \sum_{i=1}^{N} \hat{H}_{\mathbf{r}i} \qquad (16.58)$$

We now show that,

even for the multiple fermion case,

we can still write the total Hamiltonian operator exactly as in Eq. (16.49).

$$\hat{H} = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j \equiv \sum_j E_j \hat{N}_j$$

We therefore do not have to change the Hamiltonian for non-interacting fermions regardless of how many particles there are in the system

i.e., we do not have to write a sum like (16.58) over all the particles.

We begin here to see the power of the annihilation and creation operator form for multiple fermion systems.

Single-particle fermion Hamiltonians with two-particle states - 1

Consider a single-particle fermion operator and a multi-fermion system.

We now illustrate, that (16.49)

$$\hat{H} = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j \equiv \sum_j E_j \hat{N}_j$$

is still the Hamiltonian we would deduce when we create the Hamiltonian using multiple fermion wavefunction operators.

We show Hamiltonian (16.49) $\hat{H} = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j$ **works for two fermions (**$N = 2$**).**

Suppose we have a specific two-fermion state with

one fermion in single-particle state k ***and one in single-particle state*** m***.***

We can write that state as

$$\left|\psi_{TP}\right\rangle = \left|\ldots,1_k,\ldots,1_m,\ldots\right\rangle = \hat{b}_k^\dagger \hat{b}_m^\dagger \left|0\right\rangle \tag{16.59}$$

Evaluating with our new Hamiltonian form we have

$$\begin{aligned}\langle E\rangle = \left\langle\psi_{TP}\right|\hat{H}\left|\psi_{TP}\right\rangle &= \sum_j \left(\hat{b}_k^\dagger \hat{b}_m^\dagger \left|0\right\rangle\right)^\dagger E_j \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger \left|0\right\rangle \\ &= \sum_j E_j \left\langle 0\right| \hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger \left|0\right\rangle\end{aligned} \tag{16.60}$$

Single-particle fermion Hamiltonians with two-particle states - 2

Now we simplify Eq. (16.60) $\langle E\rangle = \sum_j E_j \langle 0|\hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle$

using the anticommutation relation between annihilation and creation operator pairs to push the annihilation operators to the right.

$$\begin{aligned}
\hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle &= \hat{b}_m \left(\delta_{jk} - \hat{b}_j^\dagger \hat{b}_k\right)\left(\delta_{jk} - \hat{b}_k^\dagger \hat{b}_j\right)\hat{b}_m^\dagger |0\rangle \\
&= \left(\delta_{jk}\hat{b}_m \hat{b}_m^\dagger - \delta_{jk}\hat{b}_m \hat{b}_k^\dagger \hat{b}_j \hat{b}_m^\dagger - \delta_{jk}\hat{b}_m \hat{b}_j^\dagger \hat{b}_k \hat{b}_m^\dagger + \hat{b}_m \hat{b}_j^\dagger \hat{b}_k \hat{b}_k^\dagger \hat{b}_j \hat{b}_m^\dagger\right)|0\rangle \\
&= \Big[\delta_{jk}\left(1 - \hat{b}_m^\dagger \hat{b}_m\right) - \delta_{jk}\left(\delta_{mk} - \hat{b}_k^\dagger \hat{b}_m\right)\left(\delta_{mj} - \hat{b}_m^\dagger \hat{b}_j\right) \\
&\quad - \delta_{jk}\left(\delta_{mj} - \hat{b}_j^\dagger \hat{b}_m\right)\left(\delta_{mk} - \hat{b}_m^\dagger \hat{b}_k\right) + \left(\delta_{mj} - \hat{b}_j^\dagger \hat{b}_m\right)\left(1 - \hat{b}_k^\dagger \hat{b}_k\right)\left(\delta_{mj} - \hat{b}_j^\dagger \hat{b}_m\right)\Big]|0\rangle
\end{aligned} \tag{16.61}$$

Now we have annihilation operators on the far right on every expression involving creation and annihilation operators,

so all of those terms disappear ($\hat{b}_i|0\rangle = 0$ *for any* i*).*

Hence we have

$$\hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle = \left(\delta_{jk} - \delta_{jk}\delta_{mk}\delta_{mj} - \delta_{jk}\delta_{mj}\delta_{mk} + \delta_{mj}\right)|0\rangle \tag{16.62}$$

But, by choice, m *and* k *are different states so* δ_{mk} *never has any value other than zero. Hence we have*

$$\hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle = \left(\delta_{jk} + \delta_{mj}\right)|0\rangle \tag{16.63}$$

Single-particle fermion Hamiltonians with two-particle states - 3

Substituting Eq. (16.63)

$$\hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle = \left(\delta_{jk} + \delta_{mj}\right)|0\rangle$$

back into Eq. (16.60)

$$\langle E\rangle = \sum_j E_j \langle 0| \hat{b}_m \hat{b}_k \hat{b}_j^\dagger \hat{b}_j \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle$$

we have

$$\langle E\rangle = \sum_j E_j \left(\delta_{jk} + \delta_{mj}\right)\langle 0|0\rangle = E_k + E_m \qquad (16.64)$$

which is exactly what we would expect for non-interacting fermions, one in state k and one in state m.

Hence this illustration shows how the Hamiltonian (16.49) also works for multiple particle states.

Unlike the $\mathbf{r}$ representation of the Hamiltonian,

we do not have to add separate Hamiltonians for each identical fermion,

and hence we have an elegant form of Hamiltonian for multiple fermion systems.

Representation of general single-particle fermion operators - 1

The Hamiltonian is a special case because,

for a single-particle operator,

the occupation number states were chosen as eigenstates of the Hamiltonian.

How would we represent other single-particle fermion operators

(e.g., the momentum operator or the position operator)

in this annihilation and creation operator formalism?

Having a suitable approach for this is practically quite useful;

we may need it, for example, if we are to handle

the position $\mathbf{r}$ in the electric dipole interaction $\mathbf{E}\cdot\mathbf{r}$,

or similarly to handle

the momentum in the $\mathbf{A}\cdot\mathbf{p}$ interaction.

Representation of general single-particle fermion operators - 2

Here we consider a system with N fermions.

In the $\mathbf{r}$ representation of an operator, $\hat{G}_{\mathbf{r}}$,

(e.g., such as the momentum operator)

for a multiple fermion system

we would add all of the operators corresponding to the coordinates of each particle, i.e.,

$$\hat{G}_{\mathbf{r}} = \sum_{i=1}^{N} \hat{G}_{\mathbf{r}i} \tag{16.65}$$

where $\hat{G}_{\mathbf{r}i}$ is the operator for a specific particle

(e.g., it might be the momentum operator $\hat{\mathbf{p}}_{\mathbf{r}i} = -i\hbar\nabla_{\mathbf{r}_i}$).

In the annihilation and creation operator formalism, we postulate instead that

$$\hat{G} = \int \hat{\psi}^{\dagger} \hat{G}_{\mathbf{r}} \hat{\psi} \, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N \tag{16.66}$$

where $\hat{\psi}$ is the N-particle fermion wavefunction operator.

Representation of general single-particle fermion operators - 3

Substituting the N -particle fermion wavefunction operator into (16.66) $\hat{G}=\int\hat{\psi}^\dagger\hat{G}_{\mathbf{r}}\hat{\psi}\,d^3\mathbf{r}_1 d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N$, we obtain

$$\hat{G}=\frac{1}{N}\sum_{i=1}^{N}\sum_{\substack{a,b,\ldots n\\ a',b',\ldots n'}}\hat{b}_{a'}^\dagger\hat{b}_{b'}^\dagger\ldots\hat{b}_{n'}^\dagger\hat{b}_n\ldots\hat{b}_b\hat{b}_a \qquad (16.67)$$

$$\times\int\phi_{a'}^*(\mathbf{r}_1)\phi_{b'}^*(\mathbf{r}_2)\ldots\phi_{n'}^*(\mathbf{r}_N)\hat{G}_{\mathbf{r}i}\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)\ldots\phi_n(\mathbf{r}_N)\,d^3\mathbf{r}_1 d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N$$

where each of the $a,b,\ldots n$ and each of the $a',b',\ldots n'$ ranges over all possible single-particle fermion states.

Now, all the spatial integrals,

except the one over $\mathbf{r}_i$,

lead to Kronecker deltas of the form $\delta_{k'k}$,

forcing $a'=a$, $b'=b$, etc., (except for particle i).

Hence we have

$$\hat{G}=\frac{1}{N}\sum_{i=1}^{N}\sum_{a,b,\ldots,i1,i2,\ldots n}G_{i1i2}\hat{b}_a^\dagger\hat{b}_b^\dagger\ldots\hat{b}_{i1}^\dagger\ldots\hat{b}_n^\dagger\hat{b}_n\ldots\hat{b}_{i2}\ldots\hat{b}_b\hat{b}_a \qquad (16.68)$$

where

$$G_{i1i2}=\int\phi_{i1}^*(\mathbf{r}_i)\hat{G}_{\mathbf{r}i}\phi_{i2}(\mathbf{r}_i)\,d^3\mathbf{r}_i \qquad (16.69)$$

Representation of general single-particle fermion operators - 4

We can use the anticommutation relation $\hat{b}_j \hat{b}_k + \hat{b}_k \hat{b}_j = 0$ to

progressively swap the operator $\hat{b}_{i2}$ from the right to the center,

and similarly we use the anticommutation relation $\hat{b}_j^\dagger \hat{b}_k^\dagger + \hat{b}_k^\dagger \hat{b}_j^\dagger = 0$ to

progressively swap the operator $\hat{b}_{i1}^\dagger$ from the left to the center.

Each such application of an anticommutation relation results in a sign change,

but there are equal number of swaps from the left and from the right,

so there is no net sign change in this operation.

Hence we have

$$\hat{G} = \frac{1}{N} \sum_{i=1}^{N} \sum_{a,b,\ldots,i1,i2,\ldots n} G_{i1i2} \underbrace{\hat{b}_a^\dagger \hat{b}_b^\dagger \ldots \hat{b}_n^\dagger}_{omitting\ \hat{b}_{i1}^\dagger} \hat{b}_{i1}^\dagger \hat{b}_{i2} \underbrace{\hat{b}_n \ldots \hat{b}_b \hat{b}_a}_{omitting\ \hat{b}_{i2}^\dagger} \tag{16.70}$$

Elimination of strings of operators from the Hamiltonian - 1

In practice with any operator, we are in the end always working out matrix elements for an operator.

Any two operators with identical matrix elements are equivalent operators.

We can consider two, possibly different, N-fermion basis states,

$$\left|\psi_{1N}\right\rangle \text{ and } \left|\psi_{2N}\right\rangle,$$

and consider matrix elements of the operator $\hat{G}$ in (16.70)

$$\hat{G} = \frac{1}{N}\sum_{i=1}^{N} \sum_{a,b,\ldots,i1,i2,\ldots n} G_{i1i2} \underbrace{\hat{b}_a^\dagger \hat{b}_b^\dagger \ldots \hat{b}_n^\dagger}_{omitting\ \hat{b}_{i1}^\dagger} \hat{b}_{i1}^\dagger \hat{b}_{i2} \underbrace{\hat{b}_n \ldots \hat{b}_b \hat{b}_a}_{omitting\ \hat{b}_{i2}^\dagger}$$

between such states.

Because of Pauli exclusion,

the only strings of operators that can survive in matrix elements for legal fermion states are those in which all the operators $\hat{b}_a, \hat{b}_b, \ldots \hat{b}_n$ are all different from each other

(i.e., correspond to annihilation operators for different single particle states)

and are each different from both $\hat{b}_{i1}$ and $\hat{b}_{i2}$

since otherwise we would be trying either to annihilate two fermions from the same state or create two fermions in the same state.

Elimination of strings of operators from the Hamiltonian - 2

Hence, for these states,

since no two states in our string of creation operators or our string of annihilation operators can be identical,

not only do the pairs of annihilation operators anticommute and the pairs of creation operators anticommute as usual,

so also do all the pairs of creation and annihilation operators with different subscripts (other than possibly the pair $\hat{b}_{i1}^{\dagger}\hat{b}_{i2}$*).*

Hence in Eq. (16.70)

$$\hat{G} = \frac{1}{N}\sum_{i=1}^{N}\sum_{a,b,\ldots,i1,i2,\ldots n} G_{i1i2}\underbrace{\hat{b}_a^{\dagger}\hat{b}_b^{\dagger}\ldots\hat{b}_n^{\dagger}}_{omitting\ \hat{b}_{i1}^{\dagger}}\hat{b}_{i1}^{\dagger}\hat{b}_{i2}\underbrace{\hat{b}_n\ldots\hat{b}_b\hat{b}_a}_{omitting\ \hat{b}_{i2}^{\dagger}}$$

we can swap the creation operator $\hat{b}_a^{\dagger}$ all the way from the left until we get to the left of the corresponding annihilation operator $\hat{b}_a$,

only acquiring minus signs as we do so.

Actually, however, we acquire an even number of minus signs,

because the number of swaps taken to get to the middle

is equal to

the number to get from the middle to its final position,

so there is no change in sign in all these swaps.

Elimination of strings of operators from the Hamiltonian - 3

We can repeat this procedure for each creation operator (other than $\hat{b}_{i1}^{\dagger}$, which we do not need to move anyway),

and so we have

$$\hat{G} = \frac{1}{N}\sum_{i=1}^{N} \sum_{a,b,\ldots,i1,i2,\ldots n} G_{i1i2}\hat{b}_{i1}^{\dagger}\hat{b}_{i2} \underbrace{\hat{N}_n \ldots \hat{N}_b \hat{N}_a}_{omitting\ \hat{b}_{i1}^{\dagger}\hat{b}_{i2}} \qquad (16.71)$$

When this operator operates on a specific N-fermion basis state $|\psi_{1N}\rangle$,

the only terms in the summation that can survive are those for which the list of states $a,b,\ldots n$ correspond to occupied states in $|\psi_{1N}\rangle$,

and so

the sum over $a,b,\ldots n$ (omitting $i1$ and $i2$)

and

the number operators

can be dropped without changing any matrix element.

Hence we can write

$$\hat{G} = \frac{1}{N}\sum_{i=1}^{N} \sum_{i1,i2} G_{i1i2}\hat{b}_{i1}^{\dagger}\hat{b}_{i2} \qquad (16.72)$$

General single-particle fermion operators

It makes no difference which fermion we are considering

G_{i1i2} ***is the same for every fermion***

and so we can write finally, simplifying notation in Eq. (16.72)

$$\hat{G} = \frac{1}{N}\sum_{i=1}^{N}\sum_{i1,i2} G_{i1i2}\hat{b}_{i1}^{\dagger}\hat{b}_{i2}$$

by substituting j for $i1$ and k for $i2$

$$\hat{G} = \sum_{j,k} G_{jk}\hat{b}_j^{\dagger}\hat{b}_k \tag{16.73}$$

which is the general form for a single-particle fermion operator.

The Hamiltonian, (16.49),

$$\hat{H} = \sum_j E_j\hat{b}_j^{\dagger}\hat{b}_j \equiv \sum_j E_j\hat{N}_j$$

is just a special case for a diagonal operator.

Hence we have found a very simple form for the single-particle fermion operator

valid for any number of fermions.

Two-particle fermion Hamiltonians - 1

Fermions such as electrons interact, e.g., through their Coulomb repulsion

For such cases, we need two-particle operators.

In the $\mathbf{r}$ form, we might have an operator $\hat{D}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right)$ that depends on the coordinates of both particles.

Then we postulate

$$\hat{D} = \int \hat{\psi}^{\dagger}\left(\mathbf{r}_1,\mathbf{r}_2\right)\hat{D}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right)\hat{\psi}\left(\mathbf{r}_1,\mathbf{r}_2\right)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \qquad (16.74)$$

using the two-fermion wavefunction operator $\hat{\psi}\left(\mathbf{r}_1,\mathbf{r}_2\right) = \frac{1}{\sqrt{2}}\sum_{j,k}\hat{b}_k\hat{b}_j\phi_j\left(\mathbf{r}_1\right)\phi_k\left(\mathbf{r}_2\right)$

Substituting this form into (16.74), we have

$$\hat{D} = \frac{1}{2}\sum_{a,b,c,d}\hat{b}_a^{\dagger}\hat{b}_b^{\dagger}\hat{b}_d\hat{b}_c\int \phi_a^*\left(\mathbf{r}_1\right)\phi_b^*\left(\mathbf{r}_2\right)\hat{D}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right)\phi_c\left(\mathbf{r}_1\right)\phi_d\left(\mathbf{r}_2\right)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \qquad (16.75)$$

or equivalently

$$\hat{D} = \frac{1}{2}\sum_{a,b,c,d}D_{abcd}\hat{b}_a^{\dagger}\hat{b}_b^{\dagger}\hat{b}_d\hat{b}_c \qquad (16.76)$$

where

$$D_{abcd} = \int \phi_a^*\left(\mathbf{r}_1\right)\phi_b^*\left(\mathbf{r}_2\right)\hat{D}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right)\phi_c\left(\mathbf{r}_1\right)\phi_d\left(\mathbf{r}_2\right)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \qquad (16.77)$$

Two-particle fermion Hamiltonians - 2

Note in Eq. (16.76),

$$\hat{D} = \frac{1}{2}\sum_{a,b,c,d} D_{abcd}\hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c$$

the order of the suffices on the chain of operators $\hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c$ **is not** a, b, c, d***.***

The ordering is in the opposite sense for the annihilation operators.

This different ordering emerges from the wavefunction operators and the properties of Hermitian conjugation.

We presume that the two-particle fermion operator of (16.76)

$$\hat{D} = \frac{1}{2}\sum_{a,b,c,d} D_{abcd}\hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c$$

would remain unchanged as we changed the system to have more than two fermions in it.

The arguments would be similar to those for the single-particle fermion operator (16.73) $\hat{G} = \sum_{j,k} G_{jk}\hat{b}_j^\dagger \hat{b}_k$

so we presume that (16.76) is a general statement for a two-particle fermion operator in this annihilation and creation operator approach.

Electrons interacting through the Coulomb potential - 1

Consider two electrons (of the same spin) with Coulomb repulsion.

The Hamiltonian in the $\mathbf{r}$ form is,

as in Eq. (13.22) when we considered the exchange interaction between identical electrons,

$$\hat{H}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right) = -\frac{\hbar^2}{2m_o}\left(\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2\right) + \frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \qquad (16.78)$$

Hence our two particle operator formalism gives us the new operator

$$\hat{H} = \frac{1}{2}\sum_{a,b,c,d} H_{abcd}\hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c \qquad (16.79)$$

where H_{abcd} is defined analogously to Eq. (16.77)

$$D_{abcd} = \int \phi_a^*\left(\mathbf{r}_1\right)\phi_b^*\left(\mathbf{r}_2\right)\hat{D}_{\mathbf{r}}\left(\mathbf{r}_1,\mathbf{r}_2\right)\phi_c\left(\mathbf{r}_1\right)\phi_d\left(\mathbf{r}_2\right)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \, .$$

Suppose specifically that we have the two-fermion state where

one electron is in the basis state $\phi_k(\mathbf{r})$ and the other is in the state $\phi_m(\mathbf{r})$,

i.e., the two-particle state can be written

$$\left|\psi_{TP}\right\rangle = \hat{b}_k^\dagger \hat{b}_m^\dagger \left|0\right\rangle \qquad (16.80)$$

Electrons interacting through the Coulomb potential - 2

We evaluate the expectation value of the energy in this two-particle state using the Hamiltonian (16.79)

$$\hat{H} = \frac{1}{2} \sum_{a,b,c,d} H_{abcd} \hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c$$

We have, with our chosen $|\psi_{TP}\rangle = \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle$ (Eq. (16.80))

$$\langle \psi_{TP} | \hat{H} | \psi_{TP} \rangle = \frac{1}{2} \langle 0 | \sum_{a,b,c,d} H_{abcd} \hat{b}_m \hat{b}_k \hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle \quad (16.81)$$

Now

$$\langle 0 | \hat{b}_m \hat{b}_k \hat{b}_a^\dagger \hat{b}_b^\dagger \hat{b}_d \hat{b}_c \hat{b}_k^\dagger \hat{b}_m^\dagger |0\rangle = \delta_{ak}\delta_{bm}\delta_{ck}\delta_{dm} + \delta_{am}\delta_{bk}\delta_{cm}\delta_{dk} - \delta_{am}\delta_{bk}\delta_{ck}\delta_{dm} - \delta_{ak}\delta_{bm}\delta_{cm}\delta_{dk} \quad (16.82)$$

the proof of which is left as an exercise for the reader

Hence we have for the energy expectation value

$$\langle \psi_{TP} | \hat{H} | \psi_{TP} \rangle = \frac{1}{2} \left(H_{kmkm} + H_{mkmk} - H_{mkkm} - H_{kmmk} \right) \quad (16.83)$$

Explicitly, we have

$$H_{kmkm} = H_{mkmk} = \int \phi_k^* (\mathbf{r}_1) \phi_m^* (\mathbf{r}_2) \hat{H}_{\mathbf{r}} \phi_k (\mathbf{r}_1) \phi_m (\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (16.84)$$

and

$$H_{kmmk} = H_{mkkm}^* = \int \phi_k^* (\mathbf{r}_1) \phi_m^* (\mathbf{r}_2) \hat{H}_{\mathbf{r}} \phi_m (\mathbf{r}_1) \phi_k (\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (16.85)$$

Electrons interacting through the Coulomb potential - 3

These terms are exactly the same as we previously calculated using the $\mathbf{r}$ formalism in Chapter 13:

H_{kmkm} *(or equivalently* $(1/2)(H_{kmkm} + H_{mkmk})$*) is the sum of*

the kinetic energies for the two particles and

the Coulomb potential energy for two electrons,

as in Eqs. (13.30) – (13.34)

(and is therefore the energy we would calculate if the particles were not identical);

$-(1/2)(H_{mkkm} + H_{kmmk})$ *is the exchange energy of Eq. (13.36).*

Hence this approach does reproduce the results of our previous $\mathbf{r}$ formalism.

Importantly, this formalism,

in which we never have to explicitly introduce the antisymmetry of the wavefunction for two identical fermions,

has correctly introduced the exchange energy terms.

This exchange term has emerged naturally through the use of the anticommutation relations for the fermion operators.

Interaction of different kinds of particles – 1

Reading – Sections 17.1 – 17.4 up to the start of “Spontaneous emission”

States and commutation relations for different kinds of particles

Operators for systems with different kinds of particles

Perturbation theory with annihilation and creation operators

Optical absorption with annihilation and creation operators

Interaction of different kinds of particles

So far, we have considered operators in which we are concerned with only one kind of particle

i.e., either identical bosons or identical fermions.

Many important phenomena involve interactions of different kinds of particles

e.g., interactions of photons or phonons with electrons.

To extend to this case, we need two additions.

we must include the description of the occupied single-particle states for each different particle in the overall description of the states.

we need commutation relations between operators corresponding to different kinds of particles.

States with different kinds of particles - 1

In considering the occupation number basis states,

for example for a system with two different kinds of particles,

we simply have to list which states are occupied for each different kind of particle.

Suppose we have

a set of identical electrons and

a set of identical bosons (e.g., photons).

Then for a state with

one fermion in fermion state k***, and one in state*** q***, and***

one photon in photon mode λ_d ***and three in photon mode*** λ_s***,***

we could write the state in a list form or alternatively using creation operators acting on the empty state as

$$\begin{aligned}&\left|\ldots,0_j,1_k,0_l,\ldots 0_p,1_q,0_r,\ldots;\ \ldots,0_{\lambda c},1_{\lambda d},0_{\lambda e},\ldots,0_{\lambda r},3_{\lambda s},0_{\lambda t},\ldots\right\rangle \\ &\equiv\left|N_{fm};N_{bn}\right\rangle\equiv\frac{1}{\sqrt{3!}}\hat{b}_k^\dagger\hat{b}_q^\dagger\hat{a}_{\lambda d}^\dagger\left(\hat{a}_{\lambda s}^\dagger\right)^3\left|0\right\rangle\end{aligned} \qquad (17.1)$$

States with different kinds of particles - 2

In Eq. (17.1)

$$\left|\ldots,0_j,1_k,0_l,\ldots 0_p,1_q,0_r,\ldots;\ \ldots,0_{\lambda c},1_{\lambda d},0_{\lambda e},\ldots,0_{\lambda r},3_{\lambda s},0_{\lambda t},\ldots\right\rangle$$

$$\equiv\left|N_{fm};N_{bn}\right\rangle\equiv\frac{1}{\sqrt{3!}}\hat{b}_k^\dagger\hat{b}_q^\dagger\hat{a}_{\lambda d}^\dagger\left(\hat{a}_{\lambda s}^\dagger\right)^3\left|0\right\rangle$$

N_{fm} ***is the*** m***th possible list of occupied fermion states***

here the list $\ldots,0_j,1_k,0_l,\ldots 0_p,1_q,0_r,\ldots$

and similarly N_{bn} ***is the*** n***th possible list of occupied boson states***

here the list $\ldots,0_{\lambda c},1_{\lambda d},0_{\lambda e},\ldots,0_{\lambda r},3_{\lambda s},0_{\lambda t},\ldots$**.**

Note now that the empty state $\left|0\right\rangle$ **is one that is empty both of this kind of fermion and this kind of boson.**

Commutation relations for different particles

We postulate that creation and annihilation operators corresponding to different particles commute under all conditions.

