Quantum Electronics

2. Toward quantum mechanics

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Contents: **Toward quantum mechanics**

پراش:
(diffraction)

پاشیدگی:
(dispersion)

پراکندگی:
(scattering)

تداخل:
interference

پیوند ناهمجنس :
heterostructure

برهم کنش:
(interaction)

2.1 Introduction

The basic physical building blocks forming the world, may be categorized into:

1. particles of matter (electrons);
2. carriers of force between matter (Photons);
3. composite particles made up of **elementary particles** of matter and transmitters of force (Neutrons, protons, and atoms).

All known **elementary constituents** of matter and **transmitters of force** are **quantized**. For example, **energy**, **momentum**, and **angular momentum** take on discrete quantized values.

Classical mechanics is unable to explain quantization.

Quantum mechanics can explain the nature of quantization.

The laws of quantum mechanics have been established by **experiment**.

2.1 Introduction

- Long before realizing the quantized nature of light (photons), key experiments on the wave properties of light were performed.
- The color of visible light is associated with different wavelengths of light.
- While Table 2.1 shows the range of wavelengths corresponding to different colors, Table 2.2 shows the frequencies and wavelengths corresponding to different regions of the electromagnetic spectrum.

Table 2.1 *Wavelengths of visible light*

Wavelength (nm)	Color
760–622	red
622–597	orange
597–577	yellow
577–492	green
492–455	blue
455–390	violet

2.1 Introduction

Table 2.2 *Spectrum of electromagnetic radiation*

Name	Wavelength (m)	Frequency (Hz)
radio	$> 10^{-1}$	$< 3 \times 10^{9}$
microwave	$10^{-1} - 10^{-4}$	$3 \times 10^{9} - 3 \times 10^{12}$
infrared	$10^{-4} - 7 \times 10^{-7}$	$3 \times 10^{12} - 4.3 \times 10^{14}$
visible	$7 \times 10^{-7} - 4 \times 10^{-7}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$
ultraviolet	$4 \times 10^{-7} - 10^{-9}$	$7.5 \times 10^{14} - 3 \times 10^{17}$
x-rays	$10^{-9} - 10^{-11}$	$3 \times 10^{17} - 3 \times 10^{19}$
gamma rays	$< 10^{-11}$	$> 3 \times 10^{19}$

2.1.1 Diffraction and interference of light

- light waves can exhibit diffraction, linear superposition, and interference (**Young's slits experiment** —1803).
- The interference pattern is due to the superposition of waves, for which each slit is an effective coherent source.
- Hence, the **Young's slits interference** experiment can be understood using the **principle of linear superposition.**
- The wave source at each diffracting slit (Huygen's principle) interferes to create an interference pattern, which can be observed as intensity variations on a screen.
- Intensity maxima correspond to electric fields adding coherently in phase and intensity minima correspond to electric fields adding coherently out of phase.

diffraction: پراش	principle of superposition: اصل برهم نهی	interference: تداخل

2.1.1 Diffraction and interference of light

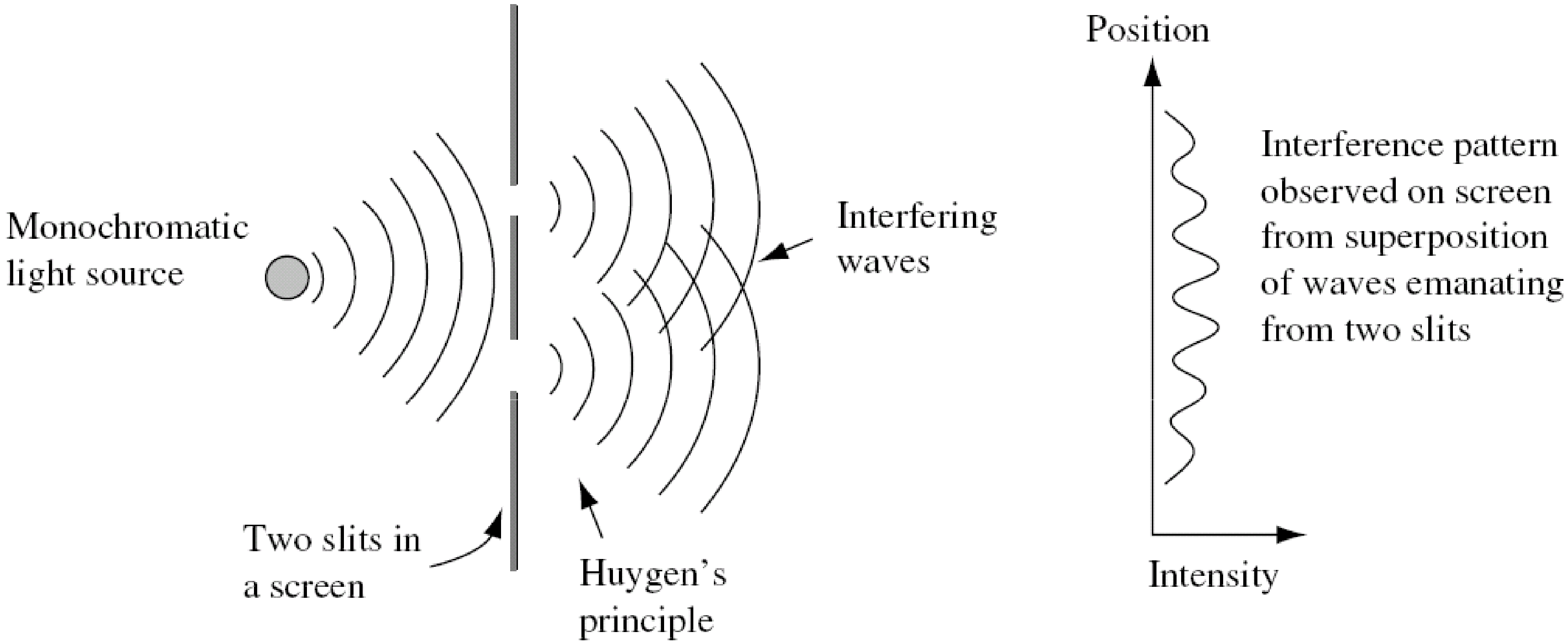


Fig. 2.1 Illustration of the Young's slits experiment.

The interference pattern is due to the superposition of waves, for which each slit is an effective coherent source.

2.1.1 Diffraction and interference of light

- **اصل برهم نهی:** خاصیتی که موج را به پدیده فیزیکی منحصربفردی تبدیل میکند، که باعث می شود ،دو موج در یک نقطه برخورد کنند و آشفتگی مرکبی را در آن نقطه به وجود آورند که از آشفتگی ناشی از هر یک از امواج، به تنهایی، بزرگتر یا کوچکتر باشد؛ و سرانجام از نقطه "برخورد" با تمام ویزگی های هر یک از این دو موج، که برخورد، هیچ گونه تغییری در آن پدید نیاورده است، خارج شوند.
- این ویزگی خاص امواج، به پدیده های تداخل و پراش می انجامد.
- تداخل سازنده: (Constructive interference) که با شدت بیشینه در آزمایش یانگ ظاهر میشود، وقتی رخ می دهد که قله موج از یک شکاف، همزمان با قله موج شکاف دیگر به یک نقطه برسند.
- تداخل ویرانگر: (Destructive interference) که با شدت کمینه در آزمایش یانگ ظاهر میشود، وقتی رخ می دهد که قله موج از یک شکاف، همزمان با دره موج شکاف دیگر به یک نقطه برسند، یا به بیانی دیگر، دو قله موج دو شکاف که به یک نقطه میرسند،با یکدیگر در فاز مخالف باشند.

2.1.1 Diffraction and interference of light

Consider two plane waves labeled j = 1 and j = 2, with wavelength $\lambda = 2\pi/k$, amplitude $|E_j|$, phase Φ_j, and frequency ω .

(In a linear system we can make any wave from a linear superposition of plane waves).

Mathematically, the two waves can be represented as:

$$\mathbf{E}_1 = \mathbf{e}_1^{\sim}|\mathbf{E}_1|e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}e^{i\phi_1} \quad (1)$$

$$\mathbf{E}_2 = \mathbf{e}_2^{\sim}|\mathbf{E}_2|e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}e^{i\phi_2} \quad (2)$$

respectively, where $\mathbf{e}\sim_j$ is the unit-vector in the direction of the electric field $\mathbf{E}_j$.

The intensity due to the linear superposition of E_1 and $\mathbf{E}_2$ with $\mathbf{e}\sim_1 = \mathbf{e}\sim_2$ is just:

$$|\mathbf{E}|^2 = |\mathbf{E}_1 + \mathbf{E}_2|^2 = |\mathbf{E}_1|^2 + |\mathbf{E}_2|^2 + 2|\mathbf{E}_1||\mathbf{E}_2|\cos(\phi) \quad (3)$$

where $\Phi = \Phi_2 - \Phi_1$ is the relative phase between the waves. Our expression for $|\mathbf{E}|^2$ is called the ***interference equation.***

2.1.1 Diffraction and interference of light

interference equation:

$$|\mathbf{E}|^2 = |\mathbf{E}_1 + \mathbf{E}_2|^2 = |\mathbf{E}_1|^2 + |\mathbf{E}_2|^2 + 2|\mathbf{E}_1||\mathbf{E}_2|\cos(\phi)$$

if: $|\mathbf{E}_1| = |\mathbf{E}_2| = |\mathbf{E}_0|$

for $\phi = 0$

intensity maximum $|\mathbf{E}|^2_{\max} = 4|\mathbf{E}_0|^2$

when $\phi = \pi$

intensity minimum $|\mathbf{E}|^2_{\min} = 0$

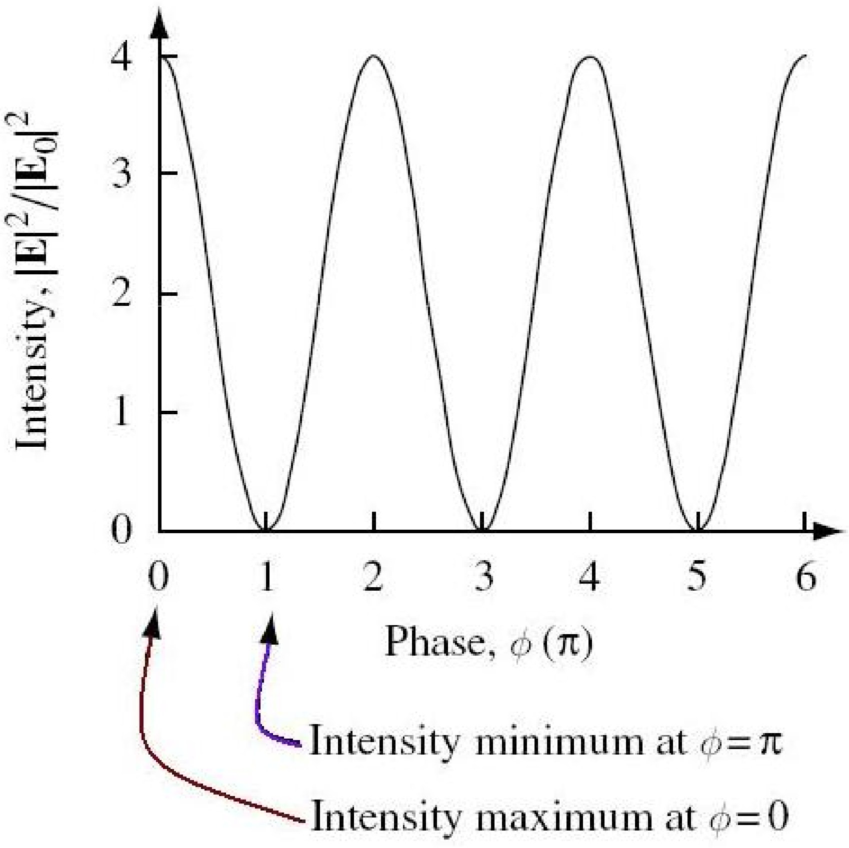


Fig. 2.2 The linear superposition of two waves at exactly the same frequency can give rise to interference if there is a relative phase delay between the waves. The figure illustrates the sinusoidal interference pattern in intensity as a function of phase delay, Φ, between two equal amplitude waves.

2.1.1 Diffraction and interference of light

- This interference pattern is periodic in Φ and exists over all space.
- In the more general case, when $|E_1| \neq |E_2|$, the interference pattern is still periodic in Φ, but:

the intensity maximum = $(|E_1| + |E_2|)^2$

the intensity minimum = $(|E_1| - |E_2|)^2$.

Usually we do not see large variations in light intensity due to interference. The reason is that the frequencies of the light waves are not exactly (i.e., are not precisely monochromatic).

There is a continuous range or spectrum of frequencies about some average value of ω. Because the light is not exactly monochromatic, even if the spectrum is sharply peaked at some value of frequency, there is a linewidth associated with the spectral line typically centered at frequency ω_0.

2.1.1 Diffraction and interference of light

By taking the Fourier transform of the continuous spectral line, we can obtain the temporal behavior of the wave.

Suppose we have a laser with light emission at wavelength **λ=1500 nm**.

The electromagnetic field oscillates at: f= 200THz or $\omega_0 = 2\pi f = 1.26\times10^{15}$ rad s^{-1}.

Assume that the pulse has a Gaussian shape (at $t=t_0$), so that the electromagnetic field can be written as:

$$\mathbf{E}_j(t) = \mathbf{e}_j^{\sim} \cos(\omega_0 t) e^{-(t-t_0)^2/\tau_0^2} \quad (4)$$

where τ_0 is proportional to the temporal width of the pulse. The Fourier transform is a Gaussian envelope centered at the frequency ω_0:

$$\mathbf{E}_j(\omega) = \mathbf{e}_j^{\sim} \frac{\tau_0}{\sqrt{2}} e^{-(\omega-\omega_0)^2 \tau_0^2/4} \quad (5)$$

2.1.1 Diffraction and interference of light

time domain field:

$$\mathbf{E}_j(t) = \mathbf{e}_j^{\sim} \cos(\omega_0 t) e^{-(t-t_0)^2/\tau_0^2} \qquad \Delta t_{\text{FWHM}} = 2\tau_0\sqrt{\ln(2)}$$ (8)

frequency domain field:

$$\mathbf{E}_j(\omega) = \mathbf{e}_j^{\sim} \frac{\tau_0}{\sqrt{2}} e^{-(\omega-\omega_0)^2\tau_0^2/4} \qquad \Delta\omega_{\text{FWHM}} = \frac{4}{\tau_0}\sqrt{\ln(2)}$$ (9)

frequency domain intensity: spectral power density

$$\mathbf{E}^*(\omega)\cdot\mathbf{E}(\omega) = \frac{\tau_0^2}{2} e^{-(\omega-\omega_0)^2\tau_0^2/2} \qquad \Delta\omega_{\text{FWHM}} = \frac{2}{\tau_0}\sqrt{2\ln(2)}$$ (10), (6, 7)

full-width at half-maximum (FWHM)

2.1.1 Diffraction and interference of light

Example: λ=1500 nm f= 200THz $\omega_0 = 2\pi f = 1.26\times10^{15}$ rad s^{-1} τ_0= 14.14 fs

$$\Delta t_{\mathrm{FWHM}} = 2\tau_0\sqrt{\ln(2)} = 23.5\,\mathrm{fs}$$

$$l = \Delta t_{\mathrm{FWHM}} \times c = 7\,\mu\mathrm{m}$$

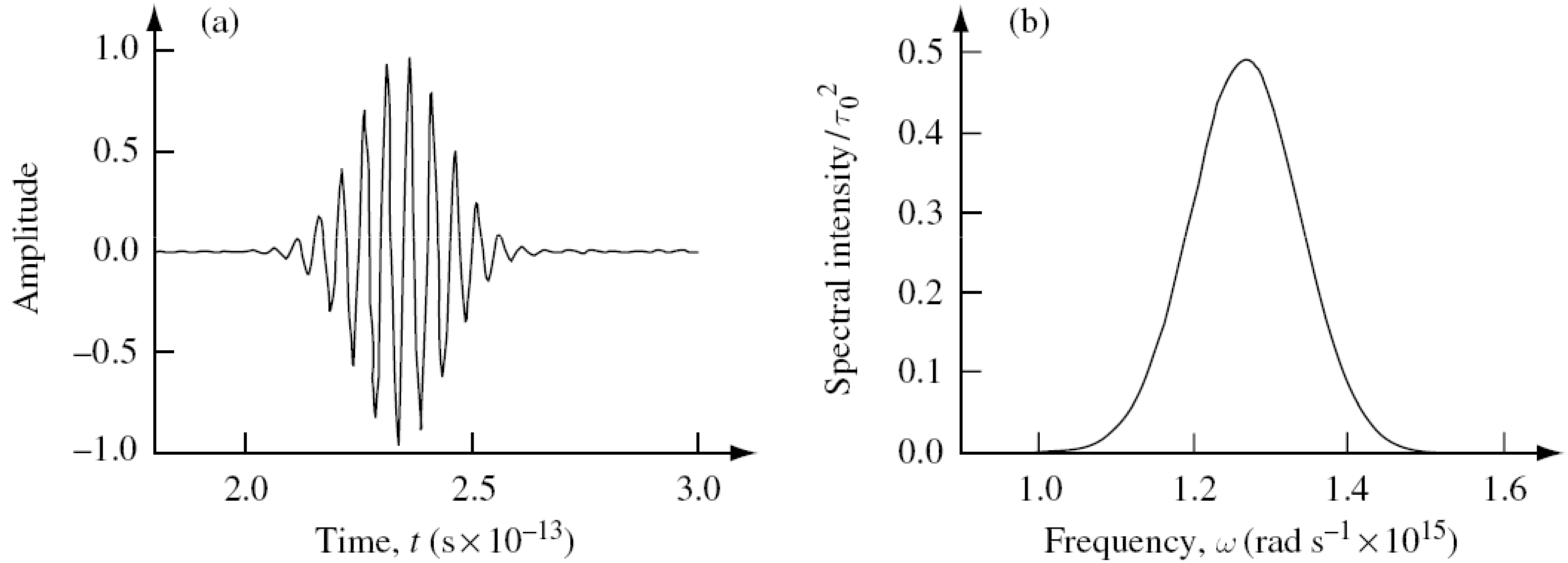


Fig. 2.3 (a) Illustration of a 200 THz electric field modulated by a Gaussian envelope function with τ_0 = 14.14 fs. **(b)** Spectral line shape centered at $\omega_0 = 1.26 \times 10^{15}$ rad s^{-1} corresponding to the 200 THz oscillating electric field in (a).

2.1.1 Diffraction and interference of light

characteristic time or length

- The fact that the oscillator can only oscillate for a finite time means that the frequency spectrum always has a finite width. This has a direct impact on the observation of interference effects.
- Interference effects can only be observed when the wave and the delayed wave overlap in space.
- We expect that interference between the pulse and the delayed pulse will only be easily observed for delays approximately equal to or less than Δt_{FWHM}.
- For a wave moving at the speed of light, this gives a characteristic length $L = \Delta t_{FWHM} \times c$, (which in our case is 7μm.)
- The normalized autocorrelation function is defined as:

$$g(\tau) = \frac{\langle f^*(t) f(t+\tau) \rangle}{\langle f^*(t) f(t) \rangle} \quad (11)$$

2.1.1 Diffraction and interference of light

coherence time:

The normalized autocorrelation function is:

$$g(\tau) = \frac{\langle f^*(t) f(t+\tau) \rangle}{\langle f^*(t) f(t) \rangle} \quad (11)$$

f(t): complex function of time (in our case it is a wave).

The value of $|g(\tau)|$ is a measure of the correlation between f(t) and f(t+τ), where τ is a time delay.

For classical **monochromatic light**, f(t) is of the form $e^{-i\omega t}$, which gives $g(\tau) = e^{-i\omega t}$, so that $|g(\tau)| = 1$.

The coherence time is defined as:

$$\tau_c = \int_{\tau=-\infty}^{\tau=\infty} |g(\tau)|^2 d\tau \quad (12)$$

So if $|g(\tau)| = 1$, the **coherence time** τ_c is infinite and the corresponding **coherence length**, which is defined as $l_c = \tau_c \times c$, is also infinite.

2.1.1 Diffraction and interference of light

In practice, because the wave source is not purely monochromatic, there is a *coherence length associated with the nonmonochromaticity.*

The coherence length gives the spatial scale over which interference from the linear superposition of fields can be observed.

For $L \gg L_c$, the phases of different wavelength components can no longer add to create either a maximum or minimum, and all interference effects are effectively washed out.

Table 2.3 *Relationship between spectral line-width and coherence time*

Spectral intensity line-shape	Spectral width $\Delta\omega_{\mathrm{FWHM}}$
Gaussian	$2(2\pi \ln(2))^{1/2}/\tau_c$
Lorentzian	$2/\tau_c$
Rectangular	$2\pi/\tau_c$

2.1.2 Black-body radiation and evidence for quantization of light

Experimental evidence for the quantization of light into particles called photons initially came from measurement of the emission spectrum of thermal light (called black-body radiation). Application of **classical statistical** thermodynamics and electromagnetics gives the **Rayleigh–Jeans formula** (1900) for electromagnetic field radiative energy density emitted from a **black body** at absolute temperature **T** as:

$$U_S(\omega) = \frac{k_B T}{\pi^2 c^3}\omega^2 \qquad \textbf{(13)}$$

Radiative energy density is the energy per unit volume per unit angular frequency, and it is measured in J s m^{-3}. Equation (13) predicts a physically impossible infinite radiative energy density as $\omega \rightarrow \infty$.

This divergence in radiative energy density with decreasing wavelength is called the classical ultraviolet catastrophe. (فاجعه فرابنفش کلاسیک)

2.1.2 Black-body radiation and evidence for quantization of light

Planck (in 1900) assumed emission and absorption of discrete energy quanta of electromagnetic radiation, so that ***E*=ħ*ω*.**

This gives a radiative energy density measured in units of **J s m⁻³**:

$$U_S(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

(14)

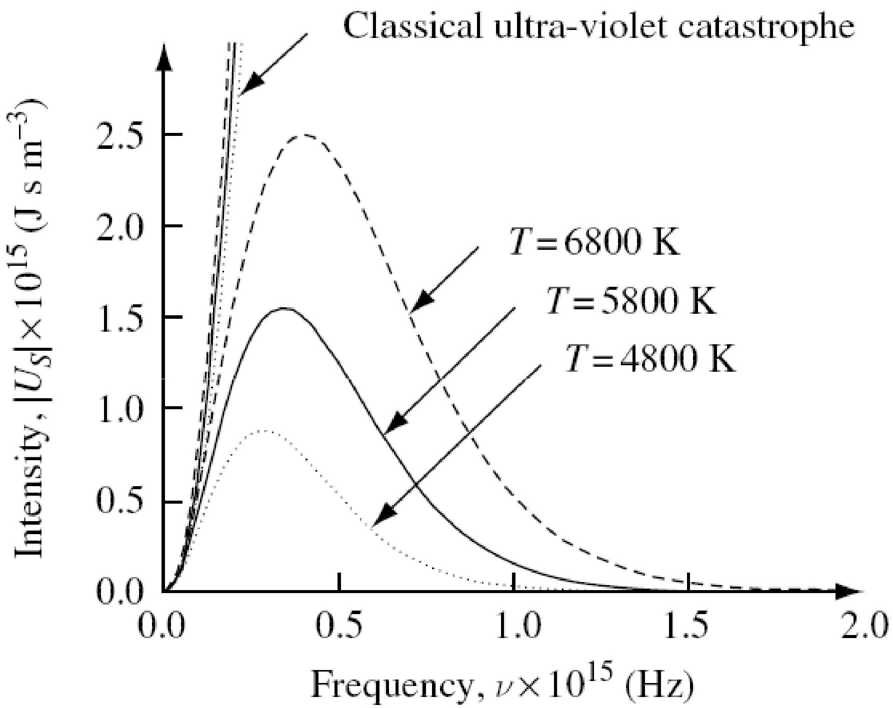


Fig. 2.4 Radiative energy density of black-body radiation emitted by unit surface area into a fixed direction from a black body as a function of frequency ($\nu = \omega / 2\pi$).

2.1.3 Photoelectric effect and the photon particle

When light of angular frequency ω is incident on a metal, electrons can be emitted from the metal surface if $\hbar\omega > e\phi$, where ϕ is the work function of the metal. $+e\phi$ is the minimum energy for an electron to escape the metal into vacuum.

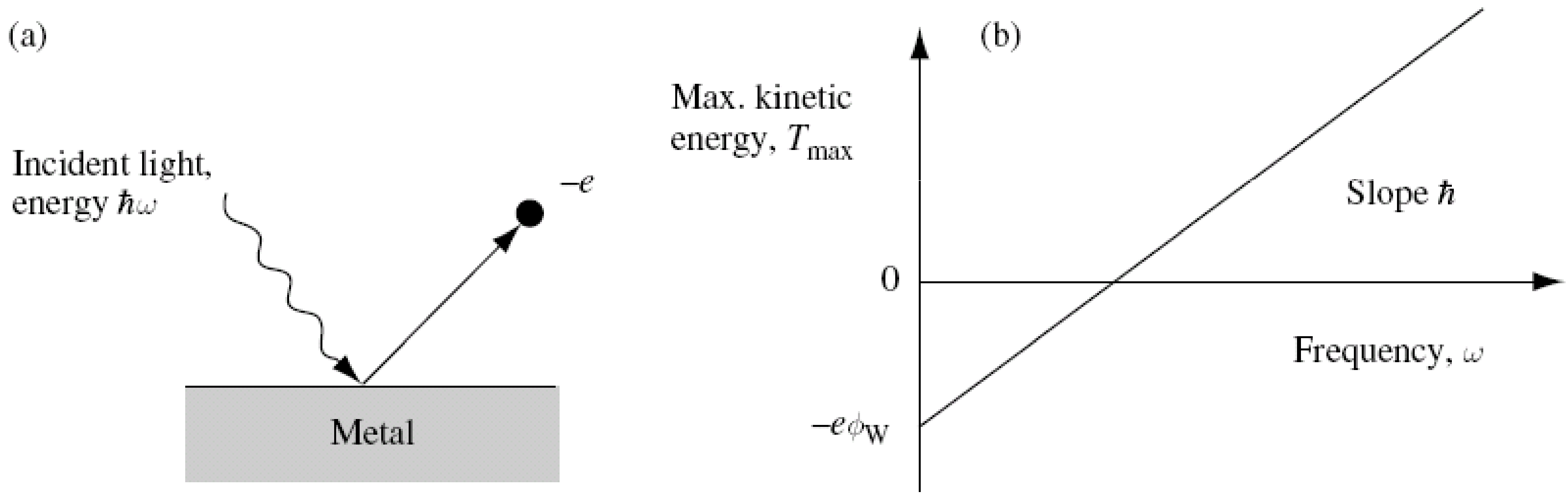


Fig. 2.5 (a) Light of energy $\hbar\omega$ can cause electrons to be emitted from the surface of a metal. **(b)** The maximum kinetic energy of emitted electrons is proportional to the frequency of light, ω. The proportionality constant is $\hbar$.

2.1.3 Photoelectric effect and the photon particle

In addition, such photoelectric-effect experiments show that the ***number of electrons leaving** the surface* depends upon the intensity of the incident electromagnetic field.

This evidence suggests that light can behave as a particle.

The maximum excess kinetic energy of the electron leaving the surface is observed in experiments to be $T_{max} = \hbar\omega - e\Phi$, where is the slope of the curve in Fig. 5(b).

The maximum kinetic energy of any ejected electron depends only upon the angular frequency, , of the light particle with which it collided, and this energy is *independent of light intensity.*

Each light particle has energy , and light intensity is given by the particle flux.

This is different from the classical case which predicts that energy is proportional to light intensity.

2.1.3 Photoelectric effect and the photon particle

In 1905, **Einstein** explained the photoelectric effect by postulating that light behaves as a **particle** and that (in agreement with Planck's work) it is quantized in energy, so that:

$$\boxed{E = \hbar\omega} \quad \textbf{(15)}$$

$\hbar = 1.054\,592\times10^{-34}$ **J s** (***Planck's constant)***

dimensions of ħ: **J s** or kg $m^2\ s^{-1}$. (**action**)

E =ħω , comes directly from **experiment**.

The **quantum of light** is called a ***photon****.*

*A **photon** has zero mass and is an example of* an elemental quantity in quantum mechanics.

In quantum mechanics, one talks of light being quantized into particles called photons.