Specifically then for the boson and fermion operators we would have

$$\begin{aligned} \hat{b}_j^\dagger \hat{a}_\lambda^\dagger - \hat{a}_\lambda^\dagger \hat{b}_j^\dagger &= 0 \quad & \hat{b}_j \hat{a}_\lambda - \hat{a}_\lambda \hat{b}_j &= 0 \\ \hat{b}_j^\dagger \hat{a}_\lambda - \hat{a}_\lambda \hat{b}_j^\dagger &= 0 \quad & \hat{b}_j \hat{a}_\lambda^\dagger - \hat{a}_\lambda^\dagger \hat{b}_j &= 0 \end{aligned} \qquad (17.2)$$

Note such relations also would hold for annihilation and creation operators corresponding to two different kinds of fermions, such as

electrons and protons.

Operators for systems with different kinds of particles

The basic approach for constructing operators corresponding to interactions between different kinds of particles is simply

progressively to apply the methods appropriate for each particle as required.

Because of the commutation relations for annihilation and creation operators for different particles,

there is no particular necessary order for applying these methods.

The construction of such operators is likely best understood by illustration.

Electron-photon interaction

The basic approach here is that

we will use the field operators instead of the classical fields and

use the fermion wave function operators to transform the fermion position (or momentum) operator to the occupation number form.

Suppose, for example, we consider the Hamiltonian of the

electric dipole interaction between electrons and electromagnetic modes.

Suppose first we presumed we had "turned off" (mathematically at least) any interaction between the electron and the photons.

Because there is no interaction, the resulting Hamiltonian is the sum of the separate fermion (electron) and boson (photon) Hamiltonians, i.e.,

$$\hat{H}_o = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j + \sum_\lambda \hbar\omega_\lambda \hat{a}_\lambda^\dagger \hat{a}_\lambda \qquad (17.3)$$

As before, the sum over j is over all possible single-particle fermion states (modes), and the sum over λ is over all possible photon modes.

Electric dipole interaction – boson operators

Previously, for the electric dipole interaction,

we had, from a semiclassical view of the energy of an electron at position $\mathbf{r}_i$ *in an electric field* $\mathbf{E}$

$$\hat{H}_{sced\mathbf{r}} = e\,\mathbf{E}\cdot\mathbf{r} \tag{17.4}$$

Substituting the multimode electric field operator of Eq. (14.132) for the classical field $\mathbf{E}$ **gives, for any specific electron** i**,**

we have now instead

$$\hat{H}_{ed\mathbf{r}i} = \sqrt{-1}\,e\sum_{\lambda}\left(\hat{a}_{\lambda} - \hat{a}_{\lambda}^{\dagger}\right)\sqrt{\frac{\hbar\omega_{\lambda}}{2\varepsilon_{o}}}\mathbf{u}_{\lambda}\left(\mathbf{r}_{i}\right).\mathbf{r}_{i} \tag{17.5}$$

For N **electrons, we have to add all these Hamiltonians, i.e.,**

$$\hat{H}_{ed\mathbf{r}} = \sum_{i=1}^{N}\sqrt{-1}\,e\sum_{\lambda}\left(\hat{a}_{\lambda} - \hat{a}_{\lambda}^{\dagger}\right)\sqrt{\frac{\hbar\omega_{\lambda}}{2\varepsilon_{o}}}\mathbf{u}_{\lambda}\left(\mathbf{r}_{i}\right).\mathbf{r}_{i} \tag{17.6}$$

Electric dipole interaction – fermion operators

Now we want to transform this Hamiltonian in $\mathbf{r}$ form into the fermion occupation number form also.

To do so, we formally use the N-fermion field operators.

Because the fermion and boson operators commute with one another,

the boson operators also commute with the (fermion) wavefunction operators,

and so we can write

$$\hat{H}_{ed} = \int \hat{\psi}^\dagger \hat{H}_{ed\mathbf{r}} \hat{\psi}\, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N$$

$$= \int \hat{\psi}^\dagger \left[\sum_{i=1}^{N} \sqrt{-1}\, e \sum_{\lambda} \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \mathbf{u}_\lambda\left(\mathbf{r}_i\right).\mathbf{r}_i \right] \hat{\psi}\; d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N \qquad (17.7)$$

$$= \sum_{\lambda} \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \int \hat{\psi}^\dagger \left[\sum_{i=1}^{N} \sqrt{-1}\, e \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \mathbf{u}_\lambda\left(\mathbf{r}_i\right).\mathbf{r}_i \right] \hat{\psi}\; d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N$$

Rewriting the single-particle fermion operator - 1

Here we have a single-particle fermion operator with a multiple fermion state,

as in Eq. (15.65), ($\hat{G}_{\mathbf{r}} = \sum_{i=1}^{N} \hat{G}_{\mathbf{r}i}$)

which we can write in the $\mathbf{r}$ form as

$$\hat{H}_{ed\lambda\mathbf{r}} = \sum_{i=1}^{N} \hat{H}_{ed\lambda\mathbf{r}i} \qquad (17.8)$$

where here

$$\hat{H}_{ed\lambda\mathbf{r}i} = \sqrt{-1}\, e \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \mathbf{u}_\lambda\left(\mathbf{r}_i\right).\mathbf{r}_i \qquad (17.9)$$

This is a single-particle fermion operator because each $\hat{H}_{ed\lambda\mathbf{r}i}$ only depends on the coordinates of one fermion.

With this notation, (17.7) becomes

$$\hat{H}_{ed} = \sum_{\lambda}\left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right)\int \hat{\psi}^\dagger \hat{H}_{ed\lambda\mathbf{r}} \hat{\psi}\; d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N \qquad (17.10)$$

Rewriting the single-particle fermion operator - 2

Now we can use our specific previous results for single-particle fermion operators with multiple fermion states,

which allow us to write (as in Eq. (15.73) $\hat{G} = \sum_{j,k} G_{jk} \hat{b}_j^\dagger \hat{b}_k$ *)*

$$\int \hat{\psi}^\dagger \hat{H}_{ed\lambda\mathbf{r}} \hat{\psi}\, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N = \sum_{j,k} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \qquad (17.11)$$

where (as in Eq. (15.69) $G_{i1i2} = \int \phi_{i1}^*(\mathbf{r}_i) \hat{G}_{\mathbf{r}i} \phi_{i2}(\mathbf{r}_i) d^3\mathbf{r}_i$ **)**

$$H_{ed\lambda jk} = \int \phi_j^*(\mathbf{r}_i) \hat{H}_{ed\lambda\mathbf{r}i} \phi_k(\mathbf{r}_i) d^3\mathbf{r}_i = \sqrt{-1}\, e \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \int \phi_j^*(\mathbf{r}_i) \left[\mathbf{u}_\lambda(\mathbf{r}_i).\mathbf{r}_i\right] \phi_k(\mathbf{r}_i) d^3\mathbf{r}_i \qquad (17.12)$$

Hence, substituting back into expression (17.7)

$$\hat{H}_{ed} = \sum_\lambda \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right) \int \hat{\psi}^\dagger \left[\sum_{i=1}^{N} \sqrt{-1}\, e \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \mathbf{u}_\lambda(\mathbf{r}_i).\mathbf{r}_i\right] \hat{\psi}\, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N$$

for this electron-dipole Hamiltonian, we have

$$\hat{H}_{ed} = \sum_{j,k,\lambda} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right) \qquad (17.13)$$

Here, all the details of the specific form of the single-particle fermion states and of the electromagnetic modes are contained within the constants $H_{ed\lambda jk}$***.***

Operators and processes

The annihilation and creation operators identify specific processes that could occur given appropriate starting states.

We can open up the creation and annihilation operator expression

$$\hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) = \hat{b}_j^\dagger \hat{b}_k \hat{a}_\lambda - \hat{b}_j^\dagger \hat{b}_k \hat{a}_\lambda^\dagger \qquad (17.14)$$

Hence, for example,

if fermion state k *was occupied, and fermion state* j *was empty,*

and we had at least one photon in mode λ*,*

then we could have a process,

corresponding to the operators $\hat{b}_j^\dagger \hat{b}_k \hat{a}_\lambda$*,*

which involves annihilating a photon in mode λ

and changing an electron from state k **to state** j**,**

i.e., we are describing an absorption process in which absorption of a photon takes an electron from one state to another.

Similarly, the process corresponding to the operators $\hat{b}_j^\dagger \hat{b}_k \hat{a}_\lambda^\dagger$ **is one of emission of a photon as an electron goes from state** k **to state** j**.**

We will evaluate transition rates for such processes once we have discussed time-dependent perturbation theory for this formalism.

Time-dependent perturbation theory with annihilation and creation operators - 1

The time-dependent perturbation theory we derived above

> ***remains valid as we change the way we write the Hamiltonian and the states***

When we use perturbation theory for states and operators in this occupation number form,

> ***we are usually considering transitions caused by interactions between different particles.***

We will have an unperturbed Hamiltonian, $\hat{H}_o$,

> ***such as the one for non-interaction fermions and bosons in Eq. (17.3) (** $\hat{H}_o = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j + \sum_\lambda \hbar\omega_\lambda \hat{a}_\lambda^\dagger \hat{a}_\lambda$ **).***

Then we will consider the interactions between particles,

> ***such as the electric dipole interaction discussed above for electrons and photons, Eq. (17.13) (** $\hat{H}_{ed} = \sum_{j,k,\lambda} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right)$ **),***

as a perturbation.

Time-dependent perturbation theory with annihilation and creation operators - 2

Note, incidentally, that

> ***this approach works for any kinds of particles;***
>
> > **we could, for example, apply it the electron-electron scattering.**

It is not necessary that the interaction is between different kinds of particles.

For the sake of definiteness here

> ***we will discuss a system in which there is one kind of fermion***
>
> > **(which we can think of as electrons of a given spin)**
>
> ***and one kind of boson (which we can think of as photons),***

though this general approach is appropriate for any different kinds of particles.

Perturbation theory with occupation number states - 1

We briefly review first-order time-dependent perturbation theory in the current notation.

First note the quantum mechanical states are those of the entire system.

Previously, we might have considered only the electron state,

treating the perturbation,

such as an electric dipole perturbation,

as being from something external to the quantum system,

such as a classical field.

Now our basis states must describe both

the occupation of each single-particle electron state and

the occupation of each boson mode.

Hence we write our basis states in the same way as in Eq. (17.1), e.g.,

$$\left|\ldots,0_j,1_k,0_l,\ldots 0_p,1_q,0_r,\ldots;\ \ldots,0_{\lambda c},1_{\lambda d},0_{\lambda e},\ldots,0_{\lambda r},3_{\lambda s},0_{\lambda t},\ldots\right\rangle$$

$$\equiv\left|N_{fm};N_{bn}\right\rangle\equiv\frac{1}{\sqrt{3!}}\hat{b}_k^{\dagger}\hat{b}_q^{\dagger}\hat{a}_{\lambda d}^{\dagger}\left(\hat{a}_{\lambda s}^{\dagger}\right)^3\left|0\right\rangle$$

Perturbation theory with occupation number states - 2

Specifically, the mth state of this entire (non-interacting) fermion-boson system can be written as $\left|N_{fm};N_{bm}\right\rangle$,

where N_{fm} is the list of all the occupation numbers of each possible single-particle fermion state, and

N_{bm} is similarly the list of all the occupation numbers of each possible boson mode.

These states will be the eigenstates of the unperturbed Hamiltonian,

which we take as the $\hat{H}_o$ of Eq. (17.3) ($\hat{H}_o = \sum_j E_j \hat{b}_j^\dagger \hat{b}_j + \sum_\lambda \hbar\omega_\lambda \hat{a}_\lambda^\dagger \hat{a}_\lambda$).

Analogous to Eq. (7.3) ($\hat{H}_o\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle$) we therefore have

$$\hat{H}_o\left|N_{fm};N_{bm}\right\rangle = E_m\left|N_{fm};N_{bm}\right\rangle \qquad (17.15)$$

where E_m would be the energy of this fermion-boson system in state m in the absence of any interaction between the fermions and bosons.

Perturbation theory with occupation number states - 3

The actual state of the system is some linear superposition $|\psi\rangle$ where we expand this state in the above basis,

i.e., analogous to Eq. (7.4) ($|\Psi\rangle = \sum_n a_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle$), we have

$$|\psi\rangle = \sum_m c_m \exp(-iE_m t/\hbar)|N_{fm};N_{bm}\rangle \tag{17.16}$$

where we have explicitly added the time varying factors $\exp(-iE_m t/\hbar)$ so that we can leave them out of the states $|N_{fm};N_{bm}\rangle$.

Note again that,

in contrast to previous approaches that treated perturbations as external phenomena,

E_m *is the energy of the complete (unperturbed) fermion-boson system in this state* m*, not merely the energy of the fermion.*

The state $|\psi\rangle$ is presumed to obey the time-dependent Schrödinger equation with the complete Hamiltonian,

including the perturbing Hamiltonian $\hat{H}_p$,

i.e., analogous to Eq. (7.2)

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \left(\hat{H}_o + \hat{H}_p\right)|\psi\rangle \tag{17.17}$$

Perturbation theory with occupation number states - 4

Using (17.16) $\left|\psi\right\rangle = \sum_m c_m \exp\left(-iE_m t/\hbar\right)\left|N_{fm};N_{bm}\right\rangle$ **in (17.17)** $i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \left(\hat{H}_o + \hat{H}_p\right)\left|\psi\right\rangle$

eliminating terms on both sides using (17.15) $\hat{H}_o\left|N_{fm};N_{bm}\right\rangle = E_m\left|N_{fm};N_{bm}\right\rangle$***,***

and premultiplying by the bra for state q **of the fermion-boson system,** $\left\langle N_{fq};N_{bq}\right|$**,**

gives,

analogously to Eq. (7.7)

$$i\hbar\dot{a}_i\left(t\right)\exp\left(-iE_i t/\hbar\right) = \sum_n a_n\left(t\right)\exp\left(-iE_n t/\hbar\right)\left\langle\psi_i\left|\hat{H}_p\left(t\right)\right|\psi_n\right\rangle$$, the result

$$i\hbar\dot{c}_q\exp\left(-iE_q t/\hbar\right) = \sum_m c_m\exp\left(-iE_m t/\hbar\right)\left\langle N_{fq};N_{bq}\left|\hat{H}_p\right|N_{fm};N_{bm}\right\rangle \qquad (17.18)$$

Taking the usual perturbation approach of basing the first-order change in wavefunctions on the zeroth-order state

(i.e., on the unperturbed wavefunctions),

we have, analogously to Eq. (7.10) ($\dot{a}_i^{(1)}\left(t\right) = \frac{1}{i\hbar}\sum_n a_n^{(0)}\exp\left(i\omega_{in}t\right)\left\langle\psi_i\left|\hat{H}_p\left(t\right)\right|\psi_n\right\rangle$ ***),***

$$\dot{c}_q^{(1)} \simeq \frac{1}{i\hbar}\sum_m c_m^{(0)}\exp\left[-i\left(E_m - E_q\right)t/\hbar\right]\left\langle N_{fq};N_{bq}\left|\hat{H}_p\right|N_{fm};N_{bm}\right\rangle \qquad (17.19)$$

Stimulated emission, spontaneous emission, and optical absorption

Suppose the electron-photon system starts in some specific basis state s,

so that $c_s^{(0)} = 1$ and all other such coefficients are zero.

Then (17.19) $\dot{c}_q^{(1)} \simeq \frac{1}{i\hbar}\sum_m c_m^{(0)} \exp\left[-i\left(E_m - E_q\right)t/\hbar\right]\left\langle N_{fq};N_{bq}\left|\hat{H}_p\right|N_{fm};N_{bm}\right\rangle$ **becomes**

$$\dot{c}_q^{(1)} \simeq \frac{1}{i\hbar}\exp\left[i\left(E_q - E_s\right)t/\hbar\right]\left\langle N_{fq};N_{bq}\left|\hat{H}_p\right|N_{fs};N_{bs}\right\rangle \qquad (17.20)$$

Now let us take as our perturbing Hamiltonian the electric dipole interaction of Eq.(17.13),

$$\hat{H}_p = \hat{H}_{ed} = \sum_{j,k,\lambda} H_{ed\lambda jk}\hat{b}_j^{\dagger}\hat{b}_k\left(\hat{a}_\lambda - \hat{a}_\lambda^{\dagger}\right) \qquad (17.21)$$

For simplicity here,

we presume we have only one electron, and that

there are only two single-particle states of interest for this electron,

State 1 – the lowest energy state of the electron, with energy E_1

State 2 – the upper state of the electron, with energy E_2

We will consider the three possible processes of

photon absorption, spontaneous emission and stimulated emission.

Absorption - 1

Suppose

the electron is initially in state 1 (the lower state),

there is one photon in mode λ_1, and

there are no photons in any other modes.

Then we can write the initial state as

$$\left|N_{fs};N_{bs}\right\rangle = \hat{b}_1^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle \tag{17.22}$$

This state will have an energy

$$E_s = E_1 + \hbar\omega_{\lambda_1} \tag{17.23}$$

(Here and below we will emit all of the additional $\hbar\omega_\lambda / 2$ contributions to the energy that we usually acquire from the zero point energy of the harmonic oscillator. This merely corresponds to a choice of energy origin.)

Now we have

$$\hat{H}_p \left|N_{fs};N_{bs}\right\rangle = \sum_{j,k,\lambda} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right) \hat{b}_1^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle \tag{17.24}$$

Absorption - 2

Examining the sequence of operators in (17.24)

$$\hat{H}_p \left| N_{fs}; N_{bs} \right\rangle = \sum_{j,k,\lambda} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \hat{b}_1^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle$$

we have

$$\begin{aligned} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \hat{b}_1^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle &= \hat{b}_j^\dagger \hat{b}_k \hat{b}_1^\dagger \left(\hat{a}_\lambda \hat{a}_{\lambda_1}^\dagger - \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \right) \left| 0 \right\rangle \\ &= \hat{b}_j^\dagger \left(\delta_{k1} - \hat{b}_1^\dagger \hat{b}_k \right) \left(\delta_{\lambda\lambda_1} + \hat{a}_{\lambda_1}^\dagger \hat{a}_\lambda - \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \right) \left| 0 \right\rangle \\ &= \hat{b}_j^\dagger \delta_{k1} \left(\delta_{\lambda\lambda_1} - \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \right) \left| 0 \right\rangle \\ &= \delta_{k1} \delta_{\lambda\lambda_1} \hat{b}_j^\dagger \left| 0 \right\rangle - \delta_{k1} \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle \end{aligned} \qquad (17.25)$$

Hence,

when we form $\left\langle N_{fq}; N_{bq} \right| \hat{H}_p \left| N_{fs}; N_{bs} \right\rangle$,

only two possible choices for the final state $\left| N_{fq}; N_{bq} \right\rangle$ give non-zero results.

$$\left| N_{fq}; N_{bq} \right\rangle = \hat{b}_j^\dagger \left| 0 \right\rangle$$

and

$$\left| N_{fq}; N_{bq} \right\rangle = \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle$$

First possibility for the final state

(i) Consider

$$\left|N_{fq};N_{bq}\right\rangle = \hat{b}_j^\dagger\left|0\right\rangle \tag{17.26}$$

which is the state with

one electron in state j, and

no photons in any modes.

This state will have energy

$$E_q = E_j \tag{17.27}$$

which leads to

$$\begin{aligned}\dot{c}_q^{(1)} &\simeq \frac{1}{i\hbar}\exp\left[i\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t/\hbar\right]\sum_{k,\lambda} H_{ed\lambda jk}\delta_{k1}\delta_{\lambda\lambda_1}\left\langle 0\left|\hat{b}_j\hat{b}_j^\dagger\right|0\right\rangle \\ &= \frac{1}{i\hbar}\exp\left[i\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t/\hbar\right]H_{ed\lambda_1 j1}\end{aligned} \tag{17.28}$$

Fermi's Golden Rule revisited - 1

Now we integrate over time.

By definition, we choose $c_q^{(1)}(t=0)=0$

since we regard the system as starting in the specified initial state at $t=0$**.**

Hence integrating from $t=0$ ***to*** t_o***, we have***

$$c_q^{(1)}(t_o) = -\frac{H_{ed\lambda_1 j1}}{E_j - E_1 - \hbar\omega_{\lambda_1}}\left\{\exp\left[i\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t_o/\hbar\right]-1\right\}$$

$$= -2iH_{ed\lambda_1 j1}\exp\left[i\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t_o/2\hbar\right]\frac{\sin\left[\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t_o/2\hbar\right]}{E_j - E_1 - \hbar\omega_{\lambda_1}} \quad (17.29)$$

So

$$\left|c_q^{(1)}(t_o)\right|^2 = 4\left|H_{ed\lambda_1 j1}\right|^2\frac{\sin^2\left[\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t_o/2\hbar\right]}{\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)^2}$$

$$= \frac{2\pi}{\hbar}t_o\left|H_{ed\lambda_1 j1}\right|^2\left\{\frac{1}{t_o}\frac{2\hbar}{\pi}\frac{\sin^2\left[\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)t_o/2\hbar\right]}{\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)^2}\right\} \quad (17.30)$$

Fermi's Golden Rule revisited - 1

Now the function in curly brackets $\{\ldots\}$ in Eq. (17.30)

$$\left\{\frac{1}{t_o}\frac{2\hbar}{\pi}\frac{\sin^2\left[\left(E_j-E_1-\hbar\omega_{\lambda_1}\right)t_o/2\hbar\right]}{\left(E_j-E_1-\hbar\omega_{\lambda_1}\right)^2}\right\}$$

is a sharply peaked function near $E_j-E_1-\hbar\omega_{\lambda_1}=0$***, and***

it has unit area when integrated over this energy argument

(note that $\int_{-\infty}^{\infty}\left[\left(\sin^2 x\right)/x^2\right]dx=\pi$*).*

Hence, in the limit of large t_o, it can be replaced by the Dirac δ-function, i.e.,

$$\left|c_q^{(1)}\left(t_o\right)\right|^2=\frac{2\pi}{\hbar}t_o\left|H_{ed\lambda_1 j1}\right|^2\delta\left(E_j-E_1-\hbar\omega_{\lambda_1}\right) \tag{17.31}$$

which gives a steadily rising occupation probability for this state q***.***

Hence the transition rate is

$$w_q\simeq\frac{2\pi}{\hbar}\left|H_{ed\lambda_1 j1}\right|^2\delta\left(E_j-E_1-\hbar\omega_{\lambda_1}\right) \tag{17.32}$$

Use of Fermi's Golden Rule to select final states

Now, for $j=1$, the δ-function

$$\delta\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)$$

vanishes for any finite $\hbar\omega_{\lambda_1}$,

so the only final state q that will give a transition rate is the state $j=2$,

with the corresponding restriction that

$$E_2 - E_1 = \hbar\omega_{\lambda_1} \qquad (17.33)$$

Hence our process is

we start with one photon in mode λ_1 and the electron in state 1

we finish with no photons and the electron in state 2

which describes a normal absorption process,

correctly now requiring the destruction of the photon in the process, with transition rate given by Eq. (17.32) $w_q \simeq \frac{2\pi}{\hbar}\left|H_{ed\lambda_1 j1}\right|^2 \delta\left(E_j - E_1 - \hbar\omega_{\lambda_1}\right)$.

Second possibility for the final state

(ii) The other possibility for the final state that we have to consider is

$$\left|N_{fq};N_{bq}\right\rangle = \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle \qquad (17.34)$$

with a corresponding energy

$$E_q = E_j + \hbar\omega_\lambda + \hbar\omega_{\lambda_1} \qquad (17.35)$$

But $E_q - E_s = E_j - E_1 + \hbar\omega_\lambda$ **cannot be close to zero because**

$E_j - E_1 \geq 0$ ***and*** $\hbar\omega_\lambda$ ***is also positive.***

Hence on integrating over time as above,

this term will not give rise to any steady transition rate.

Hence this possibility can be discarded here.