2.1.3 Photoelectric effect and the photon particle

From classical electrodynamics:

electromagnetic *plane waves* *carry* ***momentum of magnitude p = U/c,***

U*: electromagnetic energy density*

➡ momentum of photon: **p = E/c**.

Because **E** =ħω is quantized , ➡ **momentum** should also be **quantized**.

➡ p= ħω /c or, since ω = c2π/λ = ck, **(k=2π/λ)**

photon momentum can be written as:

$$\mathbf{p} = \hbar \mathbf{k} \quad \textbf{(16)}$$

$$\lambda_{\text{photon}}(\text{nm}) = \frac{1240}{E(\text{eV})} \quad \textbf{(17)}$$

Example: **λ= 1000nm** ; ➡ E = 1.24 eV; p = 6.63×10^{-28} kgms^{-1}.

Compare: room temperature thermal energy k_BT = 25 meV,

2.1.3 Photoelectric effect and the photon particle

•فوتون یک ذره بنیادی پایدار بدون جرم است که تنها با سرعت **c** وجود دارد.

•فوتون را برخلاف اجسام معمولی نمی توان مستقیما مشاهده کرد؛ تنها نتیجه خلق یا نابودی آنها مشاهده می شود.

•فوتون را هرگز نمی توان در حال پیمودن فضا مشاهده کرد. فوتون را تنها می توان هنگام اثرگذاری بر محیط اطراف مشاهده کرد، و تنها موقعی اثر قابل مشاهده دارد که به وجود می آید یا نابود میشود.

•فوتون از ذرات باردار به وجود می آید و روی ذرات باردار نابود می شود؛ در اکثر موارد فوتون از الکترون به وجود می آید و توسط الکترون جذب می شود.

چند خاصیت اساس فوتونها:

۱- فوتونها مانند موج الکترومغناطیسی، با سرعت نور حرکت می کنند.

۲- جرم و انرژی سکون آنها صفر است.

۳- حامل انرژی و اندازه حرکت هستند؛ که بین فرکانس و طول موج الکترومغناطیسی رابطه $p=\hbar\omega/c=\hbar k=h/\lambda$ و $E=\hbar\omega=h\nu$ برقرار است.

۴- در گسیل و جذب تابش، فوتونها میتوانند تولید یا نابود شوند.

۵- فوتونها مانند الکترونها، میتوانند با سایر ذرات برخوردهای ذره گونه انجام دهند.

2.1.4 Secure quantum communication

- An electromagnetic wave consists of elementary particles called **photons**.
- Each photon has **energy**.
- Electromagnetic waves can be **polarized** and **linearly** superimposed.
- we can use the **combination** of these facts to create a **secure** communication channel.

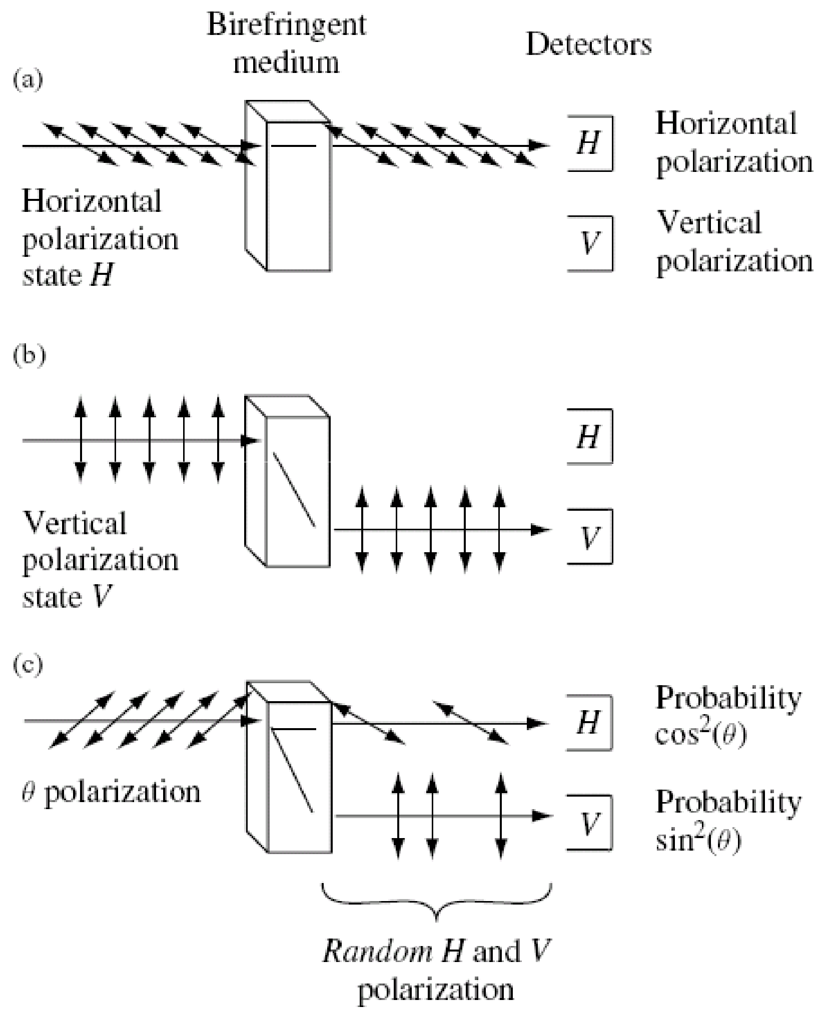


Fig. 2.6: A polarized optical wave that passes through a **birefringent** medium (such as a **calcite** crystal).

2.1.4 Secure quantum communication

The **polarization state** of each horizontally **H** or vertically **V** polarized photon can be used to reliably carry one bit of information.

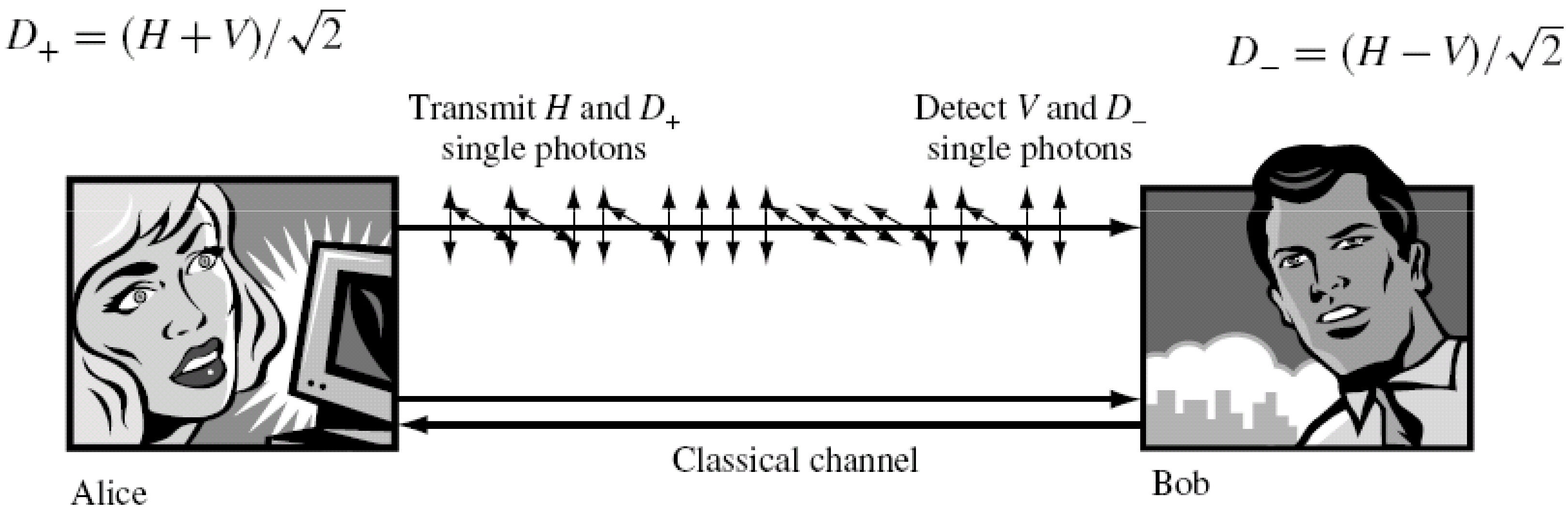


Fig. 2.7 Alice can transmit information to Bob via a **quantum communication** channel that uses **single photons** and **nonorthogonal** polarization states. Alice and Bob can also communicate via a classical channel.

2.1.4 Secure quantum communication

Alice's bit value	$H=0$	$H=0$	$D_+=1$	$D_+=1$
	↔	↔	↔ + ↕	↔ + ↕
Bob tests with	$V=1$	$D_-=0$	$V=1$	$D_-=0$
	↕	↔ − ↕	↕	↔ − ↕
Observation probability	$P=0$	$P=½$	$P=½$	$P=0$

Fig. 2.8 Transmission and detection using nonorthogonal basis ensures security. This inefficiency is the overhead that is paid for security using **quantum key distribution** (QKD).

2.1.4 Secure quantum communication

Alice generates a random number sequence and transmits binary bit 0 and bit 1 as H and D_+ respectively

Bit	1	1	1	0	1	0	0	0	1	0	1	1	1	1	0	1	1
Photon state	D_+	D_+	D_+	H	D_+	H	H	H	D_+	H	D_+	D_+	D_+	D_+	H	D_+	D_+

Bob tests with randomly chosen D_- or V for bit 0 and bit 1 respectively

Detector state	V	V	D_-	D_-	D_-	D_-	V	D_-	D_-	V	V	D_-	D_-	D_-	D_-	V	D_-
Probability Bob detects	½	½	-	½	-	½	-	½	-	-	½	-	-	-	½	½	-
Bob detects	1	1	-	0	-	0	-	0	-	-	1	-	-	-	0	0	-
Alice keeps bits	1	1	-	0	-	0	-	0	-	-	1	-	-	-	0	0	-

Fig. 2.9 Alice generates a secret random binary number sequence and agrees with Bob through the public channel that she will transmit using a nonorthogonal basis, **D+** and **H** for binary bit **1** and bit **0** respectively.

2.1.5 The link between quantization of photons and other particles

If **photons** are particles with energy $E = \hbar\omega$, wavelength λ, and quantized momentum $p = \hbar k_{photon}$, **then there may be other particles that are also characterized by** E, λ, and $p = \hbar k$.

The **essential link** between quantization of **photons** and **quantization of other particles** such as electrons is **momentum**. In general, ***interaction*** *between particles involves exchange of* ***momentum.***

We already know that ***both photons*** and **electrons** have **momentum** and that they can **interact** with **each other**.

If **photon momentum** is **quantized** it is natural to assume that **electron momentum** is **quantized**.

2.1.5 The link between quantization of photons and other particles

In a **photoelectric-effect experiment** a photon with quantized **momentum $\hbar k_{photon}$ and energy** $E = \hbar\omega$ collides with an electron in a metal. The photon energy is ***absorbed****, and the* **electron** is **ejected** from the metal.

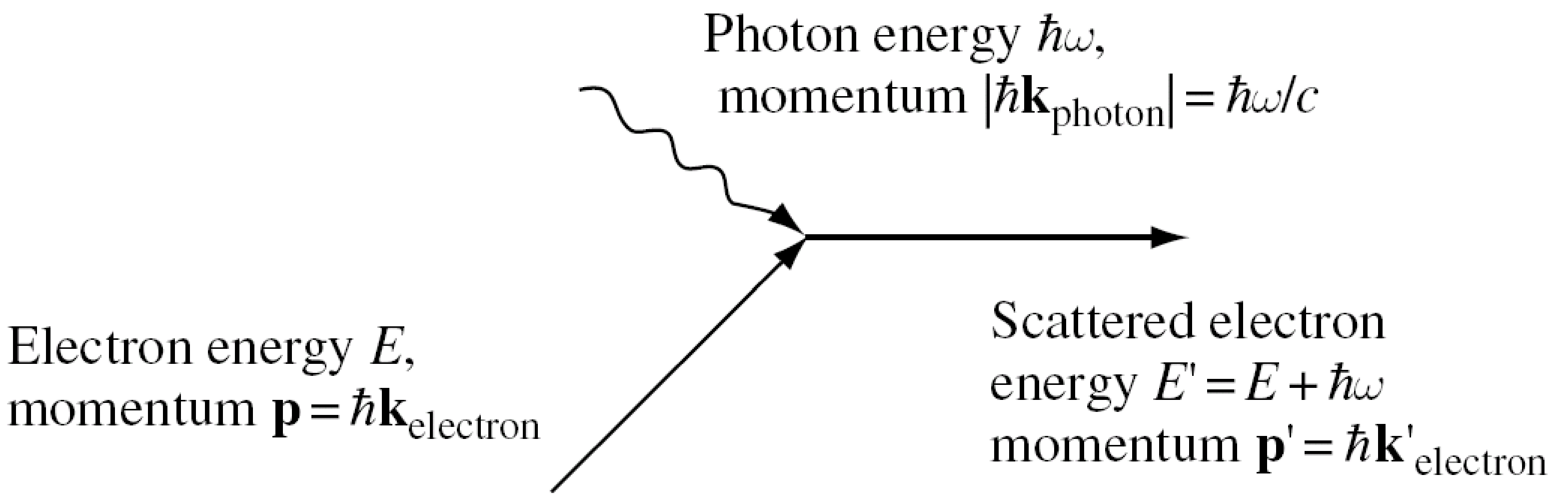


Fig. 2.10 The **momentum** and **energy** exchange between a photon and an electron.

2.1.5 The link between quantization of photons and other particles

Because **electron kinetic energy** is related to **momentum** and **quantized momentum** is related to **wavelength**, we can estimate the **wavelength** λ_e an electron with **mass** m_0 and **energy** E in free space would have:

$$\lambda_e = 2\pi\hbar/\sqrt{2m_0E} \qquad (13)$$

For an electron with E = 1eV gives a quite small wavelength λ_e =1.226nm.

In addition, **unlike photons**, **electrons** can **interact** quite strongly with **themselves** via the **coulomb potential**.