(As we will see below,

this term would actually correspond to photon emission,

but we cannot emit a photon because we are starting in the lowest energy electron state,

and hence there is no lower state to which we can emit.)

Interaction of different kinds of particles – 2

Reading – Section 17.4 from "Spontaneous emission"

Spontaneous and stimulated emission with annihilation and creation operators

Multiple-photon case

Total spontaneous emission

Spontaneous emission - 1

Suppose now that

the electron is initially in state 2 (the upper state),

and there are no photons in any mode.

This situation is not like any we considered before in semiclassically.

Indeed, semiclassically it would be trivial;

with no electromagnetic field, there would be no transitions.

The result now, though, will be different.

Our starting state now is

$$\left|N_{fs};N_{bs}\right\rangle = \hat{b}_2^\dagger \left|0\right\rangle \tag{17.36}$$

with a corresponding energy

$$E_s = E_2 \tag{17.37}$$

Spontaneous emission - 2

Now in forming $\hat{H}_p \left| N_{fs}; N_{bs} \right\rangle$ with our expression (17.21)

$$\hat{H}_p = \hat{H}_{ed} = \sum_{j,k,\lambda} H_{ed\lambda jk} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right)$$

with our starting state $\left| N_{fs}; N_{bs} \right\rangle = \hat{b}_2^\dagger \left| 0 \right\rangle$, we encounter the string of operators

$$\begin{aligned} \hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \hat{b}_2^\dagger \left| 0 \right\rangle &= \hat{b}_j^\dagger \hat{b}_k \hat{b}_2^\dagger \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \left| 0 \right\rangle \\ &= \hat{b}_j^\dagger \left(\delta_{2k} - \hat{b}_2^\dagger \hat{b}_k \right) \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger \right) \left| 0 \right\rangle \qquad (17.38) \\ &= -\delta_{2k} \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \left| 0 \right\rangle \end{aligned}$$

So that we get a non-zero result for $\left\langle N_{fq}; N_{bq} \right| \hat{H}_p \left| N_{fs}; N_{bs} \right\rangle$,

we must therefore choose for state q

$$\left| N_{fq}; N_{bq} \right\rangle = \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \left| 0 \right\rangle \qquad (17.39)$$

which is the state with

the electron now in state j*,*

and a photon in mode λ*.*

This state q ***has energy***

$$E_q = E_j + \hbar \omega_\lambda \qquad (17.40)$$

Spontaneous emission - 3

Hence we now have, for this state q (making some specific choice of mode λ and electron state j in the perturbation theory result Eq. (17.19)

$$\dot{c}_q^{(1)} \simeq \frac{1}{i\hbar}\sum_m c_m^{(0)} \exp\left[-i\left(E_m - E_q\right)t/\hbar\right]\left\langle N_{fq};N_{bq}\right|\hat{H}_p\left|N_{fm};N_{bm}\right\rangle$$ **)**

$$\begin{aligned}\dot{c}_q^{(1)} &\simeq \frac{1}{i\hbar}\exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda\right)t/\hbar\right]\sum_k H_{ed\lambda jk}\delta_{k2}\left\langle 0\right|\hat{a}_\lambda\hat{b}_j\hat{a}_j^\dagger\hat{b}_\lambda^\dagger\left|0\right\rangle \\ &= \frac{1}{i\hbar}\exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda\right)t/\hbar\right]H_{ed\lambda j2}\end{aligned} \qquad (17.41)$$

Integrating and taking $\left|c_q^{(1)}\right|^2$ to get the transition rate gives

$$w_q = \frac{2\pi}{\hbar}\left|H_{ed\lambda j2}\right|^2 \delta\left(E_j - E_2 + \hbar\omega_\lambda\right) \qquad (17.42)$$

As before, for any finite $\hbar\omega_\lambda$

the only possible choice is $j=1$ for the final state if there is to be any transition rate,

with the requirement

$$E_2 - E_1 = \hbar\omega_\lambda \qquad (17.43)$$

i.e., we have

$$w_q = \frac{2\pi}{\hbar}\left|H_{ed\lambda 12}\right|^2 \delta\left(E_1 - E_2 + \hbar\omega_\lambda\right) \qquad (17.44)$$

Spontaneous emission - 4

This transition process is spontaneous emission.

The electron starts in its higher state 2 with no photons present,

and ends in its lower state 1 with one photon present.

This photon can be in any mode λ that has the correct photon energy to match the energy separation $E_2 - E_1$

(and for which the coefficient $H_{ed\lambda 12}$ is not formally zero for some other reason).

This process has emerged naturally as a consequence of quantizing the electromagnetic field,

requiring essentially no additional physics other than that quantization.

Stimulated emission - 1

We have one final and important process to consider,

which is stimulated emission.

This process is strong in laser light,

though it is also present in small amounts all the time,

and is necessary in order to make the statistical mechanics of light agree with observation.

Suppose now we have

a photon in mode λ_1 and

an electron in its upper state 2.

The initial state is therefore

$$\left| N_{fs}; N_{bs} \right\rangle = \hat{b}_2^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle \tag{17.45}$$

with an energy

$$E_s = E_2 + \hbar \omega_{\lambda_1} \tag{17.46}$$

Stimulated emission - 2

Then, with algebra similar to that used before (e.g., in Eq. (17.25))

$$\hat{b}_j^\dagger \hat{b}_k \left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right) \hat{b}_2^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle = \delta_{k2}\delta_{\lambda\lambda_1} \hat{b}_j^\dagger \left|0\right\rangle - \delta_{k2} \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle \qquad (17.47)$$

The first term here is simply the absorption term,

but this will vanish because there is no electron state into which we can absorb,

given that we are starting in the upper state.

The second term has two possibilities in the summation,

which we will now consider,

$\lambda \neq \lambda_1$ i.e., both final photons in different modes $\left|N_{fq};N_{ba}\right\rangle = \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left|0\right\rangle$

$\lambda = \lambda_1$ i.e., both final photons in the same mode $\left|N_{fq};N_{bq}\right\rangle = \frac{1}{\sqrt{2!}} \hat{b}_j^\dagger \left(\hat{a}_{\lambda_1}^\dagger\right)^2 \left|0\right\rangle$

Final two photons in different modes - 1

(a) Suppose $\lambda \neq \lambda_1$.

Then for some specific λ,

to get a non-zero result for $\left\langle N_{fq}; N_{bq} \middle| \hat{H}_p \middle| N_{fs}; N_{bs} \right\rangle$

the final state will have to be

$$\left| N_{fq}; N_{ba} \right\rangle = \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \left| 0 \right\rangle \tag{17.48}$$

with energy

$$E_q = E_j + \hbar\omega_\lambda + \hbar\omega_{\lambda_1} \tag{17.49}$$

corresponding to a state with

the electron in level j and

a photon in each of the different modes λ and λ_1.

We will have, for some specific λ and j

$$\begin{aligned} \dot{c}_q^{(1)} &\simeq \frac{-1}{i\hbar} \exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda \right) t / \hbar \right] H_{ed\lambda j2} \left\langle 0 \middle| \hat{a}_{\lambda_1} \hat{a}_\lambda \hat{b}_j \hat{b}_j^\dagger \hat{a}_\lambda^\dagger \hat{a}_{\lambda_1}^\dagger \middle| 0 \right\rangle \\ &= \frac{-1}{i\hbar} \exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda \right) t / \hbar \right] H_{ed\lambda j2} \end{aligned} \tag{17.50}$$

Final two photons in different modes - 2

This expression, Eq. (17.50)

$$\begin{aligned}\dot{c}_q^{(1)} &\simeq \frac{-1}{i\hbar}\exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda\right)t/\hbar\right]H_{ed\lambda j2}\left\langle 0\middle|\hat{a}_{\lambda_1}\hat{a}_\lambda\hat{b}_j\hat{b}_j^\dagger\hat{a}_\lambda^\dagger\hat{a}_{\lambda_1}^\dagger\middle|0\right\rangle \\ &= \frac{-1}{i\hbar}\exp\left[i\left(E_j - E_2 + \hbar\omega_\lambda\right)t/\hbar\right]H_{ed\lambda j2}\end{aligned}$$

leads to a transition rate

$$w_q = \frac{2\pi}{\hbar}\left|H_{ed\lambda j2}\right|^2 \delta\left(E_j - E_2 + \hbar\omega_\lambda\right) \tag{17.51}$$

for which the only possibility here for non-zero transition rate is $j=1$***, and***

$$E_2 - E_1 = \hbar\omega_\lambda \tag{17.52}$$

with a transition rate

$$w_q = \frac{2\pi}{\hbar}\left|H_{ed\lambda 12}\right|^2 \delta\left(E_1 - E_2 + \hbar\omega_\lambda\right) \tag{17.53}$$

This process is just spontaneous emission into mode λ***,***

and the transition rate Eq. (17.53) is identical to that of Eq. (17.44).

The only point of this current derivation is to show explicitly that

the presence of a photon in another mode has no influence on spontaneous emission.

Final two photons in the same mode - 1

(b) Suppose now we consider the case $\lambda = \lambda_1$.

Now

to get a non-zero result for $\langle N_{fq}; N_{bq} | \hat{H}_p | N_{fs}; N_{bs} \rangle$

the final state will have to be

$$|N_{fq}; N_{bq}\rangle = \frac{1}{\sqrt{2!}} \hat{b}_j^\dagger \left(\hat{a}_{\lambda_1}^\dagger\right)^2 |0\rangle \tag{17.54}$$

with energy

$$E_q = E_j + 2\hbar\omega_{\lambda_1} \tag{17.55}$$

Note that, to have a normalized state here,

we have had to introduce the factor $1/\sqrt{2!}$

see, e.g., Eq. (14.72) or Eq. (14.126)

$$|n_1, n_2, \ldots, n_\lambda, \ldots\rangle = \frac{1}{\sqrt{n_1! n_2! \ldots n_\lambda! \ldots}} \left(\hat{a}_1^\dagger\right)^{n_1} \left(\hat{a}_2^\dagger\right)^{n_2} \ldots \left(\hat{a}_\lambda^\dagger\right)^{n_\lambda} \ldots |0\rangle$$

Final two photons in the same mode - 2

Hence we obtain a term in

$$\left\langle N_{fq};N_{bq}\middle|\hat{H}_p\middle|N_{fs};N_{bs}\right\rangle = \left\langle N_{fq};N_{bq}\middle|\sum_{j,k,\lambda} H_{ed\lambda jk}\hat{b}_j^\dagger\hat{b}_k\left(\hat{a}_\lambda - \hat{a}_\lambda^\dagger\right)\middle|N_{fs};N_{bs}\right\rangle \qquad (17.56)$$

that is

$$\begin{aligned} H_{ed\lambda_1 j2}\left\langle 0\right|\frac{1}{\sqrt{2!}}\left(\hat{a}_{\lambda_1}\right)^2\hat{b}_j\hat{b}_j^\dagger\left(\hat{a}_{\lambda_1}^\dagger\right)^2\left|0\right\rangle &= \sqrt{2!}\,H_{ed\lambda_1 j2}\left\langle 0\right|\frac{1}{\sqrt{2!}}\left(\hat{a}_{\lambda_1}\right)^2\hat{b}_j\frac{1}{\sqrt{2!}}\hat{b}_j^\dagger\left(\hat{a}_{\lambda_1}^\dagger\right)^2\left|0\right\rangle \\ &= \sqrt{2}H_{ed\lambda_1 j2} \end{aligned} \qquad (17.57)$$

The $\sqrt{2}$ is very important

it shows we are getting a larger amplitude for this process than we did for the spontaneous emission term.

This $\sqrt{2}$ can be traced back to the fact that we started with one photon in this mode λ_1 and created another one.

Final two photons in the same mode - 3

Hence for this process we have

$$\dot{c}_q^{(1)} \simeq \frac{-1}{i\hbar} \exp\left[i\left(E_j - E_2 + \hbar\omega_{\lambda_1} \right) t/\hbar \right] \sqrt{2}\, H_{ed\lambda_1 j2} \quad (17.58)$$

leading to a transition rate into this final state of

$$w_q = \frac{2\pi}{\hbar} 2 \left| H_{ed\lambda_1 j2} \right|^2 \delta\left(E_j - E_2 + \hbar\omega_{\lambda_1} \right) \quad (17.59)$$

for which the only possibility for finite transition rate is with $j=1$ and

$$E_2 - E_1 = \hbar\omega_{\lambda_1} \quad (17.60)$$

with a corresponding transition rate, finally, of

$$w_q = \frac{2\pi}{\hbar} 2 \left| H_{ed\lambda_1 12} \right|^2 \delta\left(E_1 - E_2 + \hbar\omega_{\lambda_1} \right) \quad (17.61)$$

Note in particular the additional factor of 2 that has appeared in (17.61).

This process is stimulated emission into mode λ_1.

Note that, other things being equal (e.g., matrix elements and energies),

the transition rate into the mode already occupied with a photon is twice as high as the spontaneous emission into an unoccupied mode.

Bosons want to go into modes that are already occupied!

Multiphoton case - 1

It is left as an exercise to analyze the case of n_{λ_1} photons initially in mode λ_1.

Stimulated emission

The result for stimulated emission is

$$w_q = \frac{2\pi}{\hbar}\left(n_{\lambda_1}+1\right)\left|H_{ed\lambda_1 12}\right|^2 \delta\left(E_1 - E_2 + \hbar\omega_{\lambda_1}\right) \tag{17.62}$$

with the transition rate into the mode λ_1 being $n_{\lambda_1}+1$ times larger than the spontaneous rate into an otherwise similar mode.

Spontaneous emission

The spontaneous emission in any other mode is unaffected by the presence of n_{λ_1} photons in mode λ_1, as can be shown directly by considering the multiphoton case.

Absorption

The result for absorption with n_{λ_1} photons initially in mode λ_1 can similarly be shown to be

$$w_q = \frac{2\pi}{\hbar} n_{\lambda_1}\left|H_{ed\lambda_1 12}\right|^2 \delta\left(E_2 - E_1 - \hbar\omega_{\lambda_1}\right) \tag{17.63}$$

Multiphoton case - 2

Note specifically that we wrote the matrix element $H_{ed\lambda_1 12}$, not the matrix element $H_{ed\lambda_1 21}$ in (17.63) ($w_q = \frac{2\pi}{\hbar} n_{\lambda_1} \left| H_{ed\lambda_1 12} \right|^2 \delta\left(E_2 - E_1 - \hbar\omega_{\lambda_1}\right)$).

Given the definition of $H_{ed\lambda_1 jk}$ above (Eq. (17.12)),

$$H_{ed\lambda jk} = \sqrt{-1}\, e \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}} \int \phi_j^*(\mathbf{r}_i)\left[\mathbf{u}_\lambda(\mathbf{r}_i).\mathbf{r}_i\right]\phi_k(\mathbf{r}_i)\, d^3\mathbf{r}_i$$

we see that

$$H_{ed\lambda_1 12} = H^*_{ed\lambda_1 21} \tag{17.64}$$

and so the squared moduli are the same.

(This is a general property for any kind of perturbing Hamiltonian since it must be Hermitian).

The relation between the absorption and stimulated emission strengths is fundamental,

as is their relation to the spontaneous emission strengths.

There is only one set of matrix elements involved in all of these processes.

Total spontaneous emission rate

To calculate rates of the decay from higher to lower (electron) states,

we add up the spontaneous emission rates for all possible modes.

We presume we start off with

the electron in an excited state (here state 2), and

no photons in any modes.

The total spontaneous transition rate will be

the sum of the transition rates into all possible final states q through spontaneous emission

$$W_{spon} = \sum_q w_q \qquad (17.65)$$

where w_q is the spontaneous emission rate into a specific mode λ, Eq.(17.44)

$$w_q = \frac{2\pi}{\hbar} \left| H_{ed\lambda 12} \right|^2 \delta\left(E_1 - E_2 + \hbar\omega_\lambda \right)$$

Since we know that the electron must start in state 2 and end in state 1,

the sum reduces to summing over all possible photon modes λ.

$$W_{spon} = \frac{2\pi}{\hbar} \sum_\lambda \left| H_{ed\lambda 12} \right|^2 \delta\left(E_1 - E_2 + \hbar\omega_\lambda \right) \qquad (17.66)$$

Matrix element evaluation

First we evaluate the matrix element $H_{ed\lambda 12}$**.**

We presume the field is approximately uniform over the quantum system, so

we replace $\mathbf{u}_\lambda(\mathbf{r})$ ***by*** $\mathbf{u}_\lambda(\mathbf{r}_o)$

($\mathbf{r}_o$ **is the approximate position of the quantum system).**

Hence for the matrix element we need here (Eq.(17.12))

$$\begin{aligned} H_{ed\lambda jk} &= i\,e\sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}}\int \phi_j^*(\mathbf{r})\left[\mathbf{u}_\lambda(\mathbf{r}).\mathbf{r}\right]\phi_k(\mathbf{r})\,d^3\mathbf{r} \\ &= i\,e\sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}}\mathbf{u}_\lambda(\mathbf{r}_o).\mathbf{r}_{jk} \end{aligned} \qquad (17.67)$$

where

$$\mathbf{r}_{jk} = \int \phi_j^*(\mathbf{r})\,\mathbf{r}\,\phi_k(\mathbf{r})\,d^3\mathbf{r} \qquad (17.68)$$

Choice of modes

For our calculation here,

we will presume that the modes of the electromagnetic field are all plane waves in unbounded, free space.

This is a standard assumption in most calculations of spontaneous emission,

though it is not always correct.

For example,

if the electron system is within some resonator,

the modes of interest will be those of the resonator,

and the result below does not necessarily apply.

It is possible even to inhibit spontaneous emission by making sure that the modes of the resonator do not coincide either

in energy or

in field amplitude distribution with electronic states.

Plane wave modes - 1

We need a normalizable form for plane wave modes.

We imagine we have a cubic box of volume V_b.

It is common for mathematical convenience to use running waves

(which technically come from the somewhat unphysical periodic boundary conditions encountered also in solid state physics for electron waves),

though one could use standing waves and get the same result for a large box.

The resulting modes have the form

$$\mathbf{u}_\lambda(\mathbf{r}) = \mathfrak{e}\frac{1}{\sqrt{V_b}}\exp(i\mathbf{k}_\lambda.\mathbf{r}) \qquad (17.69)$$

where $\mathfrak{e}$ is a unit vector in the polarization direction of the electric field.

These modes are readily seen to be normalized over the box of volume V_b.

The allowed values of k_x, are spaced by $2\pi / L_x$,

where L_x is the length of the box in the x direction,

and similarly for the y and z directions,

leading to a density of modes in $\mathbf{k}$-space of $V_b/(2\pi)^3$.

For such propagating waves, we will also have two distinct polarization directions, though we will handle polarization properties directly.

Plane wave modes - 2

We approximate the sum over the modes λ by

an integral over $\mathbf{k}$ with this density of states,

and also formally a sum over the two possible polarizations, i.e.,

$$\sum_{\lambda}\ldots\to\sum_{polarizations}\int\frac{V_b}{\left(2\pi\right)^3}d^3\mathbf{k}_{\lambda}\ldots \qquad (17.70)$$

In considering the polarizations,

we choose polarization directions at right angles to one another

and at right angles to $\mathbf{k}_{\lambda}$.

Specifically we choose them relative to the vector matrix element $\mathbf{r}_{12}$,

here we choose one polarization $\mathfrak{p}$ to be in the plane of the vectors $\mathbf{k}_{\lambda}$ and $\mathbf{r}_{12}$.

With this choice,

the other polarization direction is perpendicular to $\mathbf{r}_{12}$,

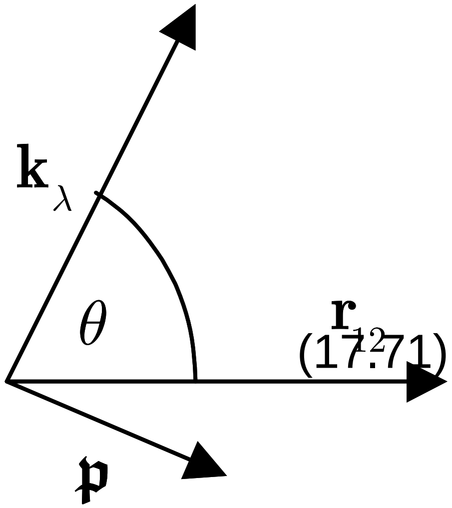
and so $\mathbf{u}_{\lambda}\left(\mathbf{r}_o\right).\mathbf{r}_{12}$ vanishes for this polarization.

Hence we need only retain the first polarization

For this choice, we therefore find that

$$\mathbf{u}_{\lambda}\left(\mathbf{r}_o\right).\mathbf{r}_{12}=u_{\lambda}\left(\mathbf{r}_o\right)r_{12}\sin\theta \qquad (17.71)$$

(the non-bold quantities refer to the vector magnitudes).



Total spontaneous transition rate - 1

Now we can use all these results to rewrite the Eq. (17.66)

$$W_{spon} = \frac{2\pi}{\hbar}\int \frac{V_b}{(2\pi)^3}\left| i\,e\sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_o}}\frac{1}{\sqrt{V_b}}\exp\left(i\mathbf{k}_\lambda.\mathbf{r}_o\right) r_{12}\sin\theta\right|^2 \delta\left(E_1 - E_2 + \hbar\omega_\lambda\right) d^3\mathbf{k}_\lambda \qquad (17.72)$$

i.e.,

$$W_{spon} = \frac{e^2\left|r_{12}\right|^2}{8\pi^2\varepsilon_o}\int \omega_\lambda \sin^2\theta\,\delta\left(E_1 - E_2 + \hbar\omega_\lambda\right) d^3\mathbf{k}_\lambda$$

$$= \frac{e^2\left|r_{12}\right|^2}{8\pi^2\varepsilon_o}\int_{k_\lambda=0}^{\infty}\int_{\theta=0}^{\pi}\omega_\lambda\,\delta\left(E_1 - E_2 + \hbar\omega_\lambda\right)\sin^2\theta\,2\pi\sin\theta k_\lambda^2 d\theta dk_\lambda \qquad (17.73)$$

Noting that $ck_\lambda = \omega_\lambda$, and changing variables to $\hbar ck_\lambda \equiv \hbar\omega_\lambda$, we have

$$W_{spon} = \frac{e^2\left|r_{12}\right|^2}{4\pi\varepsilon_o\hbar^4c^3}\int_{\hbar\omega_\lambda=0}^{\infty}\hbar\omega_\lambda\,\delta\left(E_1 - E_2 + \hbar\omega_\lambda\right)\left(\hbar\omega_\lambda\right)^2 d\hbar\omega_\lambda\int_0^{\pi}\sin^3\theta d\theta \qquad (17.74)$$

Given that

$$\int_0^{\pi}\sin^3\theta d\theta = \frac{4}{3} \qquad (17.75)$$

we finally have that the total spontaneous emission rate is

$$W_{spon} = \frac{e^2\left|r_{12}\right|^2\omega_{12}^3}{3\pi\varepsilon_o\hbar c^3} \qquad (17.76)$$

where

$$\omega_{12} = \left(E_2 - E_1\right)/\hbar \qquad (17.77)$$

Total spontaneous transition rate - 2

Such a rate gives rise to a natural lifetime, τ_{nat}, for a state

$$\tau_{nat} = 1/W_{spon} \tag{17.78}$$

A quantum mechanical system sitting in empty space in an excited state

will decay on average over this timescale to its lower state, emitting a photon.

The direction of the mode into which the photon is emitted is random

(though weighted somewhat by the polarization effects).

Quantum information -1

Reading – Sections 18.1 – 18.2

Quantum mechanical measurements and wavefunction collapse

Quantum cryptography

- No-cloning theorem
- A simple quantum encryption scheme

Representing information - 1

In a classical world

we represent information in terms of the classical state of an object.

In analog form, we could represent a number as, e.g.,

the length of a rod in meters

the value of an electrical potential in volts

In digital form,

we represent numbers usually as a sequence of “bits” that are either “1” or “0”.

We can represent the 1 and 0 physically as, e.g.,

- an object being “up” or “down”
- a device being “on” (e.g., passing current) or “off” (e.g., not passing current)
- a voltage being “high” or “low”

Representing information - 2

In quantum mechanics,

we can also use superpositions in representing information,

such as a superposition of "up" and "down."

In a classical world for one physical system, equivalently

a system that was half up and half down could be represented by it being horizontal

But in quantum mechanics, we can have superpositions of multiple systems

so-called *entangled states*

that have no classical analog

And measurement on a quantum mechanical system in a superposition can have quite a different result from that in a classical system

i.e., the process of "collapse" into an eigenstate

The processes of entanglement and collapse under measurement give different opportunities in handling and processing information

leading to the field of quantum information

e.g., quantum cryptography, quantum computing, and quantum teleportation.

Quantum mechanical measurements and collapse of the wavefunction - 1

To interpret a quantum mechanical calculation to predict the result of a measurement,

we say that

if the quantum mechanical calculation says the state of the system is $|\psi\rangle$

then the average value we will measure for some quantity A is given by

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle \tag{18.1}$$

where $\hat{A}$ is the operator associated with the quantity A.

The measurement is a statistical process –

we must repeat the experiment many times from the start

including the process that puts the system into the state $|\psi\rangle$

and take the average answer.

We also find that

every measurement we make returns a value corresponding to one of the possible eigenvalues, A_n, of $\hat{A}$.

Quantum mechanical measurements and collapse of the wavefunction - 2

Not every measurement returns the same value.

If we decompose the state into a linear combination of the normalized eigenstates $\left|\psi_n\right\rangle$ of the operator $\hat{A}$, i.e.,

$$\left|\psi\right\rangle = \sum_n a_n \left|\psi_n\right\rangle \qquad (18.2)$$

then we find that the probability of measuring a particular value A_n is given by $\left|a_n\right|^2$.

Furthermore, if we make any subsequent measurements on this system,

presuming no external influence is applied in the meantime,

we will always subsequently get the same answer A_n on measuring the quantity A.

This behavior is called the

"collapse of the wavefunction".

Measuring a quantity A appears to force it into one of its eigenstates.

As far as we know empirically, this collapse is totally random.

Quantum cryptography

We can use this randomness for a specific practical application, which is the secure distribution of information.

Unlike conventional cryptography,

which relies on it being very difficult mathematically to decode some information if one does not have the key,

quantum cryptography relies on fundamental properties of quantum mechanics

allowing exchange of information with apparently absolute security.

To see how this works,

we first show that it is impossible to clone a quantum mechanical state reliably.

No-cloning theorem

The security of quantum cryptography relies on it being impossible to make an exact replica of an arbitrary quantum mechanical state of a system.

For example,

we might want to take an electron that is in a particular spin state,

and make another electron have exactly the same spin state,

leaving the first electron in its original state.

Equivalently,

we might want to take a photon in a particular polarization state

and make another photon with exactly the same polarization state,

leaving the first photon in its original polarization state.

In the case of photons,

the two polarization basis states can be, respectively, horizontally polarized and vertically polarized.

A general linear combination of those two states is an elliptically polarized photon,

i.e., some specific ratio of amplitudes of horizontal and vertical polarization with some phase difference between the amplitudes.

In both these cases, we can if we wish write the state as a simple two-element vector with complex elements.

Proof of the no-cloning theorem

We can show that, starting from

the first system in an arbitrary state $\left|\psi_{1a}\right\rangle$

and the second system in some prescribed starting state, $\left|\psi_{2s}\right\rangle$**,**

we cannot in general create the second system in the state $\left|\psi_{2a}\right\rangle$**, leaving the first system in state** $\left|\psi_{1a}\right\rangle$**.**

In this proof, our initial state of the two systems is therefore

the (direct product) state $\left|\psi_{1a}\right\rangle\left|\psi_{2s}\right\rangle$**.**

We then imagine that we have some operation that, over time,

turns this state into the state $\left|\psi_{1a}\right\rangle\left|\psi_{2a}\right\rangle$**.**

This operation is just some time-evolution operation that we can describe by a (unitary) linear operator $\hat{T}$**,**

such as the time-evolution operator we devised in Chapter 3,

$$\hat{T} = \exp\left[-i\hat{H}\left(t - t_o\right)/\hbar\right] \qquad (18.3)$$

where t **is the time we finish and** t_o **is the time when we started.**

Cloning system properties

We presume we have engineered our cloning system to give $\hat{T}$ the required properties.

Specifically we need at least two properties for $\hat{T}$.

First we want $\hat{T}$ to perform the operation

$$\left|\psi_{1a}\right\rangle\left|\psi_{2a}\right\rangle = \hat{T}\left|\psi_{1a}\right\rangle\left|\psi_{2s}\right\rangle \tag{18.4}$$

cloning the state a of system 1 also into system 2.

Of course, we want to have this work for any initial state of system 1.

Suppose we choose some other state $\left|\psi_{1b}\right\rangle$ as the initial state of system 1

(we will choose this orthogonal to $\left|\psi_{1a}\right\rangle$).

Then we also want $\hat{T}$ now to perform the operation

$$\left|\psi_{1b}\right\rangle\left|\psi_{2b}\right\rangle = \hat{T}\left|\psi_{1b}\right\rangle\left|\psi_{2s}\right\rangle \tag{18.5}$$

cloning state b into system 2.

There is in general no problem in principle with constructing such an operator with these two properties.

Cloning a linear superposition state - 1

The problem comes when we want to clone a linear superposition state.

Suppose the initial state of system 1 is the linear superposition

$$\left|\psi_{1Sup}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{1a}\right\rangle + \left|\psi_{1b}\right\rangle\right) \qquad (18.6)$$

Hence the initial state of the pair of systems is

$$\frac{1}{\sqrt{2}}\left(\left|\psi_{1a}\right\rangle + \left|\psi_{1b}\right\rangle\right)\left|\psi_{2s}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{1a}\right\rangle\left|\psi_{2s}\right\rangle + \left|\psi_{1b}\right\rangle\left|\psi_{2s}\right\rangle\right) \qquad (18.7)$$

By postulation in quantum mechanics, the operators are linear –

operating on a linear superposition must give the linear superposition of the operations, i.e.,

$$\begin{aligned}\hat{T}\frac{1}{\sqrt{2}}\left(\left|\psi_{1a}\right\rangle\left|\psi_{2s}\right\rangle + \left|\psi_{1b}\right\rangle\left|\psi_{2s}\right\rangle\right) &= \frac{1}{\sqrt{2}}\left(\hat{T}\left|\psi_{1a}\right\rangle\left|\psi_{2s}\right\rangle + \hat{T}\left|\psi_{1b}\right\rangle\left|\psi_{2s}\right\rangle\right) \\ &= \frac{1}{\sqrt{2}}\left(\left|\psi_{1a}\right\rangle\left|\psi_{2a}\right\rangle + \left|\psi_{1b}\right\rangle\left|\psi_{2b}\right\rangle\right)\end{aligned} \qquad (18.8)$$

This is not the result we wanted for our cloning operation, which was

$$\frac{1}{2}\left(\left|\psi_{1a}\right\rangle + \left|\psi_{1b}\right\rangle\right)\left(\left|\psi_{2a}\right\rangle + \left|\psi_{2b}\right\rangle\right) \qquad (18.9)$$

Such a result would have cloned the superposition state of system 1 into system 2.

Cloning a linear superposition state - 2

The linearity properties of the quantum mechanical operator determined that,

if we got the cloning properties we wanted for the individual states a and b,

we did not get the cloning result we wanted for the superposition.

This result is not special to the particular superposition we chose –

any other superposition would give us a similar "wrong" answer.

Hence,

though we could in principle make a device to clone specific basis states,

that device could not clone superpositions of those basis states,

and hence we cannot make a device that will clone an arbitrary quantum state.

We can use this no-cloning property to ensure the security of communications through quantum cryptography.

A simple quantum encryption scheme - 1

A simple single-photon scheme for quantum encryption was devised by Bennett and Brassard in 1984

Similar schemes have been demonstrated over

a 48 km optical fiber network, and

through the atmosphere over 1.6 km.

Such a horizontal atmospheric distance tests whether we can send quantum encrypted signals to a satellite and back.

The communication rate ,

~ 100's of bits per second,

is fast enough for distributing simple messages or secret cryptographic keys for use with classical cryptography.

A simple quantum encryption scheme - 2

The sender is Alice.

The recipient is Bob.

“Eve” is an eavesdropper.

Consider (i).

For a “1”,

Alice sends a vertically polarized photon

a photon in the state $|\mathrm{V}\rangle$

For a “0”,

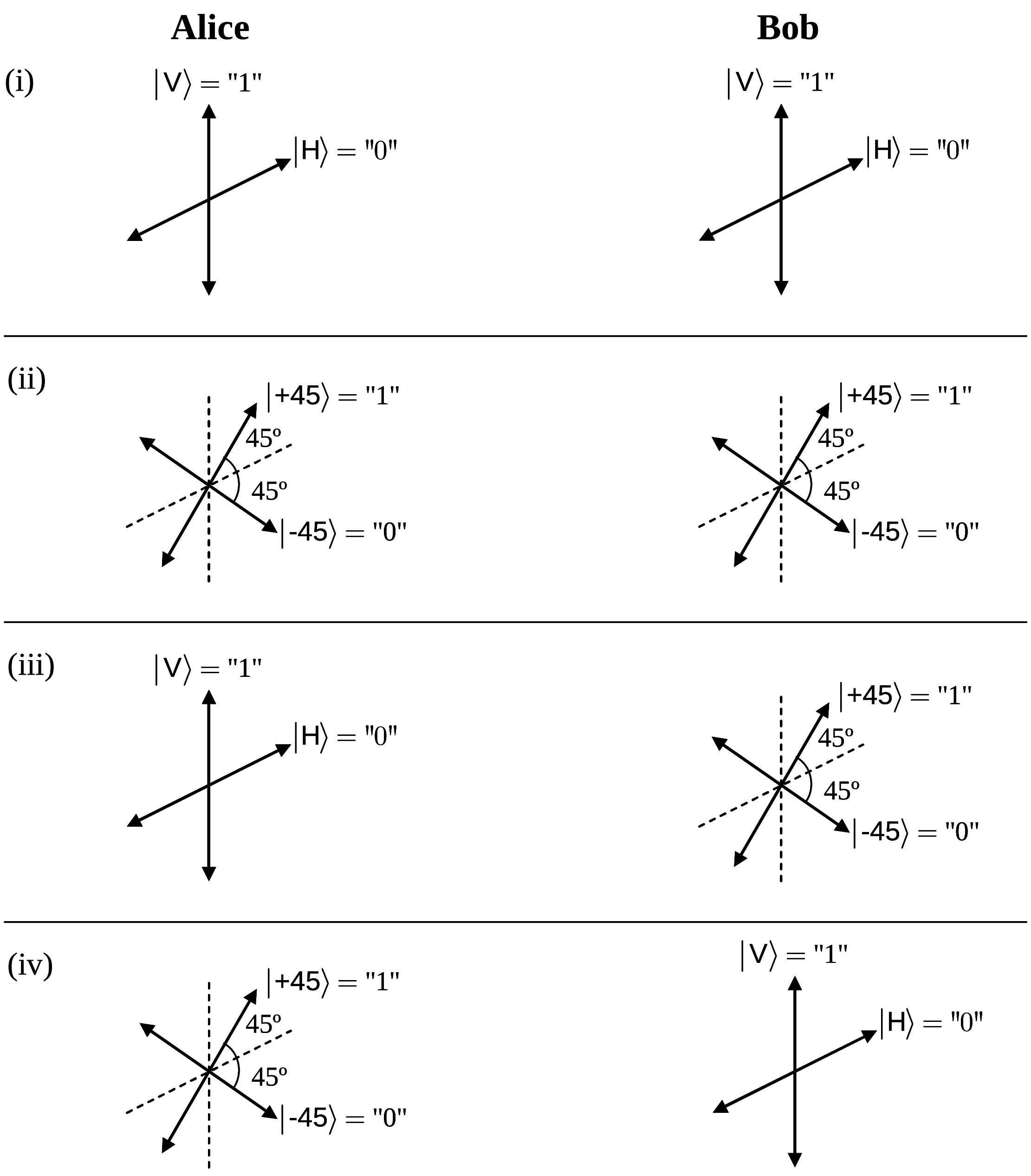
she sends a horizontally polarized photon

a photon in the state $|\mathrm{H}\rangle$.

Bob’s apparatus separates the two polarizations to different single-photon detectors

vertical for “1”,

horizontal for “0”.



A simple quantum encryption scheme - 3

Scheme (i) is not itself secure.

Eve could insert a detection system like Bob's into the path,

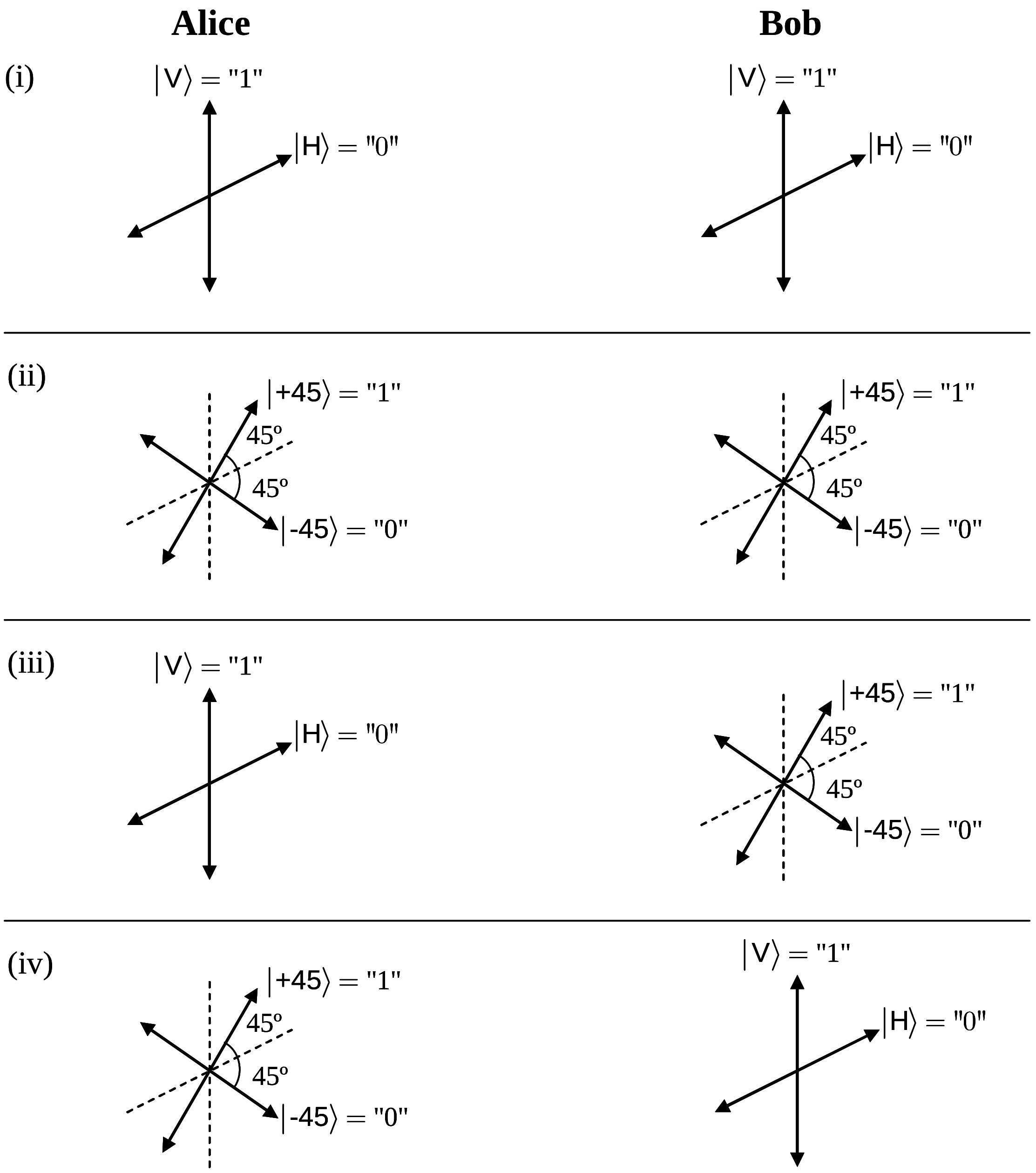
receive the photon from Alice,

write down the answer,

then, using a transmission system like Alice's,

retransmit the photon on to Bob,

with Alice and Bob being unaware of her interception.



A simple quantum encryption scheme - 4

Now rotate by 45º the apparatus Alice uses for transmission.

Now Alice transmits

a "1" using the state $|{+45}\rangle$

and

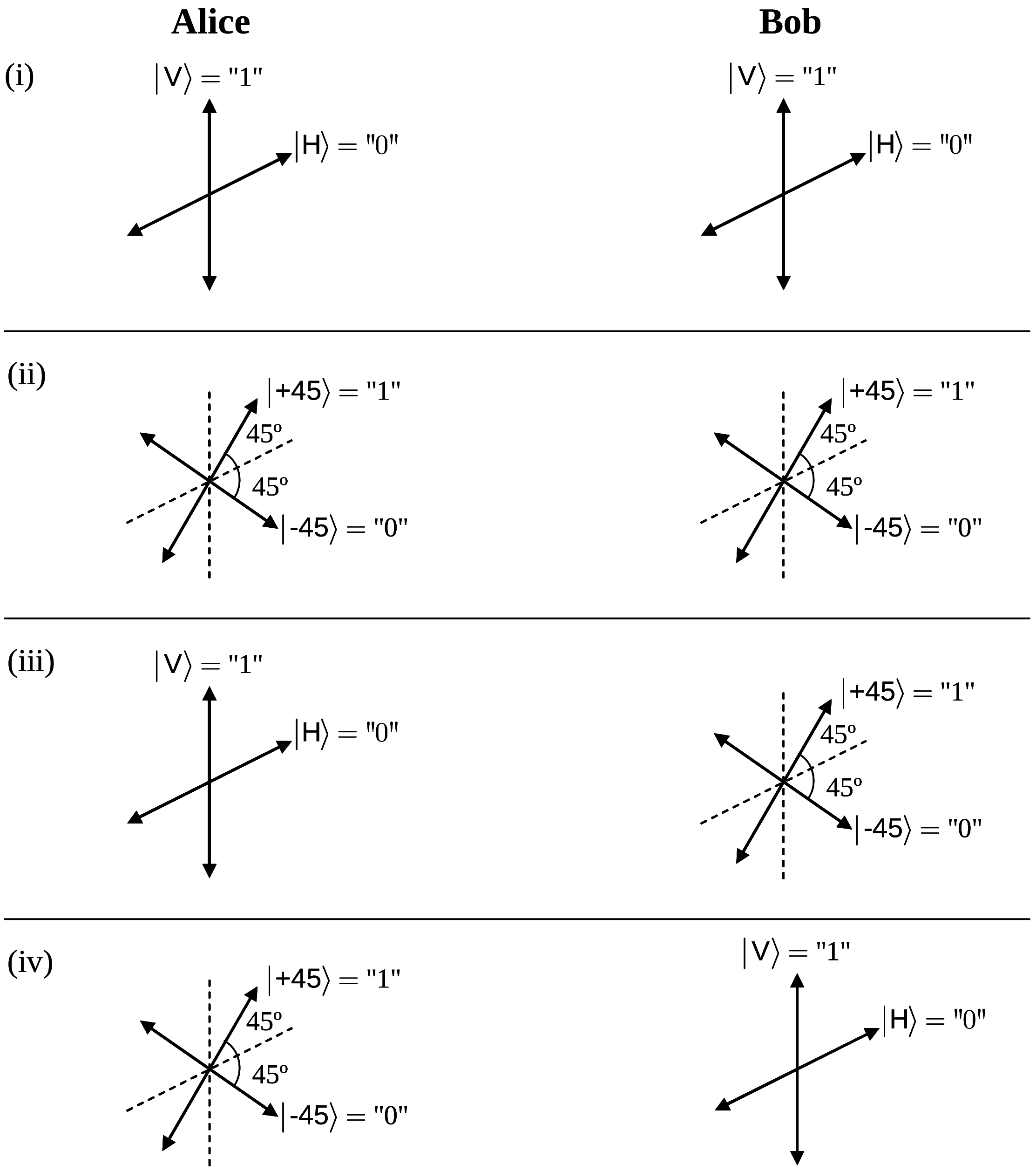
a "0" using the state $|{-45}\rangle$.

If Bob leaves his apparatus unchanged, as in (iv),

he will receive no information at all.

Note that the state $|{+45}\rangle$ can be written as a linear superposition of the horizontal and vertical states, i.e.,

$$|{+45}\rangle = \frac{1}{\sqrt{2}}\left(|H\rangle + |V\rangle\right) \qquad (18.10)$$



A simple quantum encryption scheme - 5

With the apparatus as in (iv)

Bob's apparatus will give the answer

$|\mathrm{H}\rangle$ half the time and the answer

$|\mathrm{V}\rangle$ half the time

because the expansion coefficients in these two basis states are each $1/\sqrt{2}$,

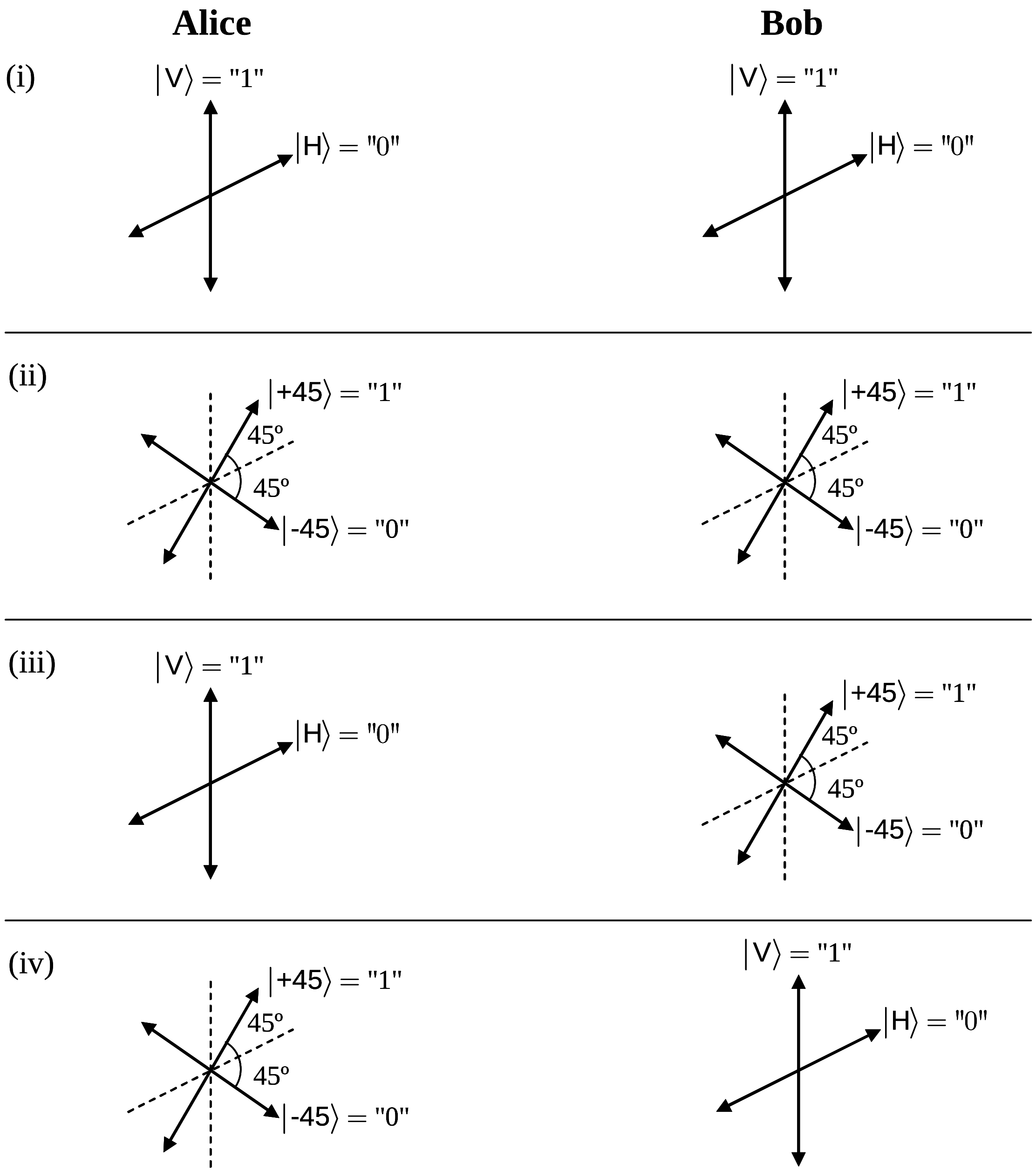
leading to probabilities of $1/2$, in what we believe to be a totally random process in quantum mechanics

Similarly the other state

$$|\text{-}45\rangle = \frac{1}{\sqrt{2}}\left(|\mathrm{H}\rangle - |\mathrm{V}\rangle\right) \qquad \textbf{(18.11)}$$

gives

$|\mathrm{H}\rangle$ half the time and the answer $|\mathrm{V}\rangle$ half the time.