2.1.6 Diffraction and interference of electrons

The **electron waves** exhibited the key features of **diffraction**, linear **superposition**, and i**nterference**.

$$\lambda_e = 2\pi\hbar\frac{1}{p} = \frac{2\pi\hbar}{\sqrt{2m_0E}}$$

The experiment of **Davisson** and **Germer**

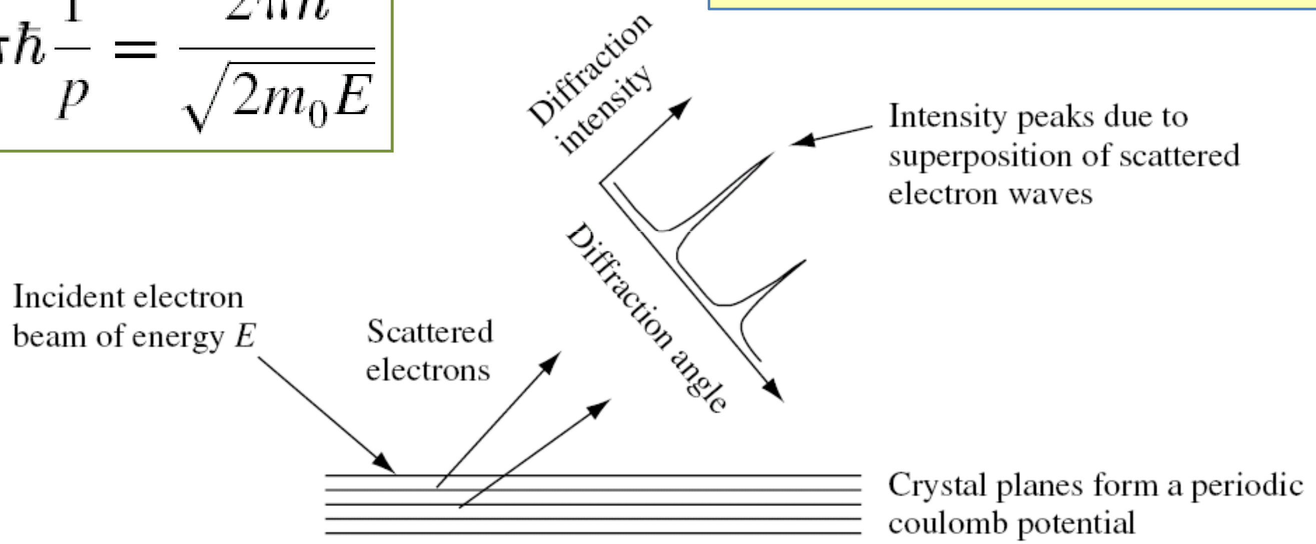


Fig. 2.11 A mono-energetic beam of **electrons** scattered from a **metal crystal** showing intensity maxima. The **periodic array** of atoms that forms the metal crystal creates a **periodic coulomb potential** from which electrons scatter.

2.1.6 Diffraction and interference of electrons

The **observation of intensity maxima** for **electrons** emerging from the **crystal** showed that **electrons behave as waves**.

The **electron waves** exhibited the **key features** of **diffraction**, **linear superposition**, and **interference**.

The experiment of **Davisson** and **Germer** supported the idea put forward by de **Broglie** in 1924 of electron "**waves**" in atoms.

An **electron** of **momentum p = ħk** (where $|\mathbf{k}| = 2\pi/\lambda$) has **wavelength**

$$\lambda_e = 2\pi\hbar\frac{1}{p} = \frac{2\pi\hbar}{\sqrt{2m_0E}} \qquad (18)$$

$$\psi(\mathbf{r}, t) \sim e^{-i(Et/\hbar - \mathbf{k}\cdot\mathbf{r})} \qquad (19)$$

Electrons of **kinetic energy** $E = p^2/2m_0$ behave as waves in such a way that $\psi(r, t)$, where **p = ħk.**

2.1.7 When is a particle a wave?

From the photoelectric effect and Young's slits experiment, it is clear that the **photon sometimes** appears to behave as a particle and **sometimes** appears to behave as a wave.

Electrons, and other atomic-scale entities such as neutrons and protons, can also behave **either as particles or waves**.

***They are both particle and* wave.**

Neutrons, protons, and electrons can seem like **particles**, with a mass and momentum.

However, if one looks on an **appropriate length** or **time scale**, they might exhibit the **key characteristics of waves**, such as **superposition** and **interference**.

2.1.7 When is a particle a wave?

wave-particle duality:

Photon energy is quantized as $E = \hbar\omega$, **photon mass** is **zero**,

photon momentum is $\mathbf{p} = \hbar\mathbf{k}$, and **photon wavelength** is $\lambda = 2\pi/k$.

The dispersion relationship for the photon moving at the speed of light in **free space** is $E = \hbar ck$ or, more simply, $\omega = ck$.

Electron momentum is quantized as $\mathbf{p} = \hbar\mathbf{k}$,

electron mass is $m_0 = 9.109\,565 \times 10^{-31}$ kg**,** and **electron energy** is $E = p^2/2m_0$.

The dispersion relationship for an isolated **electron** moving in free space is $E = \hbar^2k^2/2m_0$. If we know the energy E of the **electron** measured in **eV**, then the electron wavelength λ_e in free space measured in units of **nm** is given by the expression

$$\lambda_e(\text{nm}) = \frac{1.226}{\sqrt{E(\text{eV})}} \qquad (20)$$

2.1.7 When is a particle a wave?

electron wavelength λ_e: (in free space)

$$\lambda_e(\text{nm}) = \frac{1.226}{\sqrt{E(\text{eV})}} \quad (20)$$

For the **electron** with E =100eV , → **wavelength** of λ_e = 0.1226 nm.

Similarly, other finite-mass particles, such as the **neutron**, have a wavelength that is inversely related to the square root of the particle's kinetic energy.

Neutron wavelength λ_n :(in free space)

$$\lambda_n(\text{nm}) = \frac{0.0286}{\sqrt{E(\text{eV})}} \quad (21)$$

For the **neutron** with E =100eV , → **wavelength** of λ_n = 0.00286 nm. which is quite difficult to observe in an experiment.

2.2 The Schrödinger wave equation

There is a **need** to **generalize** what we have learned thus far about the **wave properties** of **atomic-scale particles**.

On the one hand, the **formalism** needs to incorporate the wave nature observed in experiments; on the other hand, the approach should, in the appropriate limit, **incorporate** the results of **classical physics**.

we will assume that **time**, t, is a continuous, smooth parameter and that **position**, r, is a continuous, smooth variable.

To describe the dynamics of **wavy particles**, it seems reasonable to assume that we will wish to find quantities such as particle position r and momentum p as a function of time.

We know that **waviness** is associated with the **particle**, so let us introduce a **wave function** Ψ that carries the **appropriate information**.

2.2 The Schrödinger wave equation (2)

Young's slits experiments suggest that such a **wave function**, which depends upon **position** and **time**, can be formed from a **linear superposition** of **plane waves.**

Under these conditions, it seems **reasonable** to consider the **special case** of **plane waves** without **loss of generality**. So, now we have:

$$\psi(\mathbf{r}, t) = Ae^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (22)$$

In **quantum mechanics** the **wave function** $\psi(\mathbf{r}, t)$ is a **true complex quantity**, and hence it **cannot be measured directly**. We cannot use $\psi(\mathbf{r}, t)$ to represent the **particle** directly, because it is a **complex number,** and this is at variance with our everyday experience that quantities such as **particle position are real**.

2.2 The Schrödinger wave equation (3)

The easiest way to guarantee a **real value** is to measure its **intensity**,:

$$\psi(\mathbf{r},t)^*\psi(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2$$

The probability of finding the **particle** at **position r** in space at **time** t is **proportional to** $|\psi(\mathbf{r}, t)|^2$.

we can *normalize the intensity* $|\psi(\mathbf{r}, t)|^2$ so that integration over all space is unity. This defines a ***probability density*** *for finding* the particle at position **r** in space at time t**.** If we wish to find the most likely position of our **wavy particle** in space, we need to weight the **probability distribution** with position **r** to obtain the **average position** **<r>.** The way to do this is to perform an **integral over** all space so that:

$$\langle \mathbf{r} \rangle = \int_{-\infty}^{\infty} \psi^*(\mathbf{r},t)\mathbf{r}\psi(\mathbf{r},t)d^3r = \int_{-\infty}^{\infty} \mathbf{r}|\psi(\mathbf{r},t)|^2 d^3r \qquad (23)$$

2.2 The Schrödinger wave equation (4)

$$\langle \mathbf{r} \rangle = \int_{-\infty}^{\infty} \psi^*(\mathbf{r}, t)\mathbf{r}\psi(\mathbf{r}, t)d^3r = \int_{-\infty}^{\infty} \mathbf{r}|\psi(\mathbf{r}, t)|^2 d^3r \qquad (23)$$

In **quantum mechanics**, **the average value** of **position** is **<r>** and is called the ***expectation value*** *of the* **position** ***operator*, *r*.**

For the particle **momentum** : **p = ħk**

the **average value of momentum <p> :** $\langle \mathbf{p} \rangle = \int_{-\infty}^{\infty} \psi^*(\mathbf{k}, t)\hbar\mathbf{k}\,\psi(\mathbf{k}, t)d^3k \qquad (24)$

Of course, Eq. (24) requires that we find the function ψ **(k, t)**. This can be done by taking the **Fourier transform** of ψ **(r, t).**

In the x direction only: $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(k_x)\hbar k_x\,\psi(k_x)dk_x \qquad (25)$

2.2 The Schrödinger wave equation (5)

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(k_x)\hbar k_x \psi(k_x) dk_x \quad (25)$$

The momentum operator $\hat{p}_x$ has a ^ to indicate that it is a **quantum operator** but the expectation value does not as it is just a real number.

Notice that for convenience we ignore the time dependence $e^{-i\omega t}$ of the wave function when evaluating $\psi^*\psi$, since the time-dependent terms cancel. Taking the Fourier transform of $\psi(k_x)$ to obtain $\psi(x)$ gives:

$$\langle p_x \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk_x \left(\int_{-\infty}^{\infty} dx' \psi^*(x') e^{ik_x x'} \right) \hbar k_x \left(\int_{-\infty}^{\infty} dx \psi(x) e^{-ik_x x} \right) \quad (26)$$

2.2 The Schrödinger wave equation (6)

$$\langle p_x \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk_x \left(\int_{-\infty}^{\infty} dx' \psi^*(x') e^{ik_x x'} \right) \hbar k_x \left(\int_{-\infty}^{\infty} dx \psi(x) e^{-ik_x x} \right) \quad (26)$$

Integrating the far right-hand term in the brackets by parts using:

$$\int UV'\, dx = UV - \int U'V\, dx$$

$$U = \psi(X) \;\; and \;\; V' = e^{-ik_x x}$$

$$\int_{-\infty}^{\infty} dx \psi(x) e^{-ik_x x} = \left[\frac{1}{-ik_x} e^{-ik_x x} \psi(x) \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} dx \frac{1}{ik_x} \frac{\partial \psi(x)}{\partial x} e^{-ik_x x} \quad (27)$$

The oscillatory function in the square brackets is zero in the limit x→±œ.

2.2 The Schrödinger wave equation (7)

$$\langle p_x \rangle = \frac{\hbar}{2i\pi} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dx' \psi^*(x') e^{ik_x x'} \int_{-\infty}^{\infty} dx e^{-ik_x x} \frac{\partial}{\partial x} \psi(x) \quad (28)$$

which we may rewrite as:

$$\langle p_x \rangle = -i\hbar \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx \psi^*(x') \frac{1}{2\pi} \int_{-\infty}^{\infty} dk_x e^{-ik_x(x-x')} \frac{\partial}{\partial x} \psi(x) \quad (29)$$

Recognizing that $\frac{1}{2\pi} \int_{-\infty}^{\infty} dk_x e^{-ik_x(x-x')} = \delta(x-x')$ allows one to write

$$\langle p_x \rangle = -i\hbar \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx \psi^*(x') \delta(x-x') \frac{\partial}{\partial x} \psi(x) \quad (30)$$

so that finally we have: $$\langle p_x \rangle = -i\hbar \int_{-\infty}^{\infty} dx \psi^*(x) \frac{\partial}{\partial x} \psi(x) \quad (31)$$

2.2 The Schrödinger wave equation (8)

$$\langle p_x \rangle = -i\hbar \int_{-\infty}^{\infty} dx \psi^*(x) \frac{\partial}{\partial x} \psi(x) \tag{31}$$

The important conclusion: in k space (**momentum space**) $\hat{p}_x = \hbar k_x$

in **real space** (**momentum operator**) $\hat{p}_x = -i\hbar\partial/\partial x$.

The momentum operator in **real space** is a ***spatial derivative.***

*The **momentum operator** and the **position operator** are said to* form a *conjugate pair linked by a Fourier transform.*

Summarizing, In quantum mechanics, **every particle** can be described by using a **wave function** $\psi(r, t)$, where **$|\psi(r, t)|^2$** is the **probability of finding** the particle in the volume d^3r at position **r** at time t**.** The wave function and its spatial derivative are continuous, finite, and single valued.

2.2 The Schrödinger wave equation (9)

Table 2.4 *Classical variables and quantum operators for* $\psi(\mathbf{r}, t)$

Description	Classical theory	Quantum theory
Position	r	r
Potential	$V(\mathbf{r}, t)$	$V(\mathbf{r}, t)$
Momentum	p_x	$-i\hbar\frac{\partial}{\partial x}$
Energy	E	$i\hbar\frac{\partial}{\partial t}$

The **average** or ***expectation value*** *of an operator A*ˆ is:

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi d^3 r \qquad (32)$$

2.2 The Schrödinger wave equation (10)

The **total energy function** or **Hamiltonian** of a particle mass m moving in potential V is:

$$H = T + V = \frac{p^2}{2m} + V \qquad (33)$$

1- D:

$$\hat{H}\psi(x,t) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\psi(x,t) \qquad (34)$$

3- D:

$$\hat{H}\psi(\mathbf{r},t) = \frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r},t)\psi(\mathbf{r},t) \qquad (35)$$

Where:

$$\nabla^2\psi(\mathbf{r},t) = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \qquad (36)$$

Replacing the **Hamiltonian** with the **energy operator** $i\hbar.\partial/\partial t$, we have:

$$\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \qquad (37)$$

2.2 The Schrödinger wave equation (11)

$$\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \quad (37)$$

Where: $\hat{H} = \left(\frac{-\hbar^2}{2m_0}\nabla^2 + V(\mathbf{r},t)\right)$ is the Hamiltonian operator. (38)

Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right)\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \quad (39)$$

This equation can be used to describe the behavior of quantum mechanical **particles** in **three-dimensional space**.