A simple quantum encryption scheme - 6

So now presume that Alice and Bob each rotate their apparatus by 45º, as in (ii)

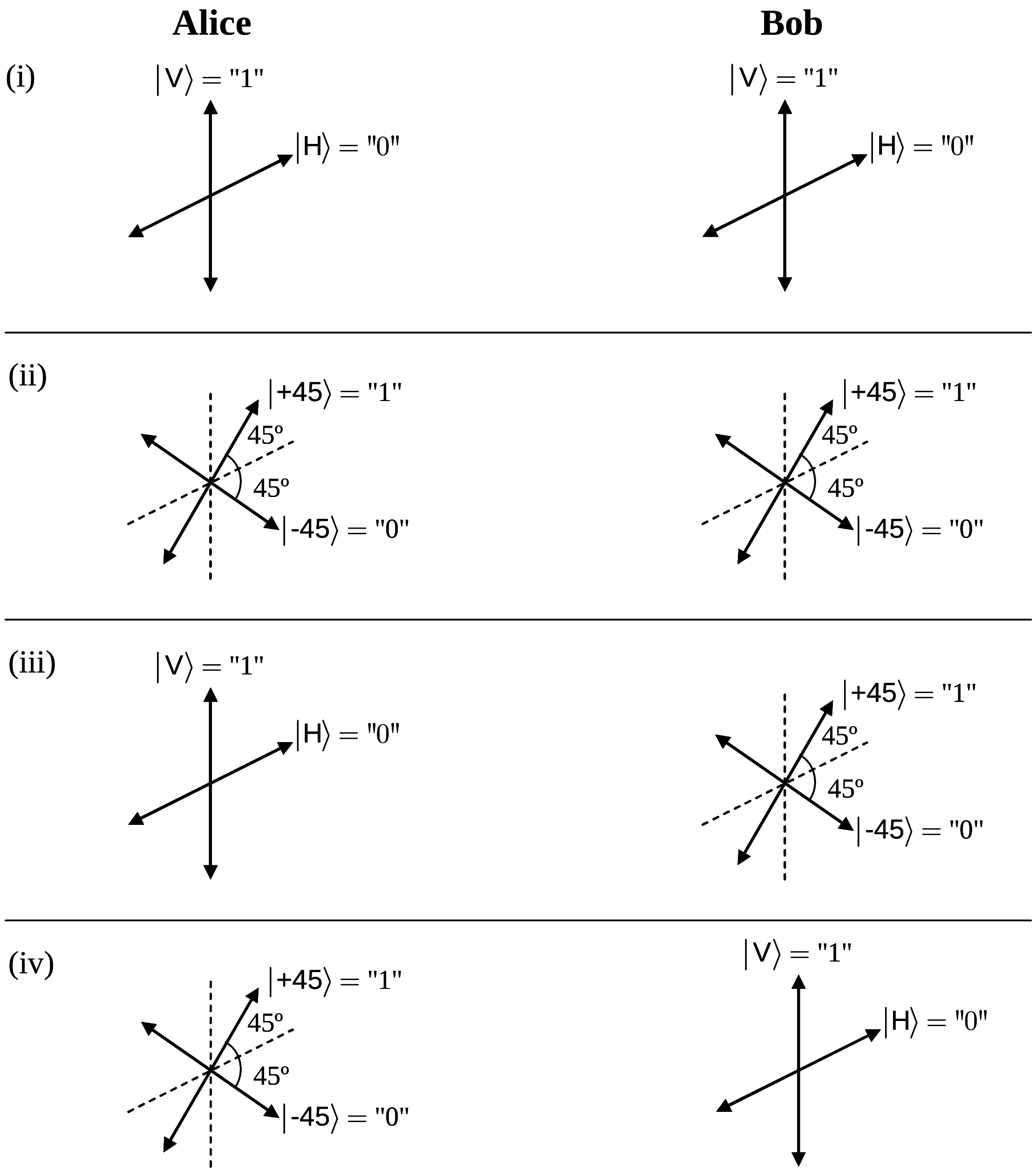
Then they can send information just as before.

If however Eve interposes her apparatus,

still oriented horizontally and vertically,

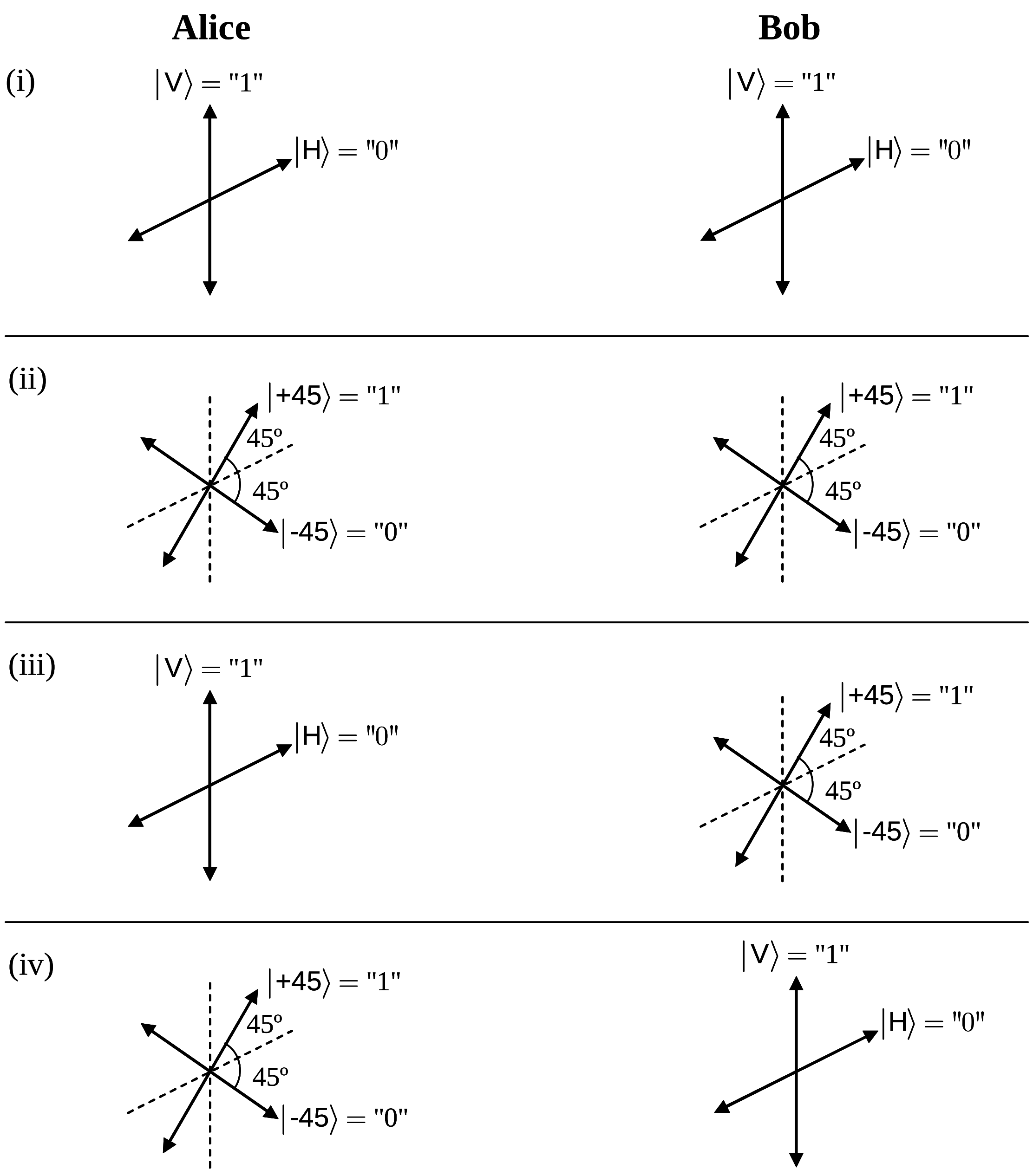
she will receive no information, and

Bob and Alice will quickly deduce that their message is being intercepted.



A simple quantum encryption scheme - 7

- **Bob and Alice can monitor errors**
  - ***talking on the telephone and checking***
    - **quite openly and publicly**
  - ***to see that they are sending and receiving the same bits on some test cases***
- **If Eve has interposed herself in this horizontal and vertical way,**
  - ***half the bits apparently received by Bob will turn out to be wrong,***
    - **and Alice and Bob will know to**
      - *discard all of the bits and to*
      - *send out a search party to find Eve and her apparatus.*



A simple quantum encryption scheme - 8

Eve

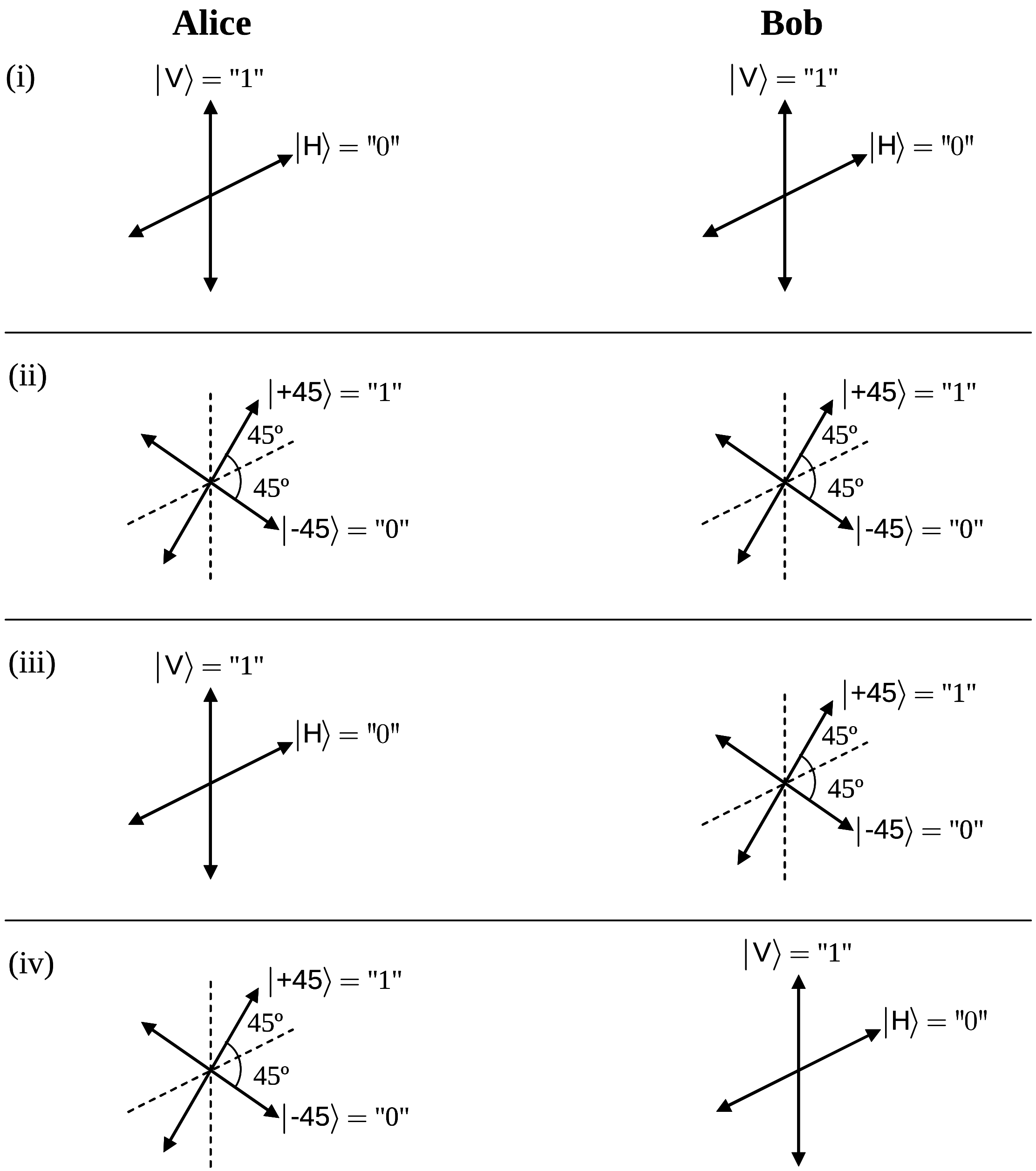
- *seeing the approaching search party*

realizes her apparatus is set incorrectly,

- *and retreats to come back another day,*
  - **then setting her apparatus in the 45° fashion.**

Alice and Bob might by that time have changed back,

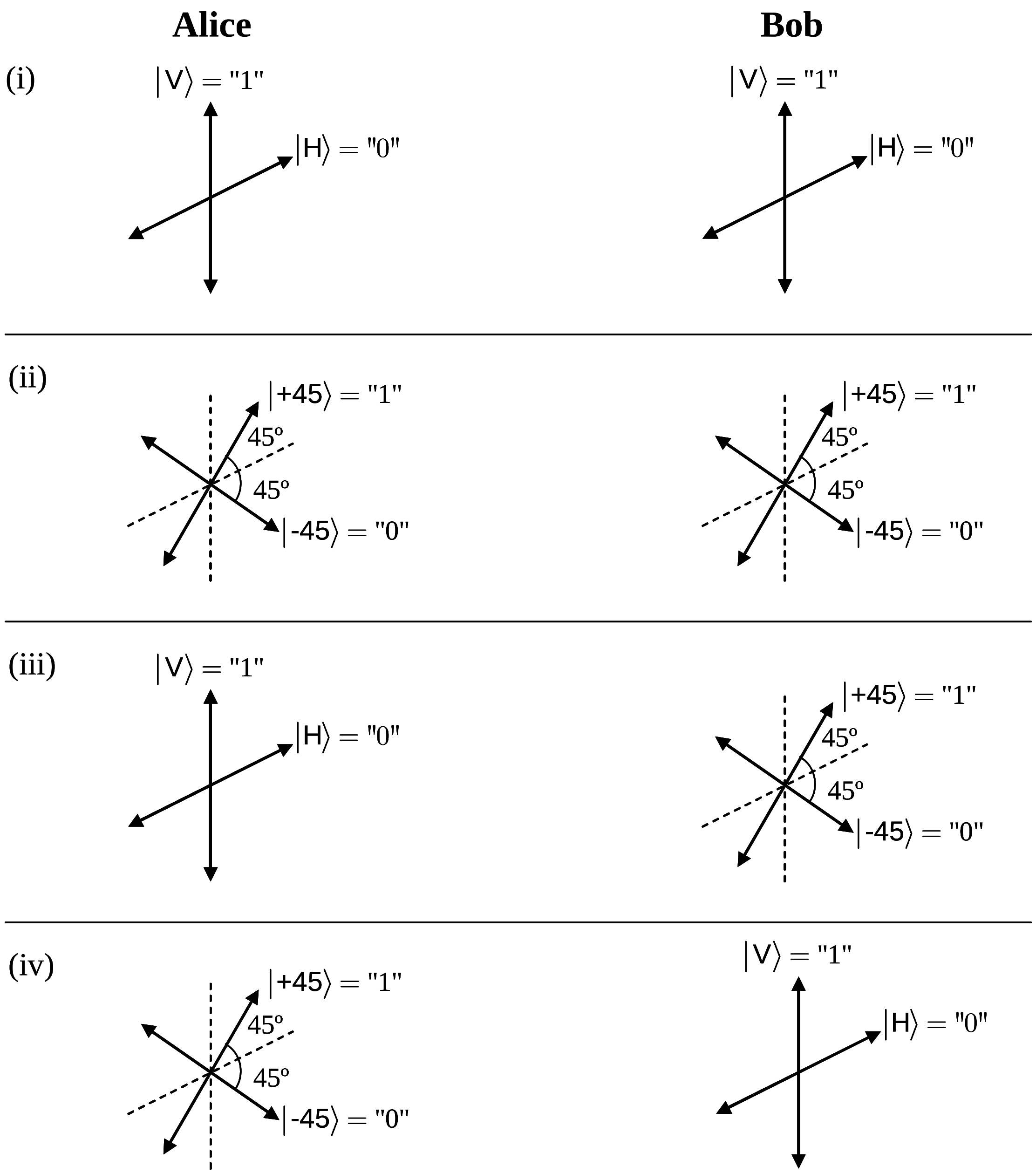
- *but there is a 50% chance that Eve could set her apparatus correctly,*
  - **and a 50% chance of interception is likely too high for Alice and Bob.**



A simple quantum encryption scheme - 9

The trick to thwarting Eve is that

- ***Alice and Bob,***
  - **for each time they want to try to communicate a bit,**
- ***each randomly choose between***
  - **the horizontal-vertical setting of their apparatus and**
  - **the 45° one.**



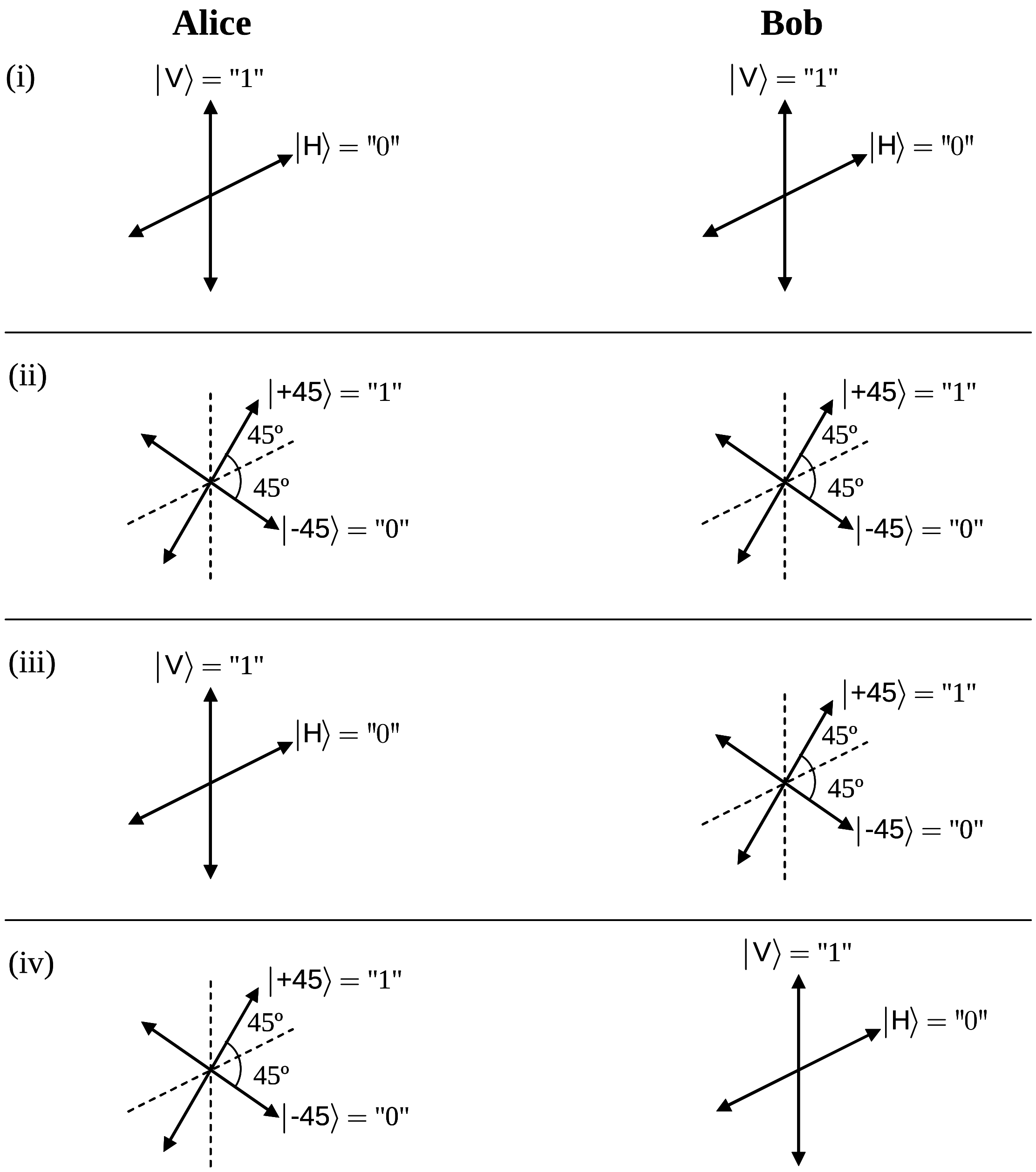
A simple quantum encryption scheme - 10

This leads to four possibilities, (i) – (iv).

- ***In two of these,***
  - **their transmission is meaningful.**
- ***In the other two no information is exchanged.***

All that is necessary now for successful secure information exchange by Alice and Bob is for them again to

- ***call one another up openly on the telephone and***
  - **agree when their polarizers were set the same**
    - *(which they can do without ever revealing what information was exchanged in each such case).*



A simple quantum encryption scheme - 11

Then at last Alice and Bob have a string of bits known only to them.

There is no strategy that Eve can choose for her apparatus that can possibly work more than half the time,

- ***and for the other half she will again generate errors half the time,***
  - **a fraction easily noticed by Alice and Bob**
    - *and stimulating the search party again.*

Eve might want to solve this problem by cloning the incoming photon,

- ***passing the clone on to Bob***
  - **who would then not notice any errors being introduced by Eve.**

If Eve could do the cloning,

- ***she could on the average deduce half of the information with random choices of her apparatus orientation,***

but no-one can do that cloning,

- ***by the no-cloning theorem proved above.***
  - **So Alice and Bob can send bits so that no-one can intercept them without Alice and Bob finding out.**
    - *If Alice and Bob find that their message is being intercepted,*
      - because they notice a large error rate,
        - they discard the bits sent and send out the search party to find Eve.

A simple quantum encryption scheme - 12

One might think that Eve has at least intercepted some of their message,

- ***but that problem is easily overcome by the strategy of not sending the actual message,***
  - **instead sending only the key.**

Once Alice and Bob have the set of shared bits that they are sure are secret,

- ***they then send their actual message.***
  - **Alice can call up Bob again,**
    - *on the public telephone,*
  - **and tell him her actual message is bits 1, 4, 5, 9, 11, and 16 on their shared list.**
- ***Only Alice and Bob then know what that message is.***
  - **Provided they only use each shared bit once in their message, their actual message is totally secure.**

As we have seen for this example, their security comes from

- ***the randomness of quantum mechanical measurement for superposition states,***
- ***and the no-cloning theorem that is a consequence of the linearity of quantum mechanics.***

Quantum information – 2

Reading – Sections 18.3 – 18.5

Entanglement

Quantum computing

Quantum teleportation

Entanglement - 1

We need to re-examine the states of more than one particle more completely.

Suppose we have two particles, e.g., two photons

- **Photon 1 is in one of a set of possible states** $|\psi_m\rangle_1$
  - *e.g., going to the left in a particular spatial mode (beam shape)*
  - *with a specific frequency,*
  - *with the different possible states being vertical or horizontal polarization.*
- **Photon 2 is similarly in one of a set of possible states** $|\phi_n\rangle_2$
  - *e.g., going to the right in a particular spatial mode (beam shape)*
  - *with a specific frequency,*
  - *with the different possible states being vertical or horizontal polarization.*

Then, appropriate basis states for the left-going photon 1 would be $|\mathrm{H}\rangle_1$ ***and*** $|\mathrm{V}\rangle_1$***,***

- **where H and V refer to horizontal and vertical polarization**

Similarly, appropriate basis states for the right-going photon 2 would be $|\mathrm{H}\rangle_2$ ***and*** $|\mathrm{V}\rangle_2$***.***

Entanglement - 2

A possible state of this two photons is

$$|\mathrm{H}\rangle_1 |\mathrm{V}\rangle_2 ,$$

which is the left-going photon horizontally polarized and the right-going photon vertically polarized.

Other examples include $|\mathrm{H}\rangle_1 |\mathrm{H}\rangle_2$, $|\mathrm{V}\rangle_1 |\mathrm{V}\rangle_2$, and $|\mathrm{V}\rangle_1 |\mathrm{H}\rangle_2$ with obvious meanings.

We can express other polarizations of a given photon as linear combinations of horizontal and vertical.

For example, the state $\left(1/\sqrt{2}\right)\left(|\mathrm{H}\rangle_1 + |\mathrm{V}\rangle_1\right)$ ***describes a left-going photon polarized at an angle of 45°.***

Hence, a state like $\left(1/\sqrt{2}\right)\left(|\mathrm{H}\rangle_1 + |\mathrm{V}\rangle_1\right)|\mathrm{H}\rangle_2$ describes a left-going photon polarized at 45° and a right-going photon horizontally polarized.

So far, we have assigned a definite polarization to each photon, just as we could classically.

But, these states are not the only ones allowed by quantum mechanics.

Entanglement - 3

For example, consider the following state of the two photons

$$|\Phi^+\rangle_{12} = \frac{1}{\sqrt{2}}\left(|H\rangle_1|H\rangle_2 + |V\rangle_1|V\rangle_2\right) \tag{18.12}$$

i.e., a linear superposition of

the state where the two photons are both horizontally polarized and

the state where the two photons are both vertically polarized

It is relatively straightforward with modern techniques,

such as spontaneous optical parametric down-conversion

a second-order nonlinear optical technique

to generate pairs of photons in such states.

A pair of photons in a state like this is sometimes called

an EPR pair (after Einstein, Podolsky and Rosen) and

the state itself is sometimes called a Bell state.

This is a linear superposition of two of the states we considered already.

Quantum mechanically, it is a valid state of the system.

we can view it as a vector in the four-dimensional Hilbert space that describes the polarization state of two photons,

a direct product space in which $|H\rangle_1|H\rangle_2$*,* $|V\rangle_1|V\rangle_2$*,* $|H\rangle_1|V\rangle_2$*, and* $|V\rangle_1|H\rangle_2$ *are appropriate orthonormal basis vectors.*

Entanglement - 4

The state in Eq. (18.12)

$$\left|\Phi^{+}\right\rangle_{12}=\frac{1}{\sqrt{2}}\left(|\mathrm{H}\rangle_{1}|\mathrm{H}\rangle_{2}+|\mathrm{V}\rangle_{1}|\mathrm{V}\rangle_{2}\right)$$

is very nonclassical.

It cannot be factorized into a product of

a state of particle 1 and

a state of particle 2.

States that cannot be factorized into a product of the states of individual systems on their own are said to be *entangled*.

In such an entangled state

particle 1 does not have a definite state of its own independent of the state of particle 2.

Imagine we measure the polarization of the left-going photon (photon 1)

and find it is horizontal

Then we have collapsed the overall state into one that now only has terms in $|\mathrm{H}\rangle_1$.

Then the state of the whole system now is $|\mathrm{H}\rangle_1|\mathrm{H}\rangle_2$

we have also collapsed the state of the second (right-going) photon into a horizontal polarization (even though we did not “touch” it).

Entanglement - 5

The state of the right-going photon depends on the state we measure for the left-going photon,

> ***even though both results are possible for the measurement of the left-going photon.***

There are three other states like Eq. (18.12)

$$\left|\Phi^{+}\right\rangle_{12} = \frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{H}\right\rangle_2 + \left|\mathrm{V}\right\rangle_1\left|\mathrm{V}\right\rangle_2\right)$$

that together constitute the four Bell states; specifically

$$\left|\Phi^{-}\right\rangle_{12} = \frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{H}\right\rangle_2 - \left|\mathrm{V}\right\rangle_1\left|\mathrm{V}\right\rangle_2\right) \qquad (18.13)$$

$$\left|\Psi^{+}\right\rangle_{12} = \frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{V}\right\rangle_2 + \left|\mathrm{V}\right\rangle_1\left|\mathrm{H}\right\rangle_2\right) \qquad (18.14)$$

$$\left|\Psi^{-}\right\rangle_{12} = \frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{V}\right\rangle_2 - \left|\mathrm{V}\right\rangle_1\left|\mathrm{H}\right\rangle_2\right) \qquad (18.15)$$

These four Bell states are orthogonal

> ***and are a complete basis for describing any such two-particle system with two available basis states per particle (here,*** $\left|\mathrm{H}\right\rangle$ ***and*** $\left|\mathrm{V}\right\rangle$***)***

Entanglement - 6

There are many bizarre and important consequences of entanglement for the meaning of quantum mechanics

Here we emphasize that

once we consider the states of more than one quantum system at a time

there is a whole additional range of states in quantum mechanics,

these entangled states,

that have no analog in the classical view of the world.

For the two particles considered here, the space is four-dimensional

the most general quantum mechanical state of these two photons is

$$|\psi\rangle = c_{\mathrm{HH}}|\mathrm{H}\rangle_1|\mathrm{H}\rangle_2 + c_{\mathrm{HV}}|\mathrm{H}\rangle_1|\mathrm{V}\rangle_2 + c_{\mathrm{VH}}|\mathrm{V}\rangle_1|\mathrm{H}\rangle_2 + c_{\mathrm{VV}}|\mathrm{V}\rangle_1|\mathrm{V}\rangle_2 \qquad (18.16)$$

where now need four (generally complex) coefficients,

the c*’s,*

to specify the state of just two photons.

Classically, we would need at most two complex numbers to specify the polarization state of two photons

and just one complex number is enough to specify the relative amplitude and phase of the two polarization components of one photon.

Entanglement - 7

As we increase the number of particles

even restricting to particles with only two basis states of interest

the dimensionality of the direct-product Hilbert space

and, hence, the number of expansion coefficients

the c'*s*

rises quickly.

For three particles,

we need eight coefficients

for four particles,

sixteen coefficients,

and so on,

leading to 2^N coefficients for N particles.

300 particles would therefore require 2^{300} coefficients,

a number that may be larger than the number of atoms in the observable universe!

Quantum computing

A quantum computer operates on a quantum state rather than a classical one.

One reason this is interesting is because

a machine dealing with N two-level quantum mechanical systems

could be performing an operation on 2^N numbers at once.

No classical machine can do that for even moderate N.

For $N = 300$ binary inputs,

there are not enough atoms to store 2^{300} numbers at one atom per number.

Perhaps such a quantum computer could solve problems that grow so fast with problem size

no classical computer could possibly solve them once they get above a certain size.

Quantum computer algorithms have been developed for two important problems of this type

finding factors of large numbers (Shor algorithm)

database searching (Grover algorithm)

Representing quantum information – qubits - 1

A classical computer takes data as bits

processes it in a "black box," and

gives an output as bits.

A quantum computer, instead of bits that are only "0" or "1"

works with "qubits"

represented as the linear superposition of two states of a quantum mechanical object.

The object might be

an electron spin in a linear superposition of spin-up and spin-down,

a photon in a linear superposition of two different polarization states,

an atom in a linear superposition of two possible states

Representing quantum information – qubits - 2

In general, the state of that qubit can be written as

$$|\psi\rangle = c_0|0\rangle + c_1|1\rangle \equiv \begin{bmatrix} c_0 \\ c_1 \end{bmatrix} \qquad (18.17)$$

where $|0\rangle$ is the quantum mechanical state that represents "0", for example,

a horizontal polarization state $|\mathrm{H}\rangle$ ***of a photon,***

a spin-down state $|\downarrow\rangle$ ***of an electron, or***

a ground state $|g\rangle$ ***of an atom***

and, similarly, $|1\rangle$ could be represented by

vertical polarization $|\mathrm{V}\rangle$***,***
spin-up $|\uparrow\rangle$***, or***
an excited atomic state $|e\rangle$***.***

Because of normalization, $|c_0|^2 + |c_1|^2 = 1$.

Running a quantum computer

First, an input quantum state is

- ***and fed into the quantum black box or "oracle"***
  - **by initializing the quantum states of the various quantum elements**
    - e.g., electrons with spins, or atoms
  - **in the box to specific quantum "starting conditions."**

Then, we "turn on" the quantum computer and

- ***let its quantum mechanical state evolve in time***
  - **because of the designed interactions between the different quantum systems.**

Running the quantum computer can involve

- ***shining specific pulses of light onto specific quantum elements at specific times***
  - **for example, in a quantum version of "clocking" the computer**
- ***to trigger the various required quantum operations.***

Then, finally, we read out the state of the system or some subset of it.

- ***That readout is a quantum mechanical measurement***
  - **so necessarily we throw away some of the information about the final quantum state of the system**

That loss of information is one of the issues in using quantum computers.

Quantum computing gates

In a classical computer,

any classical logic system can be made from

2-input NOR gates with "fan-out" of 2

i.e., capable of driving the inputs of two subsequent gates.

We might not make a computer that way,

but demonstrating such a NOR gate would be a "completeness" proof that such a classical computer could be made.

Gates in quantum computers are different.

One difference – they are reversible

Ordinary classical logic gates are not reversible

knowledge of the output state of a classical NOR gate is not sufficient to tell you what the input state was.

(It is possible, though, to make a classical computer with classically reversible gates.)

The reversibility in the quantum computer is because

the evolution of quantum mechanical states is a unitary process

and a unitary process is reversible using the inverse unitary operator.

One qubit gates - 1

The necessary basic operations for a quantum computer can be written as four different operations.

Three of these are operations on a single qubit.

We can write these operations as 2 x 2 matrices

representing the corresponding unitary operators.

One possible set is

$$U_H = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}, \quad U_Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad U_{NOTX} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad (18.18)$$

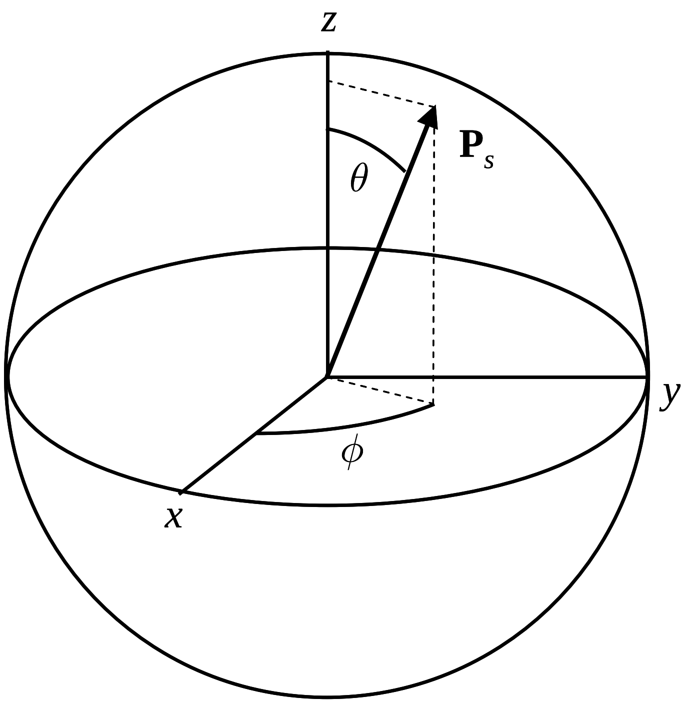
These unitary operators are known as

Hadamard (U_H),

Z (U_Z) and

NOT X (U_{NOTX}) operators.

One qubit gates - 2



We can represent a qubit using the Bloch sphere

- *the qubit is represented as a vector pointing from the center of a sphere to its surface (of unit radius)*
  - **single qubit operations corresponding to rotations of the vector on the sphere**

Single qubit operations can be achieved

- *for spins by appropriate pulses of magnetic fields in given directions*
- *for two-level "atomic" systems by pulses of electromagnetic fields*
- *for photons by changing the polarization state using various well-known polarization components*

Such single-qubit manipulations have been known for some time

- *long before qubits and quantum computing were proposed.*

Two qubit gates - 1

The fourth required operation involves an interaction between two qubits

an interaction called a Controlled-NOT (C-NOT)

One qubit is called the control

The other is called the target.

If the control is $|0\rangle$***, the target qubit is passed through unchanged,***

but if the control is $|1\rangle$***, the target qubit is inverted***

a target qubit of state $|0\rangle$ **is changed to state** $|1\rangle$ **and**

a target qubit of $|1\rangle$ **is changed to state** $|0\rangle$

hence the name Controlled-NOT*.*

Two qubit gates - 2

A two-qubit state is a vector in a four-dimensional Hilbert space

that is, like Eq. (18.16) ($|\psi\rangle = c_{\mathrm{HH}}|\mathrm{H}\rangle_1|\mathrm{H}\rangle_2 + c_{\mathrm{HV}}|\mathrm{H}\rangle_1|\mathrm{V}\rangle_2 + c_{\mathrm{VH}}|\mathrm{V}\rangle_1|\mathrm{H}\rangle_2 + c_{\mathrm{VV}}|\mathrm{V}\rangle_1|\mathrm{V}\rangle_2$ ***)***

$$\begin{aligned}|\psi\rangle &= c_{00}|0\rangle_{control}|0\rangle_{target} + c_{01}|0\rangle_{control}|1\rangle_{target} \\ &\quad + c_{10}|1\rangle_{control}|0\rangle_{target} + c_{11}|1\rangle_{control}|1\rangle_{target} \\ &= \begin{bmatrix} c_{00} \\ c_{01} \\ c_{10} \\ c_{11} \end{bmatrix}\end{aligned} \tag{18.19}$$

and so the corresponding operator can be written

$$U_{CNOT} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \tag{18.20}$$

Two qubit gates - 3

For example,

the input state with

the control as a logic 0 and

the target as a logic 1

is the state with $c_{00} = 0$*,* $c_{01} = 1$*,* $c_{10} = 0$*, and* $c_{11} = 0$*.*

Writing that state as a column vector and operating with U_{CNOT} gives

$$\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \qquad (18.21)$$

which is just the state we started with

as intended, the target qubit passes through unchanged if the control qubit is logic 0.

Two qubit gates - 4

But, if we choose to have

the control qubit be a logic 1 and

the target a logic 1

that is, if we choose the input state as $c_{00} = 0$, $c_{01} = 0$, $c_{10} = 0$, *and* $c_{11} = 1$

$$\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{18.22}$$

The resulting output state is, therefore,

$c_{00} = 0$, $c_{01} = 0$, $c_{10} = 1$, ***and*** $c_{11} = 0$,

which is the state with the target qubit now a logic 0

it has been "flipped"

and the control bit remaining at logic 1.

Implementing two-qubit gates - 1

To implement such a gate,

the two systems representing the two qubits must interact

If the system representing the control qubit is in its $|1\rangle$ state,

we want it to affect the system representing the target qubit.

One common approach is where

a light pulse shines on the target qubit system every "cycle" of operation.

This pulse carries no information

it is more like a "clock" pulse

If the control qubit system is in its $|0\rangle$ state,

then this clock pulse does nothing to the target qubit system

(e.g., perhaps the clock pulse then has the wrong optical frequency to affect the target qubit system).

If, however, the control qubit is in its $|1\rangle$ state,

perhaps it changes a transition frequency in the target qubit system

through some interaction between the control and target qubit systems.

With this change in transition energy,

the target qubit system could then be sensitive to the clock pulse

so that the clock pulse then causes an inversion of the target qubit state.

This kind of system would implement the Controlled-NOT function.

Implementing two-qubit gates - 2

Example systems for two-qubit gates include

- ***ions in ion traps,***
- ***superconducting flux and charge qubits,***
- ***quantum dots, and***
- ***spins in semiconductor impurities.***

Dephasing

A major challenge for quantum computing is that

> ***it is difficult to isolate the quantum mechanical systems enough from their environment.***
>
> > **Consequently, the phase of the quantum mechanical system keeps being disturbed,**
> >
> > > *which destroys the fidelity of the quantum mechanical states being used;*

Quantum computing relies on the phase of the quantum mechanical states being undisturbed for sufficiently long times.

> ***Essentially, we need systems with long dephasing or decoherence times.***

One possible solution is

> ***quantum error correction to restore the state,***
>
> > **though that itself requires quantum computing gates and**
> >
> > > *so we would still need to be able to get above some threshold number of quantum operations without dephasing.*

Quantum teleportation - 1

The idea of quantum teleportation is to

> ***transfer a quantum state from one place to another***
>
> > **without transferring the specific carrier of that state.**

Suppose we have a photon (photon 1)

> ***in an unknown superposition of horizontal and vertical polarization***

We want to have a different (distinguishable) photon (photon 3) be in the same superposition state somewhere else,

> ***but without sending photon 1 there.***
>
> > **In fact, we may even destroy (absorb) photon 1 in the process.**

But we know from the no-cloning theorem that

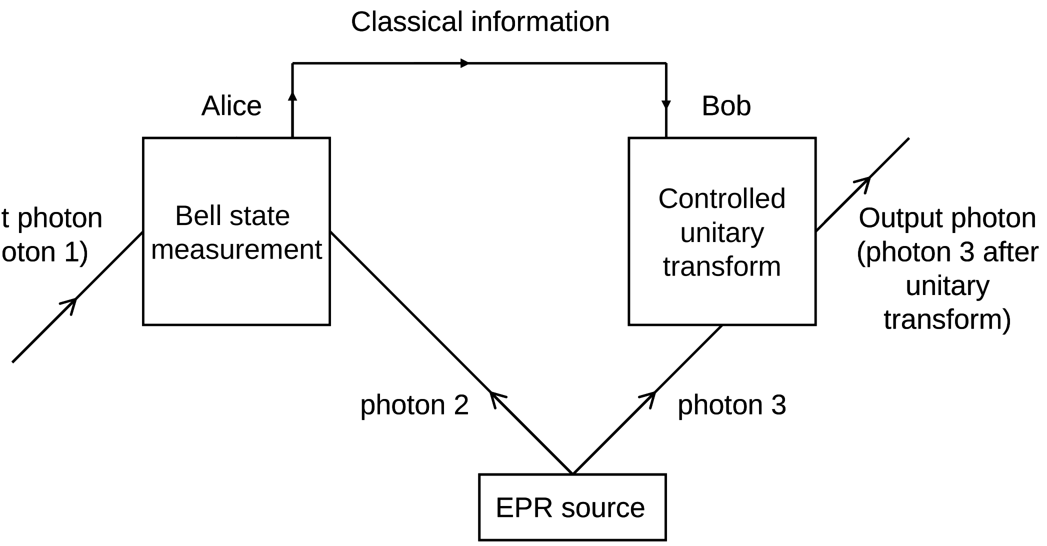
> ***we cannot clone photon 1 to produce another photon (photon 3) in the same arbitrary superposition.***
>
> ***We also know that simply making a measurement on photon 1***
>
> > > *for example with a polarizing beamsplitter or filter of some kind together with photodetectors*
> >
> > **will not reliably tell us the full quantum state of photon 1**
> >
> > > we end up statistically "collapsing" the state and throwing away information about the original quantum state of the photon.

Quantum teleportation - 2

The key to quantum teleportation is to

“share entanglement,”

by sharing an EPR pair of photons that are in a Bell (entangled) state



The EPR photon pair is presumed to be in the Bell state of Eq. (18.15)

$$\left|\Psi^{-}\right\rangle_{23}=\frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_2\left|\mathrm{V}\right\rangle_3-\left|\mathrm{V}\right\rangle_2\left|\mathrm{H}\right\rangle_3\right) \qquad (18.23)$$

The input photon is in a linear superposition of the horizontal and vertical polarizations

$$\left|\psi\right\rangle_1=c_{\mathrm{H}}\left|\mathrm{H}\right\rangle_1+c_{\mathrm{V}}\left|\mathrm{V}\right\rangle_1 \qquad (18.24)$$

The state of all three photons, therefore, can be written as

$$\left|\Psi\right\rangle_{123}=\frac{1}{\sqrt{2}}\left(c_{\mathrm{H}}\left|\mathrm{H}\right\rangle_1+c_{\mathrm{V}}\left|\mathrm{V}\right\rangle_1\right)\left(\left|\mathrm{H}\right\rangle_2\left|\mathrm{V}\right\rangle_3-\left|\mathrm{V}\right\rangle_2\left|\mathrm{H}\right\rangle_3\right) \qquad (18.25)$$

Quantum teleportation - 3

A core trick in the teleportation is to note that this state

$$\left|\Psi\right\rangle_{123}=\frac{1}{\sqrt{2}}\left(c_{\mathrm{H}}\left|\mathrm{H}\right\rangle_1+c_{\mathrm{V}}\left|\mathrm{V}\right\rangle_1\right)\left(\left|\mathrm{H}\right\rangle_2\left|\mathrm{V}\right\rangle_3-\left|\mathrm{V}\right\rangle_2\left|\mathrm{H}\right\rangle_3\right)$$

can be rewritten as

$$\begin{aligned}\left|\Psi\right\rangle_{123}=\frac{1}{2}\Big[&\left|\Phi^+\right\rangle_{12}\left(c_{\mathrm{H}}\left|\mathrm{V}\right\rangle_3-c_{\mathrm{V}}\left|\mathrm{H}\right\rangle_3\right)+\left|\Phi^-\right\rangle_{12}\left(c_{\mathrm{H}}\left|\mathrm{V}\right\rangle_3+c_{\mathrm{V}}\left|\mathrm{H}\right\rangle_3\right)\\&+\left|\Psi^+\right\rangle_{12}\left(-c_{\mathrm{H}}\left|\mathrm{H}\right\rangle_3+c_{\mathrm{V}}\left|\mathrm{V}\right\rangle_3\right)-\left|\Psi^-\right\rangle_{12}\left(c_{\mathrm{H}}\left|\mathrm{H}\right\rangle_3+c_{\mathrm{V}}\left|\mathrm{V}\right\rangle_3\right)\Big]\end{aligned} \qquad (18.26)$$

Note that we have managed to write the state in terms of Bell states of photons 1 and 2 (Eqs. (18.12)–(18.15))

$$\left|\Phi^+\right\rangle_{12}=\frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{H}\right\rangle_2+\left|\mathrm{V}\right\rangle_1\left|\mathrm{V}\right\rangle_2\right) \qquad \left|\Phi^-\right\rangle_{12}=\frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{H}\right\rangle_2-\left|\mathrm{V}\right\rangle_1\left|\mathrm{V}\right\rangle_2\right)$$

$$\left|\Psi^+\right\rangle_{12}=\frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{V}\right\rangle_2+\left|\mathrm{V}\right\rangle_1\left|\mathrm{H}\right\rangle_2\right) \qquad \left|\Psi^-\right\rangle_{12}=\frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{V}\right\rangle_2-\left|\mathrm{V}\right\rangle_1\left|\mathrm{H}\right\rangle_2\right)$$

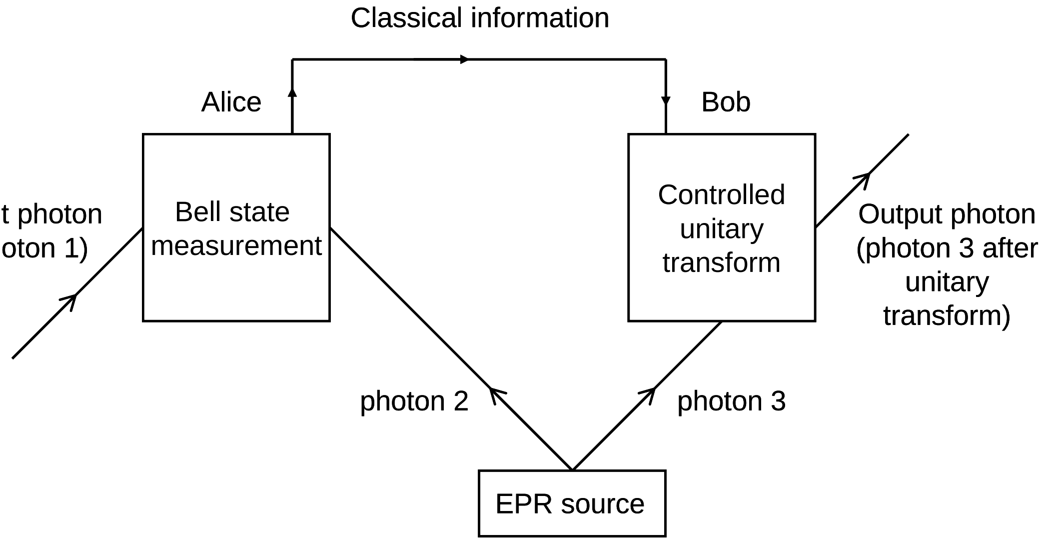
Quantum teleportation - 4

Our state is

$$|\Psi\rangle_{123} = \frac{1}{2}\Big[|\Phi^+\rangle_{12}\left(c_H|V\rangle_3 - c_V|H\rangle_3\right) + |\Phi^-\rangle_{12}\left(c_H|V\rangle_3 + c_V|H\rangle_3\right)$$
$$+|\Psi^+\rangle_{12}\left(-c_H|H\rangle_3 + c_V|V\rangle_3\right) - |\Psi^-\rangle_{12}\left(c_H|H\rangle_3 + c_V|V\rangle_3\right)\Big]$$

If we now make a measurement

- ***in Alice's Bell state measurement box***
  - **of the Bell state of this pair of photons 1 and 2,**
    - *we collapse the state into just one of those terms.*

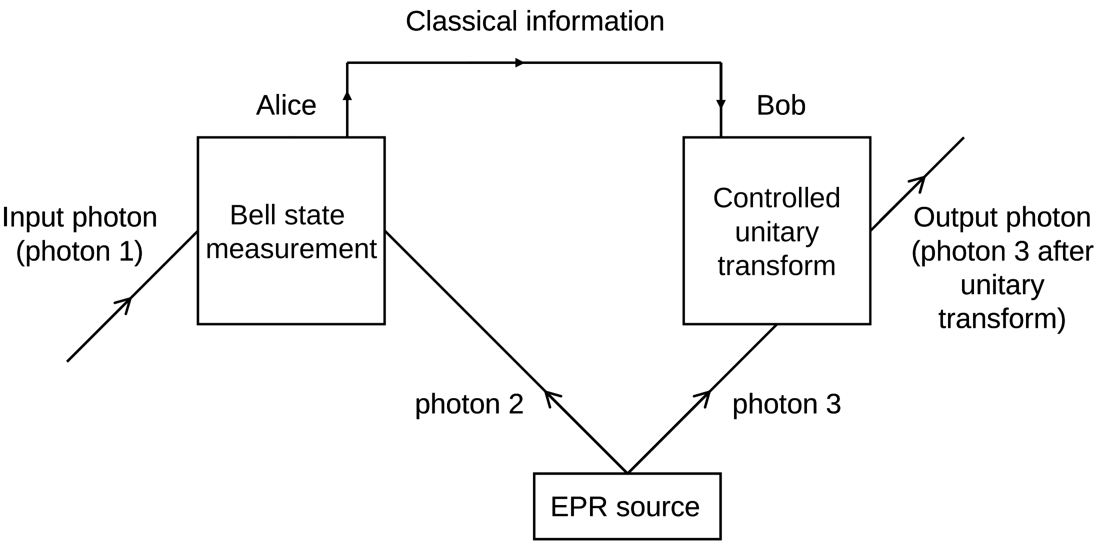


For example, suppose we measure $|\Phi^-\rangle_{12}$,

- ***an answer we can know classically because it is the result of a measurement***
  - **then, the overall system of three photons would now be in the state**

$$|\Psi\rangle_{123} = \frac{1}{2}|\Phi^-\rangle_{12}\left(c_H|V\rangle_3 + c_V|H\rangle_3\right) \tag{18.27}$$

Quantum teleportation - 5



Because Alice can tell Bob the result of her measurement by communication over an ordinary classical channel (e.g., a telephone line)

Bob now knows that photon 3 is in the state $c_H|V\rangle_3 + c_V|H\rangle_3$.