The fact that the **Schrödinger equation** is **only first-order in the time derivative** indicates that the wave function $\psi(\mathbf{r}, t)$ evolves from a single initial condition.

2.2 The Schrödinger wave equation (12)

When **energy is conserved and potential energy is time independent: V = V(r).** using the method of separation of variables:

Assuming Ψ(x, t)=Ψ(x)Ψ(t), then substitution into the 1-D Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)\phi(t) + V(x)\psi(x)\phi(t) = i\hbar\frac{\partial}{\partial t}\psi(x)\phi(t) \qquad (40)$$

We then divide both sides by ***ψ (x) ψ (t),*** so that the left-hand side is a function of x only and the right-hand side is a function of t only. This is true if **both sides are equal** to a constant E. It follows that:

time-dependent Schrödinger equation:

$$E\phi(t) = i\hbar\frac{\partial}{\partial t}\phi(t) \qquad (41)$$

time-independent Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = E\psi(x) \qquad (42)$$

2.2 The Schrödinger wave equation (13)

time-dependent Schrödinger equation:

$$E\phi(t) = i\hbar \frac{\partial}{\partial t}\phi(t) \quad (41)$$

time-independent Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = E\psi(x) \quad (42)$$

The constant E is just the ***energy eigenvalue*** *of the particle described by the* ***wave function****.*

The solution to the **time-dependent** Schrödinger equation is of **simple harmonic** form:

$$\phi(t) = e^{-i\omega t} \quad (43)$$

where $E = \hbar\omega.$

The wave function $\psi(x, t) = \psi(x)\Phi(t)$ is called a ***stationary state*** because the probability density $|\psi(x, t)|^2$ is **independent** of time.

2.2 The Schrödinger wave equation (14)

Because the **probability of finding** a particle with **wave function** $\psi_n(\mathbf{r}, t)$ somewhere in space is unity, it makes sense to require wave functions that are solutions to the **time-independent** Schrödinger equation be normalized such that:

$$\int_{-\infty}^{\infty} \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})d^3r = 1 \quad (44)$$

$$\int_{-\infty}^{\infty} \psi_n^*(\mathbf{r})\psi_m(\mathbf{r})d^3r = 0 \quad (45)$$

This n is called a quantum number. Wave functions with **different quantum numbers**, say n and m, have the **mathematical property** of **orthogonality.**

summary:

$$\int_{-\infty}^{\infty} \psi_n^*(\mathbf{r})\psi_m(\mathbf{r})d^3r = \delta_{nm}$$

Kronecker-delta function (46)

where: if $n = m$ ⇒ $\delta_{nm} = 1$; if $n \# m$ ⇒ $\delta_{nm} = 0$;

2.2.1 The wave function description of electron in free space

we start by writing down the **time-independent** Schrödinger equation for an **electron mass** m_0. The equation is:

$$\hat{H}\psi_n(\mathbf{r}) = E_n\psi(\mathbf{r}) \quad \textbf{(47)} \qquad \text{or:} \qquad \frac{-\hbar^2}{2m_0}\nabla^2\psi_n(\mathbf{r}) + V(\mathbf{r})\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}) \quad \textbf{(48)}$$

for the case of **free space** we set the potential V(**r**) = 0.

Here E_n are ***energy eigenvalues*** *and* ψ_n *are* ***eigenstates*** *so that:*

$$\psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-i\omega t} \quad \textbf{(49)}$$

For **an electron** in **free space**, V(**r**) **= 0** and so we have:

$$E_n = \frac{\hat{p}_n^2}{2m_0} = \frac{\hbar^2 k_n^2}{2m_0} = \hbar\omega_n \quad \textbf{(50)} \qquad \psi_n(\mathbf{r}, t) = (Ae^{\mathbf{ik}\cdot\mathbf{r}} + Be^{-\mathbf{ik}\cdot\mathbf{r}})e^{-i\omega_n t} \quad \textbf{(51)}$$

2.2.1 The wave function description of electron in free space

$$\psi_n(\mathbf{r}, t) = (Ae^{i\mathbf{k}\cdot\mathbf{r}} + Be^{-i\mathbf{k}\cdot\mathbf{r}})e^{-i\omega_n t} \quad (51)$$

$Ae^{ik.r}$: a wave of amplitude A traveling left to right.

$Be^{-ik.r}$: a wave of amplitude B traveling from right to left.

Selecting a boundary condition characterized by B = 0, and considering the case of motion in the x direction only, the **wave function** becomes:

$$\psi_n(x, t) = Ae^{ik_x x}e^{-i\omega_n t} \quad (52)$$

To find the momentum:

$$\hat{p}_x\psi_n(x, t) = -i\hbar\frac{\partial}{\partial x}\psi_n(x, t) = \hbar k_x Ae^{ik_x x}e^{-i\omega_n t} = \hbar k_x \psi_n(x, t) \quad (53)$$

$$p = \hbar k = \sqrt{2m_0 E} \qquad E_k = \hbar\omega = \hbar^2 k^2/2m_0 \qquad \omega(k) = \frac{\hbar k^2}{2m_0} \quad (54)$$

2.2.1 The wave function description of electron in free space

$$\omega(k) = \frac{\hbar k^2}{2m_0}$$

The Schrödinger equation does not allow an electron in free-space to have just any energy and wavelength; rather, the **electron** is constrained to values given by the dispersion relation.

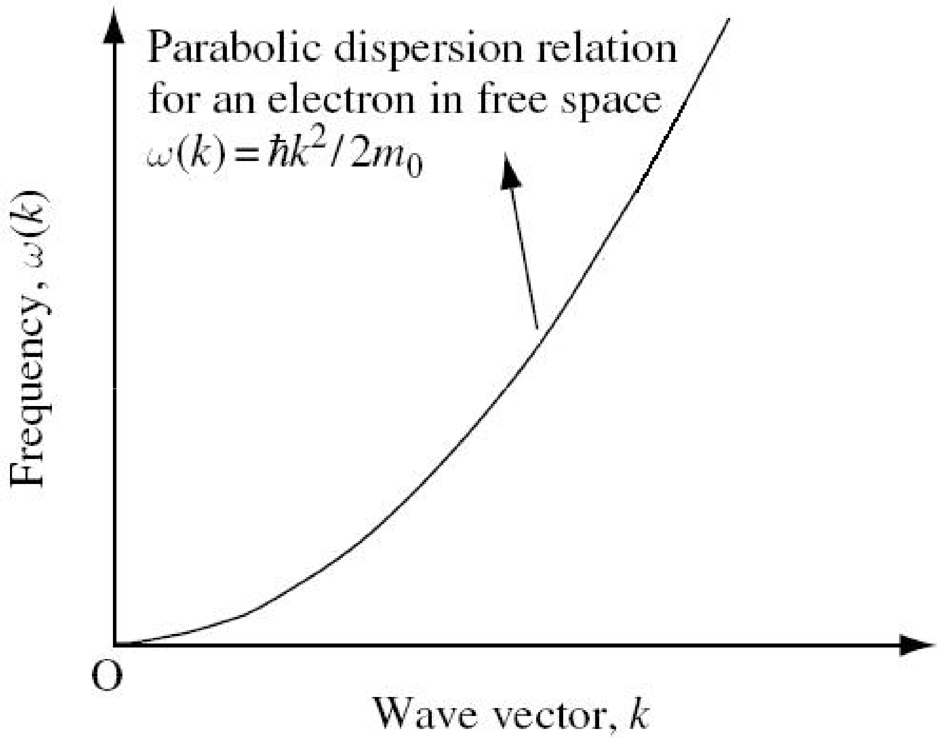


Fig. 2.12 Dispersion relation for an electron in free-space.

2.2.2 The electron wave packet and dispersion

An electron in free space was described by traveling **plane-wave states** that **extended over all space** but were well-defined points in k space. Obviously, this is an **extreme limit**.

Suppose we wish to describe **an electron** at a **particular average position** in **free space** as a sum of a **number of plane-wave eigenstates**.

We can force the electron to occupy a **finite region** of space by forming a ***wave packet*** *from a* ***continuum of plane-wave eigenstates.***

we start with a **plane wave of momentum** $\hbar k_0$ in the x direction and create a **Gaussian pulse** from this **plane wave** in such a way that at time t = 0

$$\psi(x, t=0) = A e^{ik_0 x} e^{-(x-x_0)^2/4\Delta x^2}$$

Where: $A = 1/(2\pi\Delta x^2)^{1/4}$ **(55)**

2.2.2 The electron wave packet and dispersion (2)

$$\psi(x, t=0) = Ae^{ik_0 x} e^{-(x-x_0)^2/4\Delta x^2} \quad A = 1/(2\pi\Delta x^2)^{1/4} \quad \langle x \rangle = x_0 \tag{55}$$

The **probability density** at time t = 0 is just a **normalized Gaussian function** of **standard deviation Δ**x:

$$\psi^*(x, t=0)\psi(x, t=0) = |\psi(x, t=0)|^2 = A^2 e^{-(x-x_0)^2/2\Delta x^2} \tag{56}$$

To find the **values of the momentum components** in the **Gaussian pulse**, we take the **Fourier transform** of the **wave function** $\psi(x, t = 0)$.

$$\psi(k, t=0) = \frac{1}{A\sqrt{\pi}} e^{-i(k-k_0)x} e^{-(k-k_0)^2\Delta x^2} \tag{57}$$

The corresponding **probability density** in k space **(momentum space)** is given by:

$$|\psi(k, t=0)|^2 = \frac{1}{A^2\pi} e^{-(k-k_0)^2 2\Delta x^2} = \frac{1}{A^2\pi} e^{-(k-k_0)^2/2\Delta k^2} \tag{58}$$

2.2.2 The electron wave packet and dispersion (3)

$$|\psi(k, t=0)|^2 = \frac{1}{A^2\pi} e^{-(k-k_0)^2 2\Delta x^2} = \frac{1}{A^2\pi} e^{-(k-k_0)^2/2\Delta k^2} \quad (58)$$

where k_0 is the **average value** of k, and a measure of the **spread** in the distribution of k is given by the **standard deviation** Δk = ½ Δx.

Because ΔkΔx = 1/2 is a **constant**, this indicates that localizing the **Gaussian pulse** in real space will increase the width of the corresponding distribution in k space , and Conversely. Recognizing that momentum p = ħk, we have:

$$\Delta p \Delta x = \hbar/2 \quad (59)$$

which is an example of the ***uncertainty principle***. ***Conjugate pairs of operators cannot be measured to arbitrary accuracy.*** *In this case, it is not possible to* ***simultaneously*** *know* the **exact position** of a **particle** and **its momentum.**

2.2.2 The electron wave packet and dispersion (4)

The **time evolution** of the **Gaussian wave packet**:

Each **plane wave** has a **time dependence** of the form $e^{-i\omega kt}$. For time t > 0

$$\psi(k,t) = \frac{1}{A\sqrt{\pi}} e^{-i(k-k_0)x} e^{-(k-k_0)^2 \Delta x^2} e^{-i\omega_k t} \quad (60)$$

and $E_k = \hbar\omega_k = \hbar^2 k^2/2m_0$. The Taylor expansion about k_0 for the **dispersion relation** is:

$$\omega(k) = \frac{\hbar k_0^2}{2m_0} + \frac{\hbar k_0 (k-k_0)}{m_0} + \frac{\hbar (k-k_0)^2}{2m_0} \quad (61)$$

To find the **effect of dispersion** on the Gaussian pulse as a **function of time**, we need to take the **Fourier transform** of $\psi(k, t)$ to obtain $\psi(x, t)$. The solution is:

$$\psi(x,t) = \frac{1}{A\pi\sqrt{2}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} e^{i(k-k_0)(x-x_0-(\hbar k_0 t/m_0))} e^{-(k-k_0)^2 \Delta x^2 \left(1+\frac{i\hbar t}{2m_0 \Delta x^2}\right)} dk \quad (62)$$

2.2.2 The electron wave packet and dispersion (5)

$$\psi(x,t) = \frac{1}{A\pi\sqrt{2}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} e^{i(k-k_0)(x-x_0-(\hbar k_0 t/m_0))} e^{-(k-k_0)^2 \Delta x^2 \left(1+\frac{i\hbar t}{2m_0 \Delta x^2}\right)} dk \quad (62)$$

➢The prefactor is: a **plane wave oscillating** at $\omega_0 = \hbar k_0^2/2m_0$ and moving with **momentum** $\hbar k_0$ and a *phase velocity* $v_p = \hbar k_0/2m_0$.

➢The term $\exp[i(k-k_0)(x-x_0-(\hbar k_0 t/m_0))]$: shows that the center of the **wave packet** moves a distance $\hbar k_0 t/m_0$ in time t, indicating a ***group velocity*** *for the* ***wave packet*** *of* $v_g = \hbar k_0/m_0$.

$$e^{-(k-k_0)^2 \Delta x^2 \left(1+\frac{i\hbar t}{2m_0 \Delta x^2}\right)}$$

:shows that the **width** of the **wave packet** **increases** with **time**. (63)

$$\Delta x(t) = \left(\Delta x^2 + \frac{\hbar^2 t^2}{4m_0^2 \Delta x^2}\right)^{1/2}$$

:Increase of the width (64)

2.2.2 The electron wave packet and dispersion (6)

- The **wave packet** delocalizes as a **function of time** because of **dispersion**.
- The **characteristic time** $\Delta\tau\Delta x$ for the **width** of the **wave packet** to double is $\Delta\tau\Delta x = 2m_0\Delta x^2/\hbar$.

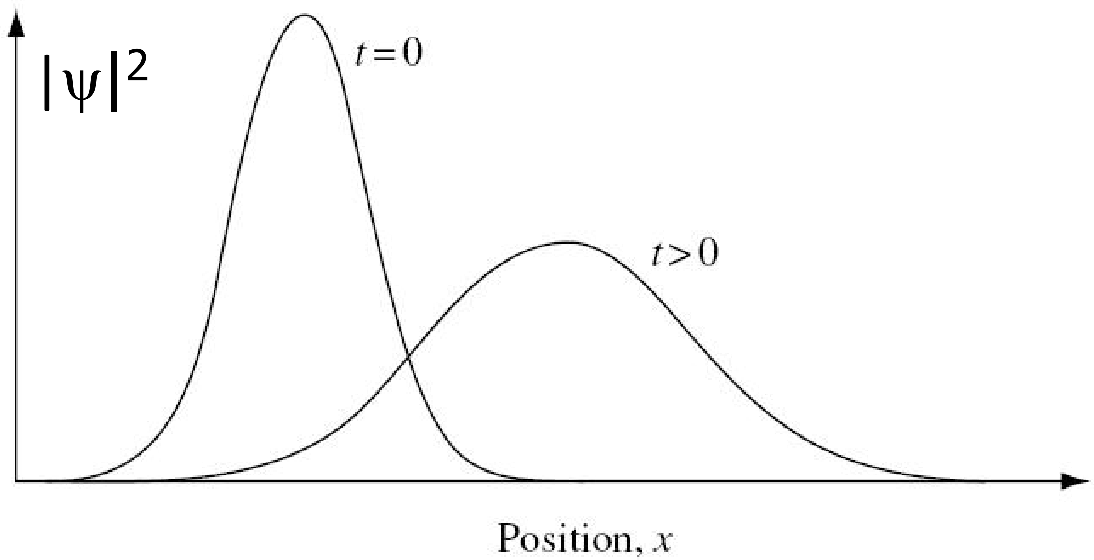


Fig. 2.13 Illustration of the **time evolution** of a **Gaussian wave packet**, showing the effect of dispersion.

2.2.2 The electron wave packet and dispersion (7)

Example 1: Consider a classical **particle** of **mass** $m = 1$ gr $= 10^{-3}$ kg, and the position of $\Delta x = 1\mu m = 10^{-6} m$.

Modeling this **particle** as a **Gaussian wave packet** gives a **characteristic time**

$\Delta\tau_{\Delta x} = 2m\Delta x^2/\hbar = 2\times10^{-3}\times(10^{-6})^2/1.05\times10^{-34} = 2\times10^{19}$ s $= 6\times10^{11}$ years.

Example 2: Consider **an electron** of **mass** $m_0 = 9.1\times10^{-31}$ kg in a circular orbit of radius $a_B = 0.529\ 177\times10^{-10} m$ around a proton.

we assume the electron is described by a **Gaussian wave packet** and that its position is known to an accuracy of $\Delta x = 10^{-11}$ m.

In this case, one obtains a characteristic time that is

$\Delta\tau_{\Delta x} = 2m_0\Delta x^2/\hbar = 2\times9.1\times10^{-31}\times(10^{-11})^2/1.05\times10^{-34} = 1.7\times10^{-18}$ s.

This time is **significantly** shorter than the **time to complete** one orbit.

($\tau_{orbit} \sim 1.5\times10^{-16}$ s).

2.2.2 The electron wave packet and dispersion (8)

We can now write the **uncertainty relation** for **momentum** and **position** more accurately as:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{65}$$

This relationship controls the **precision** with which it is possible to **simultaneously** know the **position** of a **particle** and **its momentum**.

2.2.3 The hydrogen atom

➢ we can consider **an electron** **confined** by a **potential** to motion in some local region. In 1911, Rutherford showed experimentally that electrons appear to orbit the nucleus of atoms.

➢The **electron charge** $-e=-1.602\ 176\times10^{-19}$ C , **mass** $m_0 = 9.109\ 381\times10^{-31}$ kg.

➢ The **proton charge** = +e, and the **proton mass** is $m_p = 1.672\ 621\times10^{-27}$ kg.

➢ The **ratio** of **proton mass** **to** **electron mass** is $m_p/m_0 = 1836.15$

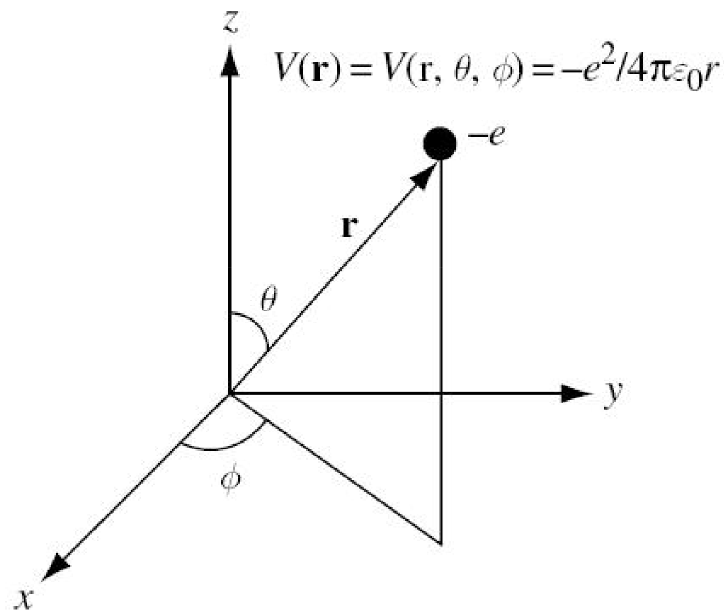


Fig. 2.14 A **hydrogen** atom consists of **an electron and a proton**. It is natural to choose a spherical coordinate system to describe a single electron moving in the coulomb potential of the single proton.

2.2.3 The hydrogen atom (2)

Experiment shows that the **classical theory does not** work! Hydrogen is observed to be stable. In addition, the spectrum of hydrogen is observed to consist of discrete spectral lines – which, again, is a feature not predicted by classical models.

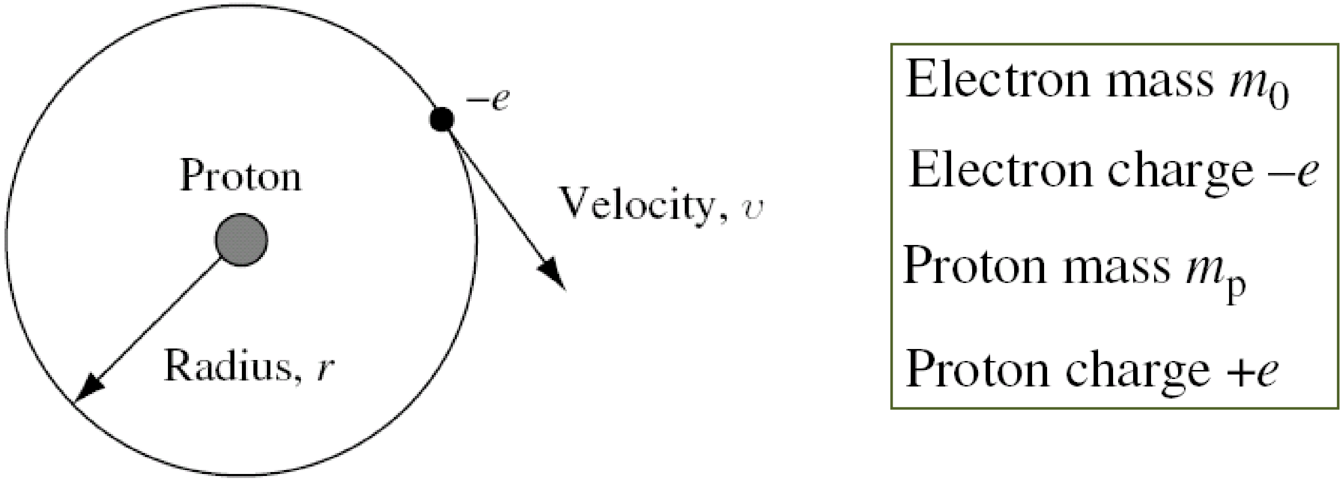
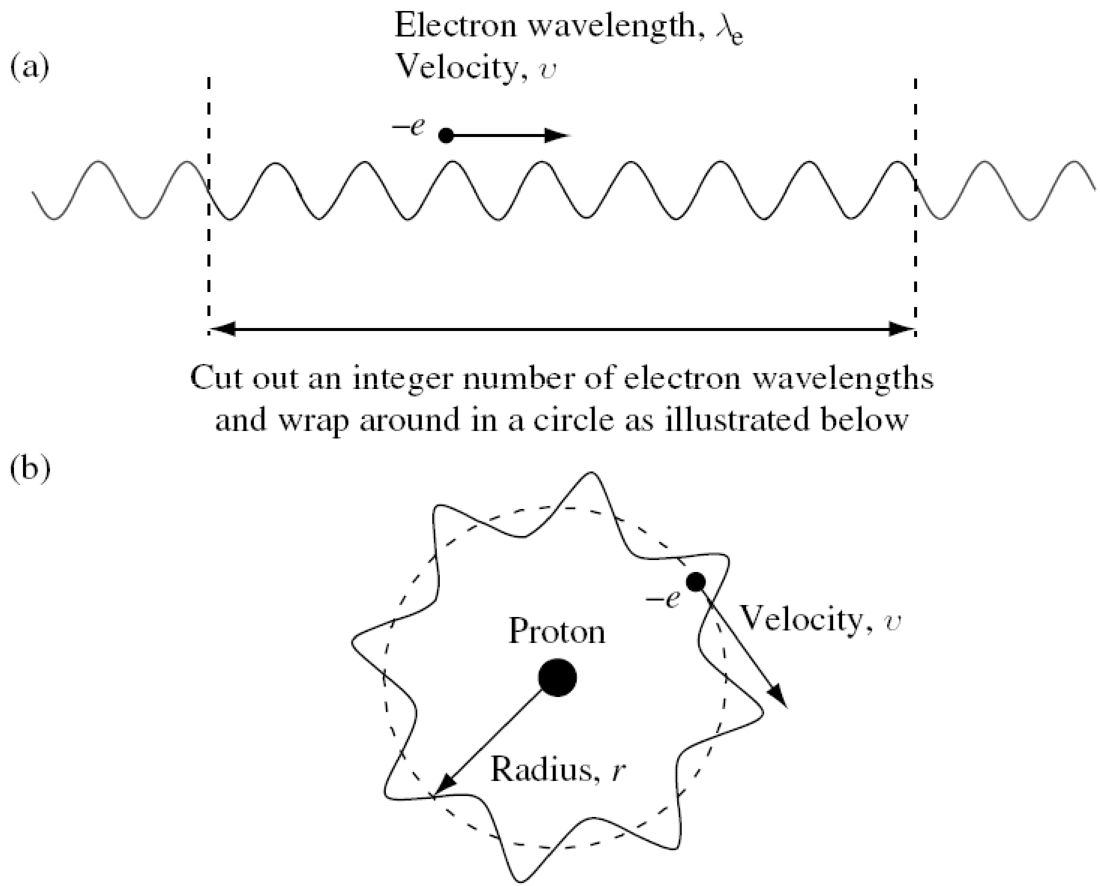


Fig. 2.15 Illustration of a **classical** circular orbit of **an electron** mass m_0 moving with velocity υ in the coulomb potential of a proton mass m_p. This classical view predicts that hydrogen is unstable.

2.2.3 The hydrogen atom (4)

Fig. 2.16 (a) Illustration of electron wave propagating in free space with wavelength e.
(b) Illustration of an electron wave wrapped around in a circular orbit about a proton. Single-valueness of the electron wave function suggests that only an integer number of electron wavelengths can fit into a circular orbit of radius r.



2.2.3 The hydrogen atom (5)

The postulates of Bohr (1913):

1. Electrons exist in stable circular orbits around the proton.

2. Electrons may make transitions between orbits by emission or absorption of a photon of energy .

3. The **angular momentum** of the electron in a given orbit is quantized according to $p_\theta = n\hbar$, where n is a non-zero positive integer. Postulate 3 admits the **wavy nature** of the **electron**.

The postulates of Bohr allowed **many parameters** to be **calculated**, such as the **average radius** of **an electron orbit** and the **energy difference** between **orbits**.

2.2.3.1 *Calculation of the average radius of an electron orbit in hydrogen*

We start by equating the electrostatic force and the centripetal force:

$$\frac{-e^2}{4\pi\varepsilon_0 r^2} = -\frac{m_0 \upsilon^2}{r} \quad (66)$$

we continue to assume an infinite proton mass and electron mass m_0 instead of using the reduced mass m_r of Eq. (1.26) such that $1/m_r = 1/m_p + 1/m_0$.

Because **angular momentum** is quantized, $p_\theta = n\hbar = m_0 \upsilon r_n$.

Since: $m_0^2 \upsilon^2 = n^2\hbar^2/r_n^2$ ⟹ $m_0\upsilon^2/r_n = (1/r_n m_0)(n^2\hbar^2/r_n^2)$.

Substituting into our expression for centripetal force gives:

$$\frac{e^2}{4\pi\varepsilon_0 r_n^2} = \frac{1}{r_n m_0}\frac{n^2\hbar^2}{r_n^2} \quad (67)$$

and hence

$$r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{m_0 e^2} \quad (68)$$

2.2.3.1 *Calculation of the average radius of an electron orbit in hydrogen* (2)

radius of the n-th orbit:

$$r_n = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{m_0 e^2} \qquad (68)$$

The **radius** of each orbit is **quantized**.

The **spatial scale** is set by the **radius** for n = 1, giving:

Bohr radius:

$$r_1 = a_B = \frac{4\pi\varepsilon_0 \hbar^2}{m_0 e^2} = 0.529\,177 \times 10^{-10}\,\mathrm{m} \qquad (69)$$

which is called the *Bohr radius*.

***Notice** that if we were to **use** the **reduced mass** then* $r_1 = 0.529\,889 \times 10^{-10}$ m.

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen*

- Calculation of the **energy difference** between orbits is **important**, since it will allow us to **predict** the optical spectra of excited hydrogen atoms.
- We start by **equating** **classical momentum** with the quantized momentum of the n-th electron orbit.
- Since **angular momentum:** $p_\theta = n\hbar = m_0 \upsilon r_n$
- and **momentum of the electron:** $m_0 \upsilon = n\hbar / r_n$

Electron velocity of the n-th orbit:

$$\upsilon = \frac{n\hbar}{m_0 r_n} = \frac{m_0 e^2}{4\pi\varepsilon_0 n^2 \hbar^2} \frac{n\hbar}{m_0} = \frac{e^2}{4\pi\varepsilon_0 n\hbar} \quad (70)$$

The value of υ for $n = 1$ is $\upsilon = 2.2\times10^6\ ms^{-1}$.