This is not the same as the original state of the photon

which was by definition $c_H|H\rangle_1 + c_V|V\rangle_1$

but that is easily fixed.

Bob could rotate the polarization of the photon by 90° clockwise,

turning vertical polarization into horizontal and horizontal into –vertical (i.e., $|V\rangle \to |H\rangle$ and $|H\rangle \to -|V\rangle$) and

insert a half wave plate to delay the vertical polarization by 180° relative to the horizontal,

turning c_V to $-c_V$.

Then, photon 3 will be in exactly the same state as photon 1 was,

without either Alice or Bob ever knowing what that state was

(i.e., without them knowing the coefficients c_H and c_V).

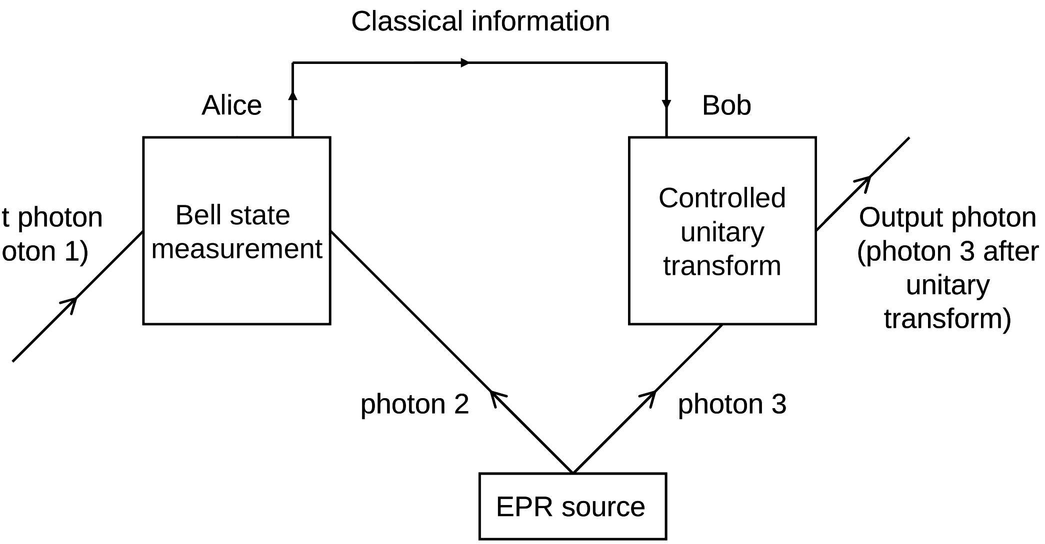
Quantum teleportation - 6

For other results from Alice's Bell state measurement,

Bob implements other polarization manipulations,

but those present no fundamental problem

e.g., he could use electrically controlled phase shifters



In general, Bob implements a specific unitary transformation on photon 3

a combination here of phase delays and polarization rotations

that depends on the outcome of Alice's Bell state measurement

Hence, for any result from Alice,

Bob can put photon 3 into exactly the same state as photon 1 originally had,

thus completing the teleportation of the quantum mechanical state.

Interpretation of quantum mechanics – 1

Reading – Section 19.1

Hidden variables and Bell's inequalities

Hidden variables and Bell's inequalities

Is quantum mechanics truly random?

Is quantum mechanics incomplete,

in the sense that classical statistical mechanics is incomplete?

Statistical mechanics discusses the most likely outcomes

based on, for example, the collisions of atoms or molecules in a gas, leading to

e.g., relations between pressure and temperature in gases.

In a classical world there is an underlying deterministic theory of colliding mechanical particles we could use if we wanted to.

If we only use statistical mechanics, these underlying variables

e.g., the actual positions and momenta of each atom or molecule

are hidden, though, classically, we presume that they exist.

Perhaps quantum mechanics rests has such hidden variables

if we could figure out what they were,

the apparent randomness of quantum mechanics would disappear.

EPR pairs

Einstein, Podolsky and Rosen came up with a famous thought-experiment they believed demonstrated

the absurdity of the quantum mechanical randomness and the wavefunction collapse and

the reasonableness of a hidden variable approach,

a thought-experiment known since then as the EPR paradox.

We can create two distinguishable particles (an EPR pair) in a quantum mechanical superposition state

of the form of one of the Bell states

for example, for two photons 1 and 2 going in different directions, like

$$\left|\Phi^{+}\right\rangle_{12} = \frac{1}{\sqrt{2}}\left(\left|\mathrm{H}\right\rangle_1\left|\mathrm{H}\right\rangle_2 + \left|\mathrm{V}\right\rangle_1\left|\mathrm{V}\right\rangle_2\right) \quad (19.1)$$

a linear superposition of

the state where the two photons are both horizontally polarized and

the state where the two photons are both vertically polarized.

Measuring an EPR state

In such a state,

if one measures one of the photons in a state $|\mathrm{H}\rangle$,

according to quantum mechanics,

the state of both particles is forced to collapse into the one element $|\mathrm{H}\rangle|\mathrm{H}\rangle$ in the linear superposition,

and a measurement on the other photon is now bound to give the result $|\mathrm{H}\rangle$ also.

Similarly, measuring the result $|\mathrm{V}\rangle$ for one photon will lead,

according to quantum mechanics,

to the inescapable conclusion that the other photon will also be in the state $|\mathrm{V}\rangle$.

Consequences of EPR behavior in quantum mechanics

According also to quantum mechanics,

neither photon has a defined polarization until it is measured,

and so one is forced to conclude that somehow the measurement of one photon leads to a change in the other one's state.

This is indeed a bizarre notion,

especially if one arranges that the photons are very widely separated at the time either of them is measured,

so that there is no possibility during the time of measurement that any signal can be conveyed, even at the velocity of light, between the two measurement apparatuses.

Einstein referred to such a change in state of the other particle as

"spooky action at a distance."

He considered such behavior strong evidence that in fact there should be hidden variables.

Hidden variables and the EPR paradox

Perhaps each photon actually does have a specific polarization at the time it leaves the apparatus,

- ***but we merely are unaware of it until the measurement takes place.***
  - **Such a definite polarization would be a hidden variable**
    - *This polarization information would presumably be carried with the photon as a local property of the photon,*
      - hence being a local hidden variable.

Einstein believed there were local hidden variables for the rest of his life,

- ***but that there was no experimental test that could answer the question as to whether local hidden variables actually existed.***

Local hidden variables would restore the belief that

- ***though we do not yet have a theory that explains exactly how such variables behave,***
  - **the world actually does agree with our apparent local determinate view**
    - *i.e., things have actual well-defined states*
      - given by properties that exist in some region of space near the things.

Bell's inequalities

In 1964, Bell proposed a way of distinguishing experimentally between

- *local hidden variable theories and*
- *the predictions of quantum mechanics.*

He showed that,

- *in a particular kind of behavior that could be seen in an EPR experiment,*
  - any local hidden variable theory would give a result that would be different from the predictions of quantum mechanics.

The experiments agree with quantum mechanics and

- *disagree with any local hidden variable theory.*

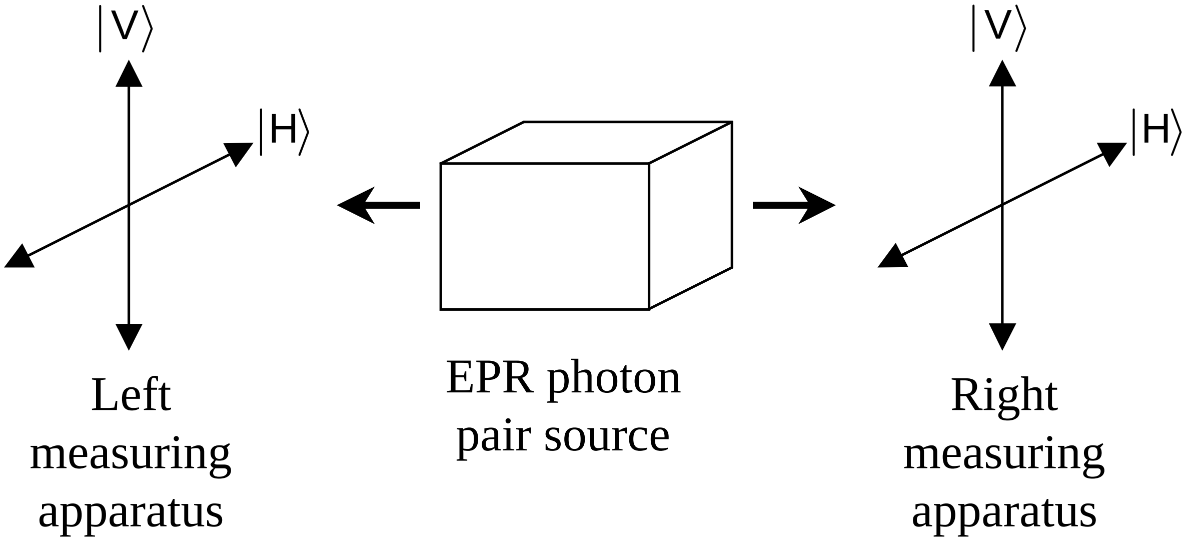
The key experiment involves the correlation between the results we would see

- *in the two different apparatuses for measuring the polarization of the two different photons, and*
  - in particular when the two apparatuses have their axes rotated at an angle.

For certain ranges of angles,

- *the results for local hidden variable theories obey a set of inequalities (Bell's inequalities).*
  - The quantum case gives correlations different from those possible in any local hidden variable theory.

EPR experiment



Suppose we presume the EPR pair of photons are heading off to two different measuring apparatuses with their axes aligned.

Quantum mechanics predicts that, for an EPR pair,

if we measure one photon to be horizontal,

then we will find the other photon also to be horizontal,

and similarly if we measure one photon to be vertical, the other photon will also be measured to be vertical.

This is the behavior we find also in experiments;

with their polarization axes aligned, both apparatuses always measure the same polarization for the two photons.

Failure of local hidden variables - 1

Suppose we asserted that the two photons had the same polarization,

- ***with that actual polarization being the hidden variable,***
  - **though we just did not know what it was until it we measured it.**

If that polarization is not aligned with either the horizontal or vertical axis,

- ***then each photon has a probability of being measured to be either horizontal or vertical,***
  - **and many times we will therefore see the two photons being measured to have different polarizations.**

Hence this simple hidden variable theory

- ***using local polarization as the hidden variable,***
  - **will not work.**

We could fix up this theory to agree with experiment for aligned polarizers,

- ***though we have to introduce attributes and behavior not present in current models for photons or electromagnetic radiation.***
  - **For example, we can simply say that each photon has some attribute that causes it to emerge on a particular axis from the polarizer,**
    - *and since both photons have the same attribute, they both emerge always on the same axis.*

Failure of local hidden variables - 2

Bell proved that once we misalign the two measuring apparatuses

- ***i.e., rotate the polarizer axes of one apparatus with respect to the other,***
  - **there are inequalities relating the correlations between the measured results on the two different apparatuses that must be obeyed for any local hidden variable theory.**

Those limiting correlations can be tested against experiment.

- ***It is found that the experimental results violate these inequalities,***
  - **so no local hidden variable theory agrees with experiment.**
    - *It is also true that the experimental results do agree with the quantum mechanical prediction for such EPR states.*

Hence reality is not local.

- ***We cannot describe reality as we see it based only on local properties.***

To be forced to this conclusion,

- ***we do not even need to believe that quantum mechanics is correct.***
  - **Even if quantum mechanics is wrong and its agreement with the experimental results is merely a coincidence,**
    - *it is still not possible to construct a local hidden variable theory that agrees with the experimental results!*

Simple example of a Bell's inequality

Consider a deterministic hidden variable theory

The hidden variables are definite properties of each particle on its own

and hence can be said to be local to the particle

The particle may also have various attributes or definite values of variables that are not hidden.

The net result of the combination of the hidden and non-hidden variables,

which we can call the local state of the particle,

determine the outcome of any measurement on the particle.

Measuring devices acting on other particles we therefore expect do not matter

and measurements made sufficiently far away and at such times that

no information can get to our particle in time cannot influence the outcome of our measurement.

Photon deterministic local variable theory - 1

In this theory,

the local state of the photon determines from which port of a polarizing beamsplitter it will emerge,

since this is by choice a deterministic theory.

So we can draw a Venn diagram

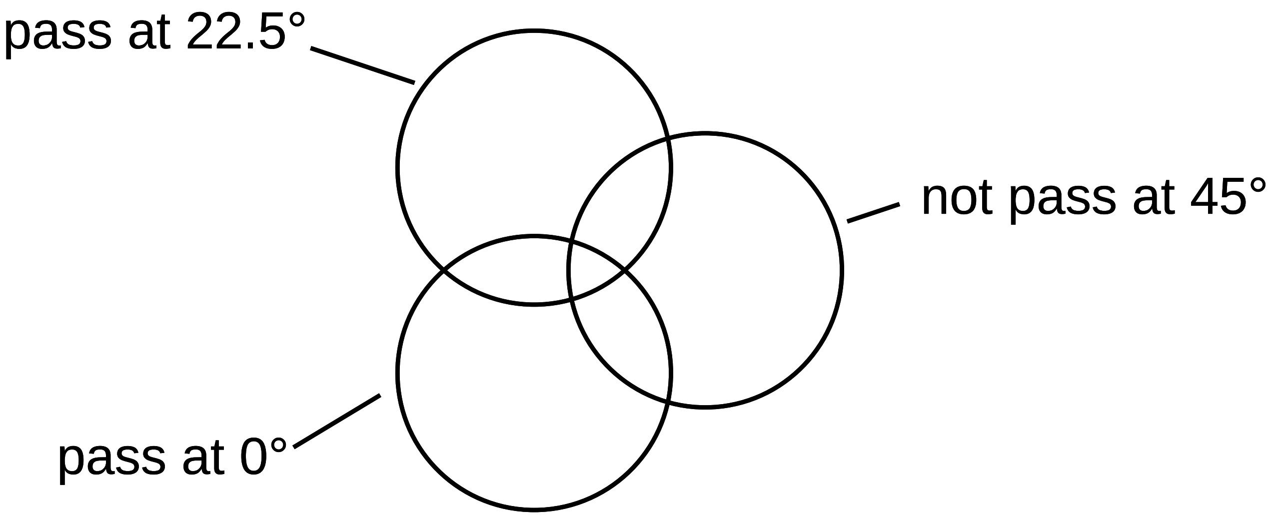
Each combination of local variables that corresponds to a particular measurable set of behaviors with polarizers at any angle is represented by a point on this Venn diagram.

All of these three regions can overlap, and still be in agreement with our observations on what happens with photons and polarizers.

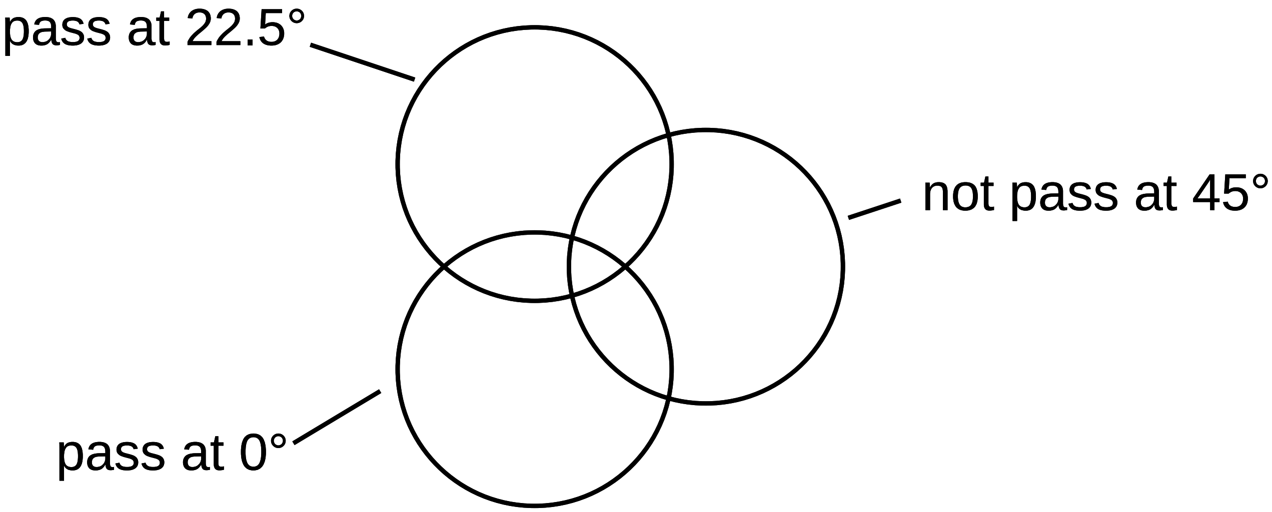
We can only perform one test on a given photon

(with a polarizer set at 0°, 22.5°, or 45°)

because that test may change the state of the photon in some way.



Photon deterministic local variable theory - 2



With our EPR photon pair source,

we have two photons to use in two different experiments

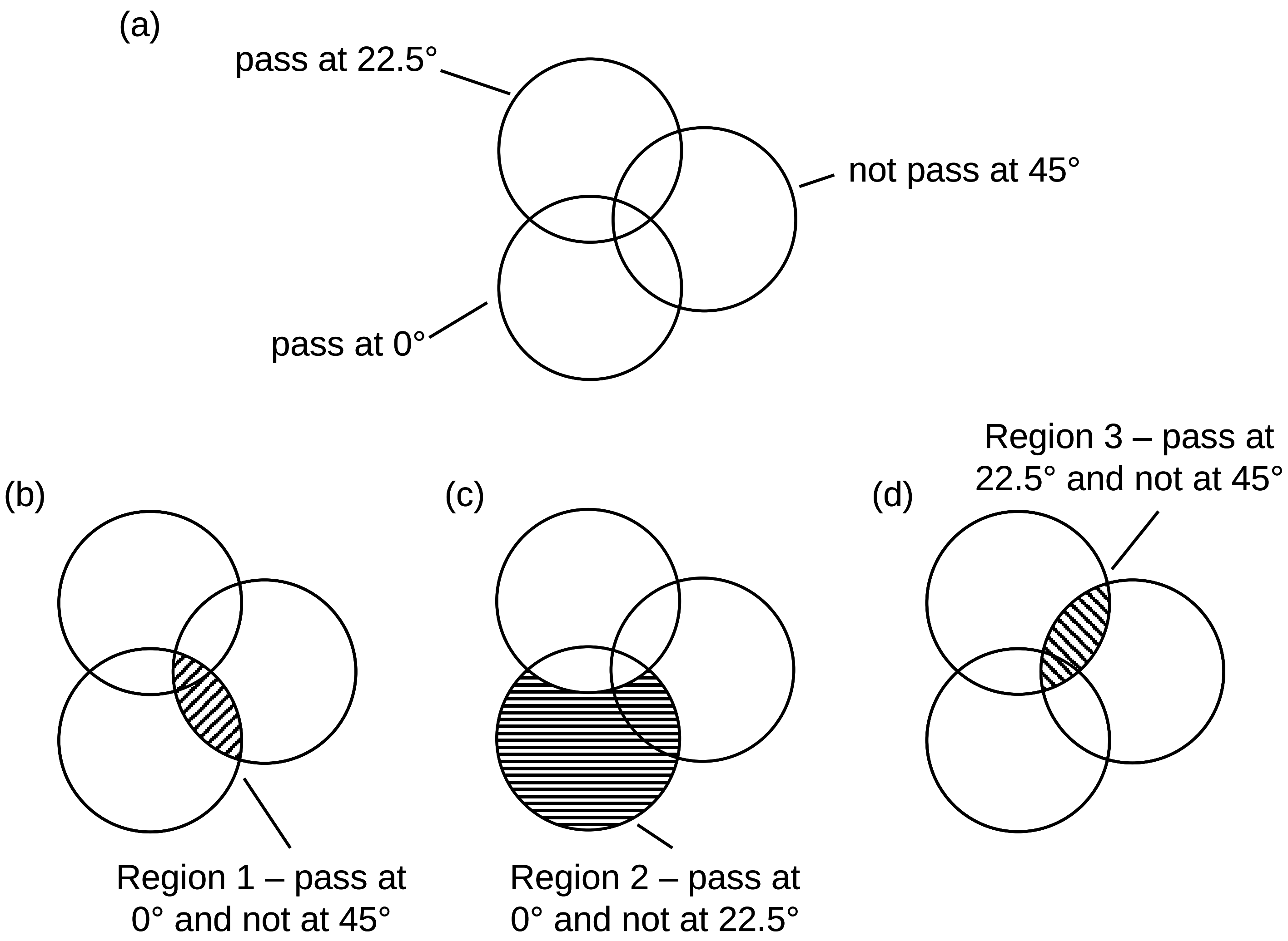
one on the left, and one on the right,

and we already know that photons prepared this way always behave identically if the polarizers are set identically.

Hence we conclude that their local states are identical in that they lie at the same point on this Venn diagram.

So now we can consider the overlap regions, corresponding to those sets of local states in which, for example, one photon passes a polarizer at 0° and the other passes a polarizer at 22.5°.

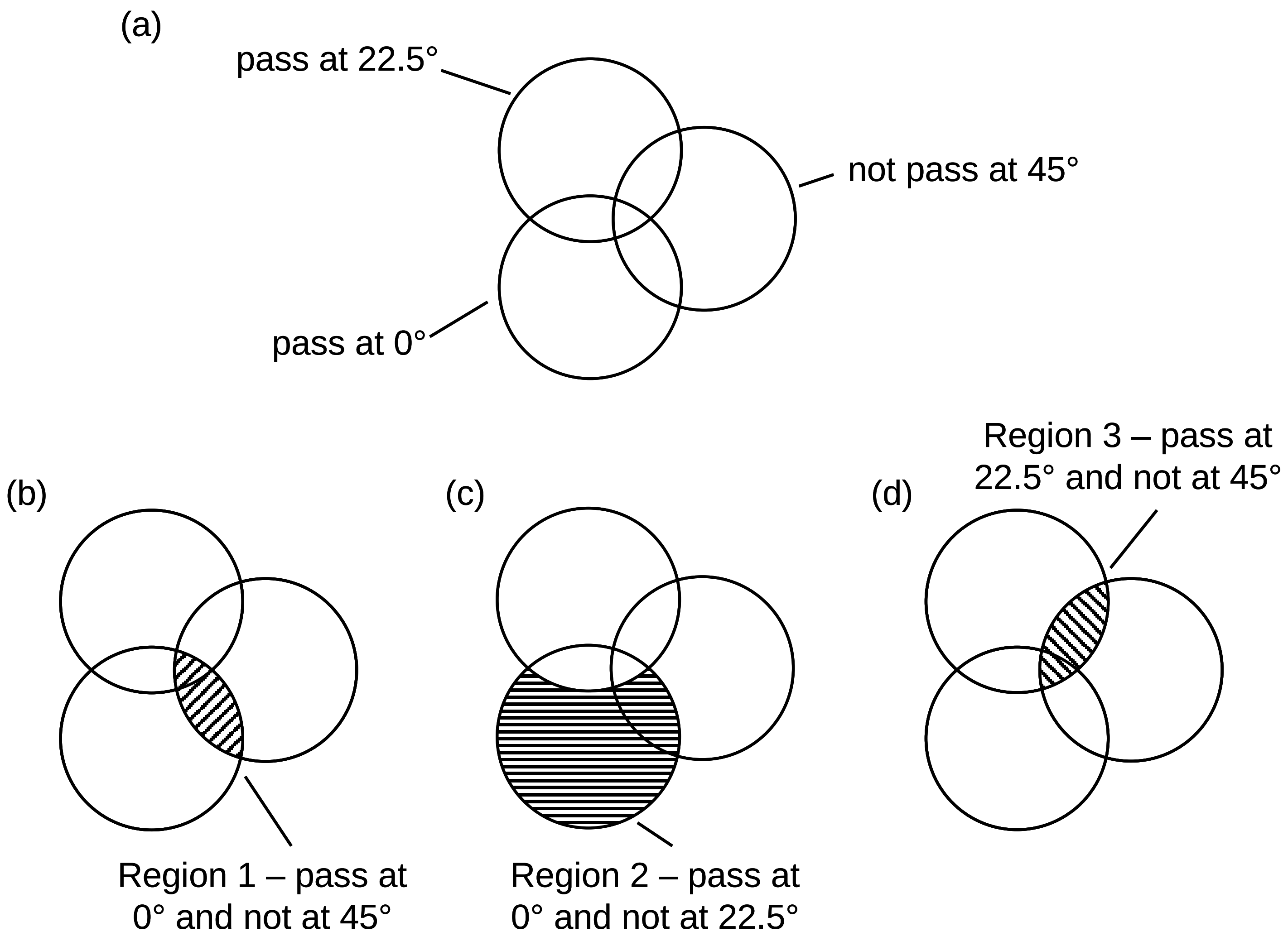
Photon deterministic local variable theory - 3



Regions 2 and 3 taken together encompass all of the states in Region 1 (i.e., Region 1 is a subset of the union of Regions 2 and 3).

The sum of the number of local states in Regions 2 and 3 taken together always either equals or exceeds the number of local states in Region 1.

Photon deterministic local variable theory - 4

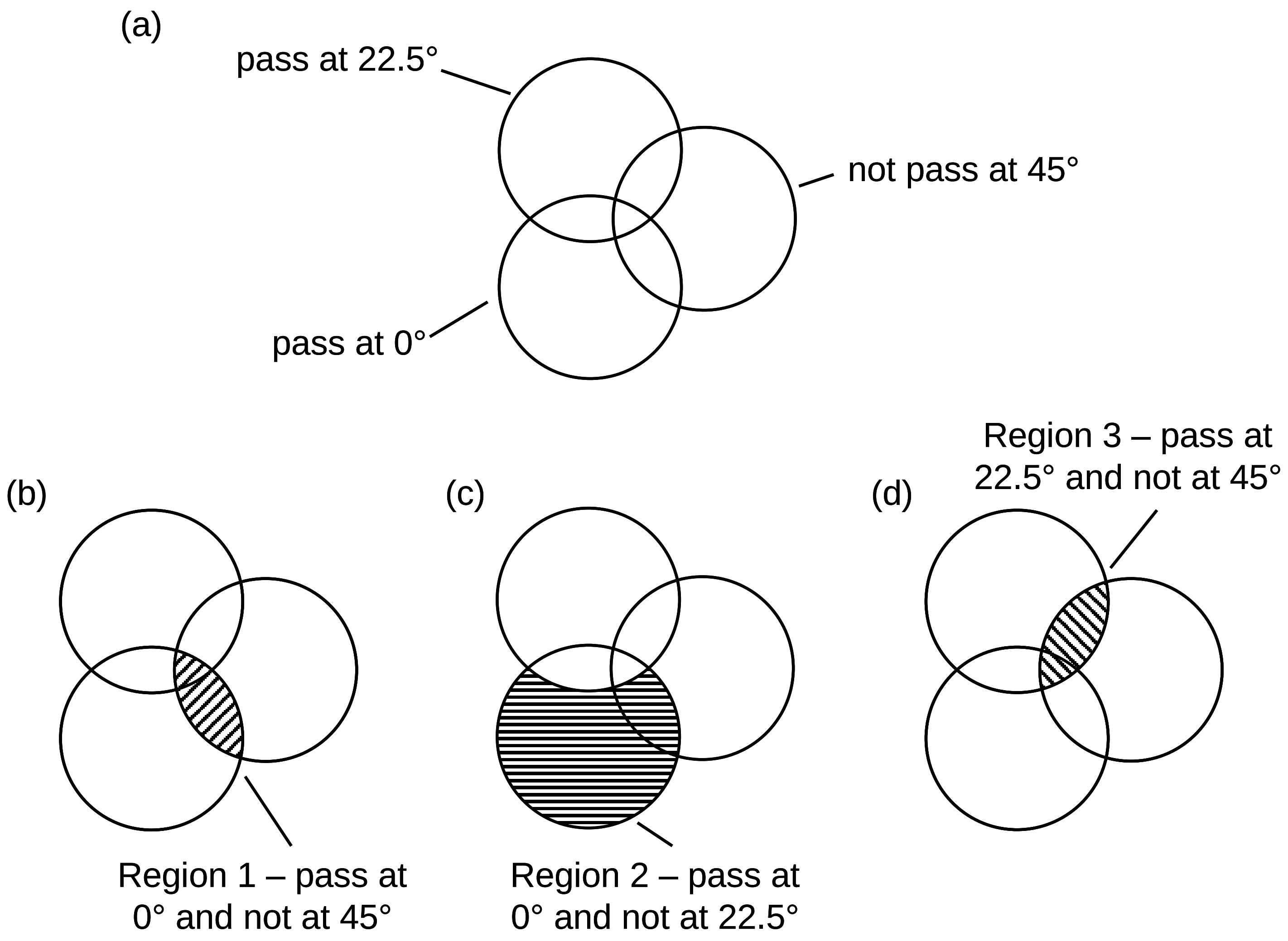


We presume that we can perform this experiment many times

with random local states

(we can verify the randomness by performing experiments on just one of the photons to see random behavior independent of polarizer angle).

Photon deterministic local variable theory - 5



The probability that the local state is found to lie in Region 1

must therefore be less than or equal to

the probability that the local state is found to lie in Region 2 or Region 3,

Photon deterministic local variable theory - 6

Restating:

The probability that the local state is found to lie in Region 1

must therefore be less than or equal to

the probability that the local state is found to lie in Region 2 or Region 3,

i.e.,

The probability that one photon will pass at 0° and the other will not pass at 22.5°
+
The probability that one photon will pass at 22.5° and the other will not pass at 45°
≥
The probability that one photon will pass at 0° while the other will not pass at 45°
(19.2)

This is a specific example for a Bell's inequality.

Simple Bell's inequality

If we therefore find in an experiment that this inequality is violated,

then we have to throw out any deterministic local hidden variable theory.

Experiments do violate this inequality.

Therefore deterministic local hidden variable theories cannot explain reality!

Note this argument does not even mention quantum mechanics.

Bell's inequalities in this sense have nothing to do with quantum mechanics.

They show that, because of the results of experiments, reality cannot be explained by local variables, hidden or otherwise.

Particles cannot simply be described deterministically by properties they carry along with them.

Quantum mechanical calculation

Of course, we find that the results of the experiments do also agree with the predictions of quantum mechanics

Consider a photon linearly polarized at an angle θ to the horizontal.

The polarization state of that photon as

$$\left|\psi(\theta)\right\rangle = \cos\theta\left|H\right\rangle + \sin\theta\left|V\right\rangle \tag{19.3}$$

where $\left|H\right\rangle$ and $\left|V\right\rangle$ are the horizontal and vertical polarization basis states, respectively.

We take the probability that such a photon will pass a horizontally-oriented beamsplitter to be

$$P_H = \left|\left\langle H\middle|\psi(\theta)\right\rangle\right|^2 = \cos^2\theta \tag{19.4}$$

EPR state

Now we consider two different photon modes,

one propagating to the left (L)

and the other to the right (R).

We presume that we have one photon in each mode,

and that this pair of photons is in an "EPR" state

with the two orthogonal polarization states now generalized to be at angles θ and $\theta + \pi/2$

instead of just horizontal and vertical.

Hence we can have the form

$$\left|\psi_{EPR}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|\psi(\theta),L\right\rangle\left|\psi(\theta),R\right\rangle + \left|\psi(\theta+\pi/2),L\right\rangle\left|\psi(\theta+\pi/2),R\right\rangle\right] \tag{19.5}$$

where $\left|\psi(\theta),L\right\rangle$ means that the photon in the left-going mode is polarized with angle θ to the horizontal axis, and so on.

Examination of EPR state with polarizers - 1

We examine this state with

a horizontal polarizer on the left

(or at least the horizontal arm of a polarizing beamsplitter)

and a polarizer at angle ϕ to the horizontal on the right.

For such an examination, we will have an amplitude

$$\begin{aligned}A&=\left(\langle H,L|\langle\psi(\phi),R|\right)|\psi_{EPR}\rangle\\&=\frac{1}{\sqrt{2}}\left(\langle H,L|\langle\psi(\phi),R|\right)\begin{pmatrix}|\psi(\theta),L\rangle|\psi(\theta),R\rangle\\+|\psi(\theta+\pi/2),L\rangle|\psi(\theta+\pi/2),R\rangle\end{pmatrix}\\&=\frac{1}{\sqrt{2}}\begin{bmatrix}\langle H,L|\psi(\theta),L\rangle\langle\psi(\phi),R|\psi(\theta),R\rangle\\+\langle H,L|\psi(\theta+\pi/2),L\rangle\langle\psi(\phi),R|\psi(\theta+\pi/2),R\rangle\end{bmatrix}\end{aligned} \tag{19.6}$$

Note that we can write

$$\langle\psi(\phi)|\psi(\theta)\rangle=\langle H|\psi(\theta-\phi)\rangle \tag{19.7}$$

because the inner product of these two vectors will not change if we rotate both of them by an angle $-\phi$.

Examination of EPR state with polarizers - 2

Hence we have

$$\begin{aligned} A &= \frac{1}{\sqrt{2}}\left[\cos\theta\cos(\theta-\phi)+\cos(\theta+\pi/2)\cos(\theta+\pi/2-\phi)\right] \\ &= \frac{1}{\sqrt{2}}\left[\cos\theta\cos(\theta-\phi)+\sin(\theta)\sin(\theta-\phi)\right] \\ &= \frac{1}{\sqrt{2}}\frac{1}{2}\left[\cos(\phi)+\cos(2\theta-\phi)+\cos(\phi)-\cos(2\theta-\phi)\right] \\ &= \frac{1}{\sqrt{2}}\cos\phi \end{aligned} \qquad (19.8)$$

independent of the angle θ of the polarization axis of the EPR pair.

Hence we can conclude that

the probability of the "left" photon passing the left polarizer at angle 0 (horizontal) and the "right" photon passing the right polarizer at angle ϕ is

$$P = |A|^2 = \frac{1}{2}\cos^2\phi \qquad (19.9)$$

Examination of EPR state with polarizers - 3

If a photon on the right passes at an angle ϕ,

then it fails to emerge from the other arm of a polarization beamsplitter,

an arm that passes a photon of polarization angle $\phi - \pi / 2$.

Hence we can finally conclude that

the probability of the "left" photon passing the left polarizer at angle 0 (horizontal) and

the "right" photon failing to pass the right polarizer at angle ϕ is

$$P_\phi = \frac{1}{2}\cos^2\left(\phi - \pi/2\right) = \frac{1}{2}\sin^2\phi \quad (19.10)$$

The choice of the polarizer orientation on the left as "horizontal" is arbitrary,

and so this expression applies when the angle between the two polarizers is ϕ. Hence we have

The probability that one photon will pass at 0° and the other will not pass at 22.5°

$$((1/2)\sin^2(22.5°) \simeq 0.0732$$

$$+$$

The probability that one photon will pass at 22.5° and the other will not pass at 45°

$$(1/2)\sin^2(22.5°) \simeq 0.0732$$

$$\simeq 0.1464$$

Examination of EPR state with polarizers - 3

But

The probability that one photon will pass at 0° while the other will not pass at 45°

$$(1/2)\sin^2(45°) \simeq 0.2500$$

Hence

because $0.2500 > 0.1464$

Bell's inequality, Eq. (19.2), for this case is violated by the quantum mechanical calculation that also agrees well with experiment.

Hence,

no local hidden variable theory can explain the results of the EPR experiment with misaligned polarizers.

Hence,

if quantum mechanics is to explain the results of experiments

(and it does),

quantum mechanics cannot be explained by local hidden variable theories either.

This is a remarkable conclusion.

Interpretation of quantum mechanics – 2

Reading – Sections 19.2 – 19.4

The measurement problem

Solutions to the measurement problem

Epilogue

The measurement problem

Thus far we have presumed we can make a measurement,

> ***and this measurement forces quantum mechanical systems into eigenstates of the quantity being measured***
>
> > **(the “collapse of the wavefunction”).**

There is, however, a major problem.

> ***We do not know what a measurement is in quantum mechanics,***
>
> > **and we cannot construct a model of it in the quantum mechanics we have constructed with linear operators acting on states.**

Proof of the measurement problem - 1

Suppose we have a measurement apparatus that is going to act on a quantum mechanical state to give the measured value.

Suppose then that this apparatus is described by the quantum mechanical operator $\hat{M}$,

which must therefore be a linear operator.

Suppose that the system starts out in one of the eigenstates of the quantity being measured by the apparatus (e.g., electron spin).

Hence, for the initial eigenstate $|\uparrow\rangle$,

we have the result of the measurement being the state

$$M|\uparrow\rangle = |\uparrow\rangle \tag{19.11}$$

i.e., the system,

when measured in an eigenstate,

stays in that eigenstate.

Similarly for the other possible initial eigenstate

$$M|\downarrow\rangle = |\downarrow\rangle \tag{19.12}$$

So far, this agrees with our observation.

Proof of the measurement problem - 2

But suppose instead that the system starts in a linear superposition state $a_\uparrow|\uparrow\rangle + a_\downarrow|\downarrow\rangle$.

Then on operating on that state, because of the linearity of $\hat{M}$, we have

$$\hat{M}\left(a_\uparrow|\uparrow\rangle + a_\downarrow|\downarrow\rangle\right) = a_\uparrow\hat{M}|\uparrow\rangle + a_\downarrow\hat{M}|\downarrow\rangle = a_\uparrow|\uparrow\rangle + a_\downarrow|\downarrow\rangle \tag{19.13}$$

Note that the resulting state is a linear superposition also.

The measurement operation has not been able to collapse the resulting state into an eigenstate,

in disagreement with our understanding of measurement.

Therefore there is no way of describing measurement using the quantum mechanics we have constructed!

Solutions to the measurement problem

There is no proposed solution to it that does not appear either

absurd, or that

invokes something outside quantum mechanics for which we have no explanation.

Also, however, there is no experiment that we know of that can discriminate between the different proposals,

and therefore all of them remain in the realm of metaphysical philosophical speculation.

Here we briefly mention some of the contenders.

The Standard Interpretation

The so-called Standard Interpretation of quantum mechanics is that

> ***we separate out the measurement process as being something different,***
>
> > **and use our simple rules to work out the probability of various outcomes.**

For engineering,

> ***this presents no apparent problems as long as it keeps working for every problem we ask it to solve.***

From a scientific or philosophical point of view

> ***because we have no description of how the measurement process works,***
>
> > **and at what point we make the boundary between the quantum mechanical world and the (presumably) macroscopic world of measurements**
>
> ***it is very unsatisfactory.***
>
> > **The quantum system evolves in superposition states until we measure it,**
> >
> > > *but we do not know what measurement is!*

The Standard Interpretation is also an example of theory in which reality

> ***specifically the determinate experience we have of things being in specific states rather than superpositions***

is created by the act of observation, whatever that is.

Schrödinger's cat

The classic illustration of the absurdity of the Standard Interpretation is Schrödinger's cat,

The cat is trapped in a box that has

a device that will go off randomly,

with a quantum mechanical process such as radioactive decay,

triggering the death of the cat.

The Standard Interpretation would say that,

if we do not open the box and make a measurement,

the cat will continue to "exist" in a linear superposition of alive and dead,

which, the criticism would say, is absurd.

Whether it is absurd or not,

and whether absurdity should be given any weight in deciding the validity of a quantum theory provided the theory agrees with experiment,

both are matters of opinion.

The Copenhagen Interpretation - 1

The Copenhagen interpretation is essentially due to Bohr.

We know that we must accept the wave-particle duality –

- ***entities such as electrons have both wave and particle character.***

Such a duality requires us to accept two views that,

- ***in a classical approach at least,***
  - **are contradictory**
    - *or, in the terminology of the Copenhagen interpretation, complementary.*

We also note that certain variables have a complementarity to them,

- ***such as position and momentum –***
  - **we can accurately only know one of these at a time,**
    - *as given by the uncertainty principle.*

Then perhaps we should extend this complementarity principle to other aspects of quantum mechanics that are also apparently contradictory,

- ***such as the "complementarity" of the linear superposition aspects of quantum mechanical states***
  - **having character seen also in waves with their linear superposition**
- ***and the apparent definite states seen as a result of measurements***
  - **having character seen also in particles with their definite discrete existence.**

The Copenhagen Interpretation - 2

Modern opinion is sometimes that

generations of physicists were misled into believing that Bohr had solved the problem of the interpretation of quantum mechanics,

including the measurement problem,

though no-one was exactly sure how precisely he had done this

e.g., Murray Gell-Mann said

"The fact that an adequate philosophical presentation has been so long delayed is no doubt caused by the fact that Niels Bohr brainwashed a whole generation of theorists into thinking that the job was done fifty years ago.".

Whatever Bohr was advocating is not clearly defined mathematically

once we go beyond aspects like the uncertainty principle and wave-particle duality,

and does not appear to offer a way of resolving the difficulties of the interpretation of quantum mechanics.

A common problem with the Copenhagen Interpretation is that one cannot find a consistent or clear definition in the literature as to what it actually is.

Bohm's Pilot Wave

We start with the time-dependent Schrödinger equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad (19.14)$$

and then we make a mathematical choice to write

$$\psi(\mathbf{r},t) = R(\mathbf{r},t)\exp(iS(\mathbf{r},t)) \qquad (19.15)$$

where *R* and *S* are real quantities.

Any complex function can be represented in this way.

If we substitute the form (19.15) into Eq. (19.14),

then, after a little algebra, we can deduce the equation

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V + Q = 0 \qquad (19.16)$$

where

$$Q = -\frac{\hbar^2}{2m}\frac{\nabla^2 R}{R} \qquad (19.17)$$

Hamilton-Jacobi equation

Eq. (19.16) without the quantum potential *Q*

$$\frac{\partial S}{\partial t}+\frac{(\nabla S)^2}{2m}+V=0$$

is known as the Hamilton-Jacobi equation of classical mechanics.

It reproduces all the usual classical behavior of a particle.

***S* is known as the "action" or Hamilton's principal function,**

and the momentum is $\mathbf{p}=\nabla S$**.**

This equation is a completely deterministic equation

in which position and momentum are both simultaneously well defined.

For a large wavepacket and a large mass,

then the quantum potential $Q=-\frac{\hbar^2}{2m}\frac{\nabla^2 R}{R}$ ***is a very small correction***

and hence,

even using the full form of Eq. (19.16),

we obtain the classical behavior with which we are familiar.

Quantum potential and the pilot wave

Bohm's assertion –

Because we can use definite position and momentum as meaningful concepts in the classical version of Eq. (19.16),

so also we can use them when we add in a finite quantum potential *Q*.

We are merely adding in the potential from another field

here a potential derived from the solution to Schrödinger's equation

to the Hamilton-Jacobi equation

just as we might add in another potential from, say, an electromagnetic field that is the solution of Maxwell's equations.

This quantum potential also acts,

together with the other potentials in the system,

to guide the particle.

As a result this potential, or the wavefunction that generates it, can be regarded as a "pilot wave".

As far as Schrödinger's equation is concerned,

there is nothing apparently wrong with Bohm's assertion.

The randomness of quantum mechanics in this picture comes from the ordinary randomness of the initial positions and momenta of the particles.

Bohm's pilot wave and the double slit experiment

This picture does correctly reproduce the results of classic experiments like diffraction through two slits.

- ***the wavefunction through the quantum potential gives the necessary additional potential to guide the particles,***
  - **one by one,**
    - *so that an ensemble of them with suitable random starting conditions will reproduce the diffraction pattern we see,*
      - with the zeros at specific points as required.

If we block a slit, we block the wavefunction from passing through that slit

- ***hence the wavefunction will not have a two-slit diffraction pattern***
  - **hence neither will the quantum potential,**
    - *and the ensemble of particles will not show a two-slit diffraction pattern either*
      - just as we expect.

Note, though, that in this picture,

- ***the particle does definitely go through one slit or the other, and any individual particle does have definite position and momentum at all times.***
- ***Because of this definiteness, there is no "collapse of the wavefunction" required to explain definite measurements.***

Objections to Bohm's picture

There have been many objections to this picture.

In this simple form as presented here,

it is not relativistically correct,

and it only applies to one particle.

Approaches to addressing such problems do exist however.

It does also appear to give a special status to position,

whereas the conventional description of quantum mechanics treats position on an equal footing with any other dynamical variable.

DAVID J. BOHM (*center*) is escorted to the House Un-American Activities Committee hearing room by Donald Appel, a staff investigator, on May 25, 1949.

Nonlinearity

The measurement problem is based on the linearity of quantum mechanics.

Perhaps quantum mechanics is not actually exactly linear,

and the effects of that nonlinearity become strong as we move to the macroscopic world in which we appear to exist.

Then it would not be mathematically impossible to discount the kind of proof we gave above and propose that some state collapse is possible.

This approach does not seem to get a lot of attention,

presumably because no-one has been able to come up with a theory that both satisfactorily explains the microscopic world

and yet gives the kind of state collapse we think we see.

Distinction between matter and mind

Perhaps the process of measurement and collapse of the wavefunction occurs when a conscious mind (whatever that is) intervenes.

- *Consciousness then lies outside quantum mechanics as stated so far.*

Such a supposition might allow us to test experimentally for the presence of consciousness in a chain of events,

- *since consciousness would collapse the wavefunction*
  - and lead to an evolution after that point that was different from the evolution we would have seen for a true superposition.

If the system that is supposed to be conscious is a relatively complex one such as a human brain,

- *it is doubtful that we could calculate the evolution of a true superposition in interacting with that system,*
  - and so we likely could not distinguish it from the evolution of a collapsed state of a complex system;
    - *hence this experiment is perhaps discouragingly hard.*

Also, having no clear definition of consciousness, it is difficult to make much progress theoretically.

- *It does raise the hypothesis that maybe consciousness has something to do with nonlinearity in quantum mechanics.*

Many-worlds hypothesis

Everett proposed in 1957 that there was no collapse of the wavefunction.

Each possible measurement outcome exists, but in different "worlds"!

Measurement causes reality to split into multiple branches or worlds,

each corresponding to a different possible result.

Multiple replicas of the observer then exist,

one for each world,

and in each world the observer believes a different outcome happened.

In this approach,

an observer can be a machine,

with the characteristic that it writes down results.

For each possible answer the machine might write down,

there is a different world.

An alternative version would have the observer have multiple different minds, one for each outcome,

in which case it is known as a many-minds hypothesis.

This approach does not obviously violate any laws of quantum mechanics,

and claims not to require anything other than linear quantum mechanics to describe everything, including the observer.

Epilogue

Perhaps instead we should have taken the advice of Willis Lamb (a Nobel Laureate).

> ***"I have taught graduate courses in quantum mechanics for over 20 years …, and for almost all of them I have dealt with measurement in the following manner. On beginning the lectures I told the students, 'You must first learn the rules of calculation in quantum mechanics, and then I will tell you about the theory of measurement and discuss the meaning of the subject.' Almost invariably, the time allotted to the course ran out before I had time to fulfill my promise."***