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen (2)*

We now obtain the **kinetic energy** of the electron:

$$T = \frac{1}{2} m_0 v^2 = \frac{1}{2} m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2} \qquad (71)$$

The **potential energy** is just the **force times the distance between charges**, so

$$V = \frac{-e^2}{4\pi\varepsilon_0 r_n} = -m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2} \qquad (72)$$

Total energy for the n-th orbit is:

$$E_n = T + V = -\frac{1}{2} m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2} \qquad (73)$$

2.2.3.2 Calculation of energy difference between electron orbits in hydrogen (3)

kinetic energy	potential energy	Total energy
$T = \frac{1}{2} m_0 v^2$	$V = \frac{-e^2}{4\pi\varepsilon_0 r_n}$	$E_n = T + V$
$\frac{1}{2} m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2}$	$-m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2}$	$-\frac{1}{2} m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2}$

Note that: **T = −V/2**. The result is a specific example of the more general **"virial theorem"** which states that **<T> = γV/2** for a **system** in a **stationary state** and with a potential proportional to r^{γ}.

The **energy difference** between **orbits** with **quantum number** n_1 and n_2 is:

$$E_{n_2} - E_{n_1} = \frac{m_0}{2} \frac{e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (74)$$

2.2.3.2 Calculation of energy difference between electron orbits in hydrogen (4)

The pre-factor: **natural energy scale**

Lowest energy state: n = 1

E_1: (R_y is called the Rydberg constant.)

$$E_n = T + V = -\frac{1}{2} m_0 \frac{e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2}$$

$$E_{n_2} - E_{n_1} = \frac{m_0}{2} \frac{e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

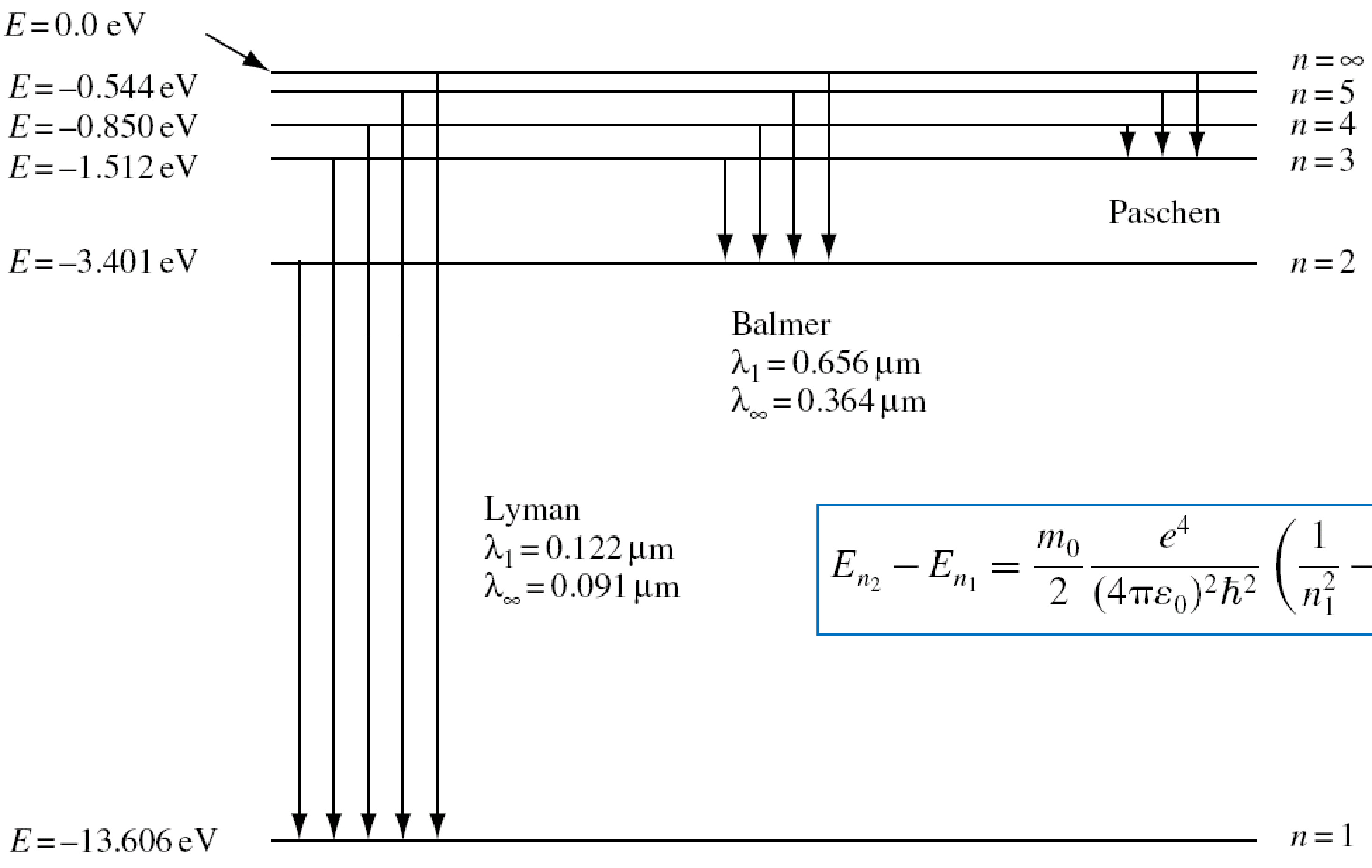
$$E_1 = Ry = \frac{-m_0}{2} \frac{e^4}{(4\pi\varepsilon_0)^2 \hbar^2} = -13.6058\,\mathrm{eV} \qquad (75)$$

The emission: transitions from high energy levels to lower energy levels.

Absorption: excitation electron from a low energy level to a higher energy level.

Different groups of energy transitions result in emission of photons of energy, . The characteristic emission line spectra have been given the **names of those who first observed them (Lyman, Balmer, Paschen)** .

Fig. 2.17 Photon emission spectra of excited hydrogen consist of a **discrete number** of spectral lines corresponding to **transitions** from high energy levels to lower energy levels. **Different groups** of characteristic emission line spectra have been given the names of those **who first observed them**.



$$E_{n_2} - E_{n_1} = \frac{m_0}{2} \frac{e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen* (6)

The **Bohr model** is **somewhat** of a hybrid between classical and quantum ideas.

The **Schrödinger equation** describes an electron moving in the **spherically symmetric coulomb potential** of the **proton charge**.

In **spherical coordinates**, the **time-independent solutions** are:

$$\psi_{nlm}(r,\theta,\phi)=R_n(r)\Theta_l^m(\theta)\Phi_m(\phi) \qquad (76)$$

The resulting three equations have wave functions that are quantized with integer **quantum numbers** *n*, *l*, and *m* and are separately normalized.

It can be shown that the function $\Phi_m(\varphi)$ must satisfy:

$$\frac{\partial^2}{\partial\phi^2}\Phi_m(\phi)+m^2\Phi_m(\phi)=0 \qquad (77)$$

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen* (7)

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0$$

2.2.3.2 Calculation of energy difference between electron orbits in hydrogen (8)

$$\frac{\partial^2}{\partial \phi^2}\Phi_m(\phi) + m^2\Phi_m(\phi) = 0 \quad (77) \quad \Rightarrow \quad \Phi_m(\phi) = Ae^{im\phi} \quad (78)$$

The normalization constant A can be found from:

$$\int_0^{2\pi} \Phi_m^*(\phi)\Phi_m(\phi)d\phi = A^2\int_0^{2\pi} e^{-im\phi}e^{im\phi}d\phi = A^2\int_0^{2\pi} d\phi = 2\pi A^2 = 1 \quad (79)$$

$$\text{Hence, } A = 1/\sqrt{2\pi} \text{ and } \quad \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \quad (80)$$

Hence, we expect $\Phi_m(\varphi)$ be **single-valued**, repeating itself **every 2π**.

This happens if m is an integer.

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen* (9)

$$\psi_{nlm}(r, \theta, \phi) = R_n(r)\Theta_l^m(\theta)\Phi_m(\phi)$$

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, \ldots, (n-1)$$

$$m = \pm l, \ldots, \pm 2, \pm 1, 0$$

The principal **quantum number** n specifies the **energy** of the Bohr orbit.

The **quantum numbers** l and m relate to the quantization of orbital **angular momentum**.

The **orbital angular momentum** quantum number is l, and the azimuthal quantum number is m.

2.2.3.2 *Calculation of energy difference between electron orbits in hydrogen* (9)

The energy level for given n is **independent** of quantum numbers l and m, hence **degeneracy** in **states of energy** E_n follow: (see Exercise 2.9)

$$\sum_{l=0}^{l=n-1} (2l+1) = n^2 \quad (77)$$

In addition to n, l , and m, the **electron** has a **spin quantum number** $s = \pm 1/2$. Electron **spin angular momentum**, $s\hbar$, is an **intrinsic** property of the electron arising from the **influence** of **special relativity** on the behavior of the electron.

2.2.4 Periodic table of elements

There are over 100 other **atoms**, each with their own **unique** characteristics. They are grouped in **periodic table**, arranged according to the **similarities** in their **chemical** behavior.

H, Li, Na and other atoms form the **column** IA elements of the periodic table because they all have a **single electron** available for chemical reaction with other atoms.

The **rules of quantum mechanics** can help us to **understand** why atoms **behave** the way they do and why chemists can **group** atoms according to the **number of electrons** available for **chemical reaction**.

2.2.4.1 *The Pauli exclusion principle and the properties of atoms*

An experimental fact: No two electrons in an interacting system can have the same quantum numbers n, l, m, and s.

This is the *Pauli exclusion principle, which determines many **properties of*** **atoms** in the **periodic table**, including the **formation** of **electron shells**.

For a given n in an atom there are only a **finite number** of values of l, m, and s that an electron may have.

If there is an electron assigned to each of these values, then a **complete shell** is formed. **Completed shells** occur in the chemically **inert noble elements** of the periodic table, which are **He, Ne, Ar, Kr, Xe**, and **Rn**.

Electrons in these **incomplete** sub-shells are available for **chemical reaction** with other atoms and therefore dominate the chemical activity of the atom.

2.2.4.1 *The Pauli exclusion principle and the properties of atoms* (2)

Table 2.5 *Electron shell states*

n	l	m	$2s$	Allowable states in sub-shell	Allowable states in complete shell
1	0	0	± 1	2	2
2	0	0	± 1	2	8
	1	-1	± 1	6	
		0	± 1		
		1	± 1		
3	0	0	± 1	2	18
	1	-1	± 1	6	
		0	± 1		
		1	± 1		
	2	-2	± 1	10	
		-1	± 1		
		0	± 1		
		1	± 1		
		2	± 1		

2.2.4.1
***The Pauli exclusion principle and the properties of atoms* (3)**

$Al[Ne]3s^2 3p^1$	group IIIB
$Si[Ne]3s^2 3p^2$	group IVB
$P[Ne]3s^2 3p^3$	group VB
$Ga[Ar]3d^{10} 4s^2 p^1$	group IIIB
$Ge[Ar]3d^{10} 4s^2 p^2$	group IVB
$As[Ar]3d^{10} 4s^2 p^3$	group VB
$In[Kr]4d^{10} 5s^2 p^1$	group IIIB

2.2.4.1 *The Pauli exclusion principle and the properties of atoms* (4)

Table 2.6 *Electron ground state for first 18 elements of the periodic table*

Atomic number	Element		$n=1$, $l=0$, $1s$	$n=2$, $l=0$, $2s$	$n=2$, $l=1$, $2p$	$n=3$, $l=0$, $3s$	$n=3$, $l=1$, $3p$	Shorthand notation
1	H		1					$1s^1$
2	He		2					$1s^2$
3	Li	[He] core		1				$1s^2 2s^1$
4	Be	2 electrons		2				$1s^2 2s^2$
5	B			2	1			$1s^2 2s^2 2p^1$
6	C			2	2			$1s^2 2s^2 2p^2$
7	N			2	3			$1s^2 2s^2 2p^3$
8	O			2	4			$1s^2 2s^2 2p^4$
9	F			2	5			$1s^2 2s^2 2p^5$
10	Ne			2	6			$1s^2 2s^2 2p^6$
11	Na	[Ne] core				1		[Ne] $3s^1$
12	Mg	10 electrons				2		[Ne] $3s^2$
13	Al					2	1	[Ne] $3s^2 3p^1$
14	Si					2	2	[Ne] $3s^2 3p^2$
15	P					2	3	[Ne] $3s^2 3p^3$
16	S					2	4	[Ne] $3s^2 3p^4$
17	Cl					2	5	[Ne] $3s^2 3p^5$
18	Ar					2	6	[Ne] $3s^2 3p^6$

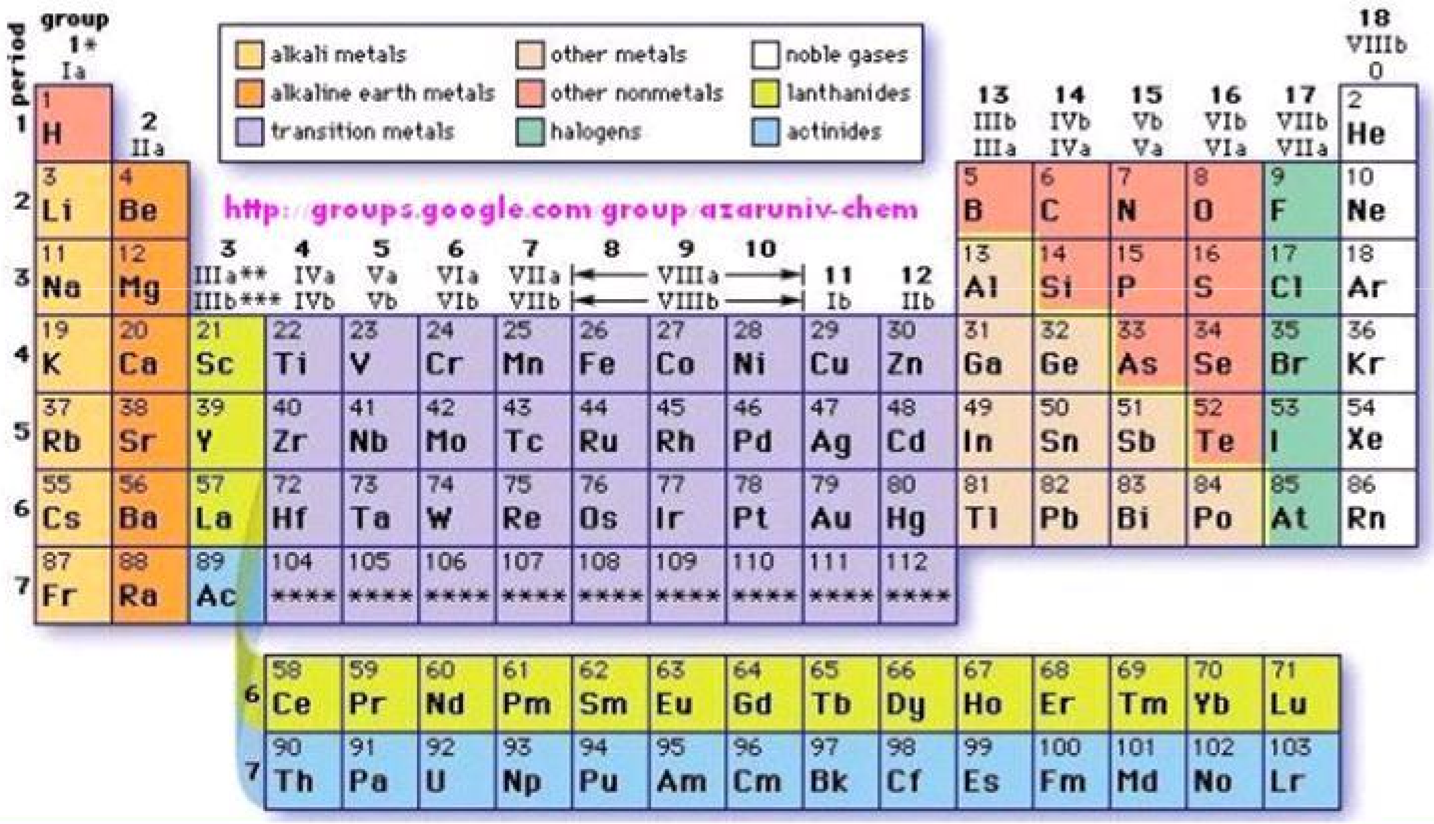
Table 2.7 *The Periodic Table of elements*

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble
Hydrogen **H** $1s^1$ 1.0079																	Helium **He** $1s^2$ 4.0026
Lithium **Li** $1s^2 2s^1$ 6.941	Beryllium **Be** $1s^2 2s^2$ 9.0122											Boron **B** $1s^2 2s^2 2p^1$ 10.81	Carbon **C** $1s^2 2s^2 2p^2$ 12.01	Nitrogen **N** $1s^2 2s^2 2p^3$ 14.007	Oxygen **O** $1s^2 2s^2 2p^4$ 15.999	Fluorine **F** $1s^2 2s^2 2p^5$ 18.998	Neon **Ne** $1s^2 2s^2 2p^6$ 20.18
Sodium **Na** [Ne] $3s^1$ 22.9898	Magnesium **Mg** [Ne] $3s^2$ 24.305											Aluminum **Al** [Ne] $3s^2 3p^1$ 26.982	Silicon **Si** [Ne] $3s^2 3p^2$ 28.086	Phosphorous **P** [Ne] $3s^2 3p^3$ 30.974	Sulfur **S** [Ne] $3s^2 3p^4$ 32.064	Chlorine **Cl** [Ne] $3s^2 3p^5$ 35.453	Argon **Ar** [Ne] $3s^2 3p^6$ 39.948
Potassium **K** [Ar] $4s^1$ 39.09	Calcium **Ca** [Ar] $4s^2$ 40.08	Scandium **Sc** [Ar] $3d^1 4s^2$ 44.956	Titanium **Ti** [Ar] $3d^2 4s^2$ 47.90	Vanadium **V** [Ar] $3d^3 4s^2$ 50.942	Chromium **Cr** [Ar] $3d^5 4s^1$ 52.00	Manganese **Mn** [Ar] $3d^5 4s^2$ 54.938	Iron **Fe** [Ar] $3d^6 4s^2$ 55.85	Cobalt **Co** [Ar] $3d^7 4s^2$ 58.93	Nickel **Ni** [Ar] $3d^8 4s^2$ 58.71	Copper **Cu** [Ar] $3d^{10} 4s^1$ 63.55	Zinc **Zn** [Ar] $3d^{10} 4s^2$ 65.38	Gallium **Ga** [Ar] $3d^{10} 4s^2 4p^1$ 69.72	Germanium **Ge** [Ar] $3d^{10} 4s^2 4p^2$ 72.59	Arsenic **As** [Ar] $3d^{10} 4s^2 4p^3$ 74.922	Selenium **Se** [Ar] $3d^{10} 4s^2 4p^4$ 78.96	Bromine **Br** [Ar] $3d^{10} 4s^2 4p^5$ 79.91	Krypton **Kr** [Ar] $3d^{10} 4s^2 4p^6$ 83.80
Rubidium **Rb** [Kr] $5s^1$ 85.47	Strontium **Sr** [Kr] $5s^2$ 87.62	Yttrium **Y** [Kr] $4d^1 5s^2$ 88.91	Zirconium **Zr** [Kr] $4d^2 5s^2$ 91.22	Niobium **Nb** [Kr] $4d^4 5s^1$ 92.91	Molybdenum **Mo** [Kr] $4d^5 5s^1$ 95.94	Technetium **Tc** [Kr] $4d^5 5s^2$ 98.91	Ruthenium **Ru** [Kr] $4d^7 5s^1$ 101.07	Rhodium **Rh** [Kr] $4d^8 5s^1$ 102.90	Palladium **Pd** [Kr] $4d^{10} 5s^0$ 106.40	Silver **Ag** [Kr] $4d^{10} 5s^1$ 107.87	Cadmium **Cd** [Kr] $4d^{10} 5s^2$ 112.40	Indium **In** [Kr] $4d^{10} 5s^2 5p^1$ 114.82	Tin **Sn** [Kr] $4d^{10} 5s^2 5p^2$ 118.69	Antimony **Sb** [Kr] $4d^{10} 5s^2 5p^3$ 121.75	Tellurium **Te** [Kr] $4d^{10} 5s^2 5p^4$ 127.60	Iodine **I** [Kr] $4d^{10} 5s^2 5p^5$ 126.90	Xenon **Xe** [Kr] $4d^{10} 5s^2 5p^6$ 131.30
Cesium **Cs** [Xe] $6s^1$ 132.91	Barium **Ba** [Xe] $6s^2$ 137.34	Lanthanum **La** [Xe] $5d^1 6s^2$ 138.91	Hafnium **Hf** [Xe] $4f^{14} 5d^2 6s^2$ 178.49	Tantalum **Ta** [Xe] $4f^{14} 5d^3 6s^2$ 180.95	Tungsten **W** [Xe] $4f^{14} 5d^4 6s^2$ 183.85	Rhenium **Re** [Xe] $4f^{14} 5d^5 6s^2$ 186.2	Osmium **Os** [Xe] $4f^{14} 5d^6 6s^2$ 190.20	Iridium **Ir** [Xe] $4f^{14} 5d^7 6s^2$ 192.22	Platinum **Pt** [Xe] $4f^{14} 5d^{10} 6s^0$ 195.09	Gold **Au** [Xe] $4f^{14} 5d^{10} 6s^1$ 196.97	Mercury **Hg** [Xe] $4f^{14} 5d^{10} 6s^2$ 200.59	Thallium **Tl** [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$ 204.37	Lead **Pb** [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$ 207.19	Bismuth **Bi** [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$ 208.98	Polonium **Po** [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$ 210	Astatine **At** [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$ 210	Radon **Rn** [Xe] $4f^{14} 5d^{10} 6s^2 6p^6$ 222
Francium **Fr** [Rn] $7s^1$ 223	Radium **Ra** [Rn] $7s^2$ 226	Actinium **Ac** [Rn] $6d^1 7s^2$ 227															

Rare earths

Lanthanides	Cerium **Ce** [Xe] $4f^2 5d^0 6s^2$ 140.12	Praseodymium **Pr** [Xe] $4f^3 5d^0 6s^2$ 140.91	Neodymium **Nd** [Xe] $4f^4 5d^0 6s^2$ 144.24	Promethium **Pm** [Xe] $4f^5 5d^0 6s^2$ 145	Samarium **Sm** [Xe] $4f^6 5d^0 6s^2$ 150.35	Europium **Eu** [Xe] $4f^7 5d^0 6s^2$ 151.96	Gadolinium **Gd** [Xe] $4f^7 5d^1 6s^2$ 157.25	Terbium **Tb** [Xe] $4f^9 5d^0 6s^2$ 158.92	Dysprosium **Dy** [Xe] $4f^{10} 5d^0 6s^2$ 162.50	Holmium **Ho** [Xe] $4f^{11} 5d^0 6s^2$ 164.93	Erbium **Er** [Xe] $4f^{12} 5d^0 6s^2$ 167.26	Thulium **Tm** [Xe] $4f^{13} 5d^0 6s^2$ 168.93	Ytterbium **Yb** [Xe] $4f^{14} 5d^0 6s^2$ 173.04	Lutetium **Lu** [Xe] $4f^{14} 5d^1 6s^2$ 174.97
Actinides	Thorium **Th** [Rn] $6d^2 7s^2$ 232.04	Protactinium **Pa** [Rn] $5f^2 6d^1 7s^2$ 231	Uranium **U** [Rn] $5f^3 6d^1 7s^2$ 238.03	Neptunium **Np** [Rn] $5f^4 6d^1 7s^2$ 237.05	Plutonium **Pu** [Rn] $5f^6 6d^0 7s^2$ 244	Americium **Am** [Rn] $5f^7 6d^0 7s^2$ 243	Curium **Cm** [Rn] $5f^7 6d^1 7s^2$ 247	Berkelium **Bk** [Rn] $5f^7 6d^2 7s^2$ 247	Californium **Cf** [Rn] $5f^8 6d^2 7s^2$ 251	Einsteinium **Es**	Fermium **Fm**	Mendelevium **Md**	Nobelium **No**	Lawrencium **Lw**

2.2.4.1 *The Pauli exclusion principle and the properties of atoms (6)*



2.2.5 Crystal structure

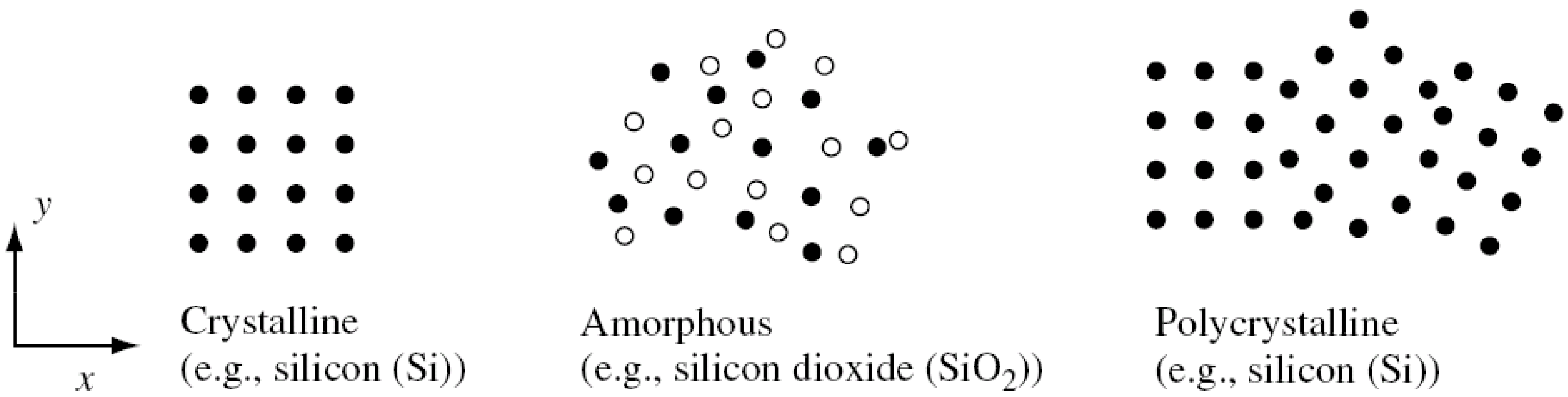


Fig. 2.18 Illustration of different types of solids according to atomic arrangement. In the figure, a dot represents the position of an atom.

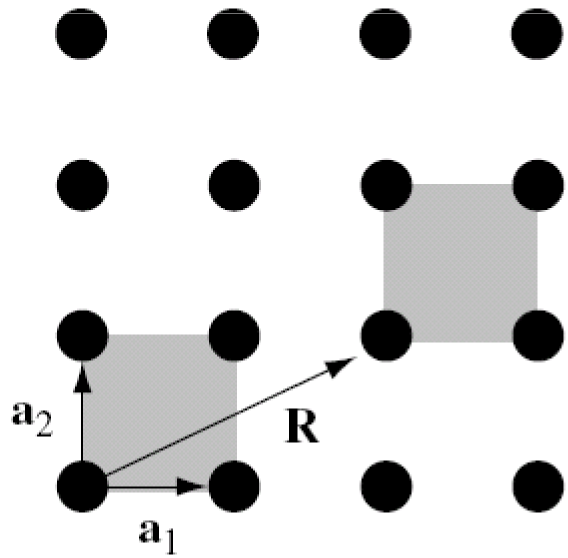
2.2.5 Crystal structure (2)

2.2.5.1 *Three types of solids classified according to atomic arrangement:*

Atoms in a crystalline solid are located in space on a *lattice*. *The unit cell is a lattice* volume, which is representative of the entire lattice and is repeated throughout the crystal. The smallest unit cell that can be used to form the lattice is called a *primitive cell.*

2.2.5.2 *Two-dimensional square lattice:*

Fig. 2.19 A **two-dimensional square lattice** can be created by **translating** the **unit vectors** a_1 and a_2 through space according to $\mathbf{R} = n_1a_1 + n_2a_2$, where n_1 and n_2 are integers.



2.2.5 Crystal structure (3)

2.2.5.3 Three-dimensional crystals:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (82)$$

where n_1, n_2, and n_3 are integers. This complete real-space lattice is called the Bravais lattice. The volume of the basic unit cell (the primitive cell) is:

$$\Omega_{cell} = a_1.(a_2 \times a_3) \quad (83)$$

A good choice for the vectors a_1, a_2, and a_3 that defines the primitive unit cell is due to Wigner and Seitz. The Wigner–Seitz cell about a lattice reference point is specified in such a way that any point of the cell is closer to that lattice point than any other.

The Wigner–Seitz cell may be found by **bisecting** with perpendicular planes all vectors connecting a reference atom position to all atom positions in the crystal. The smallest volume enclosed is the Wigner–Seitz cell.

2.2.5 Crystal structure (4)

2.2.5.4 Cubic lattices in three dimensions:

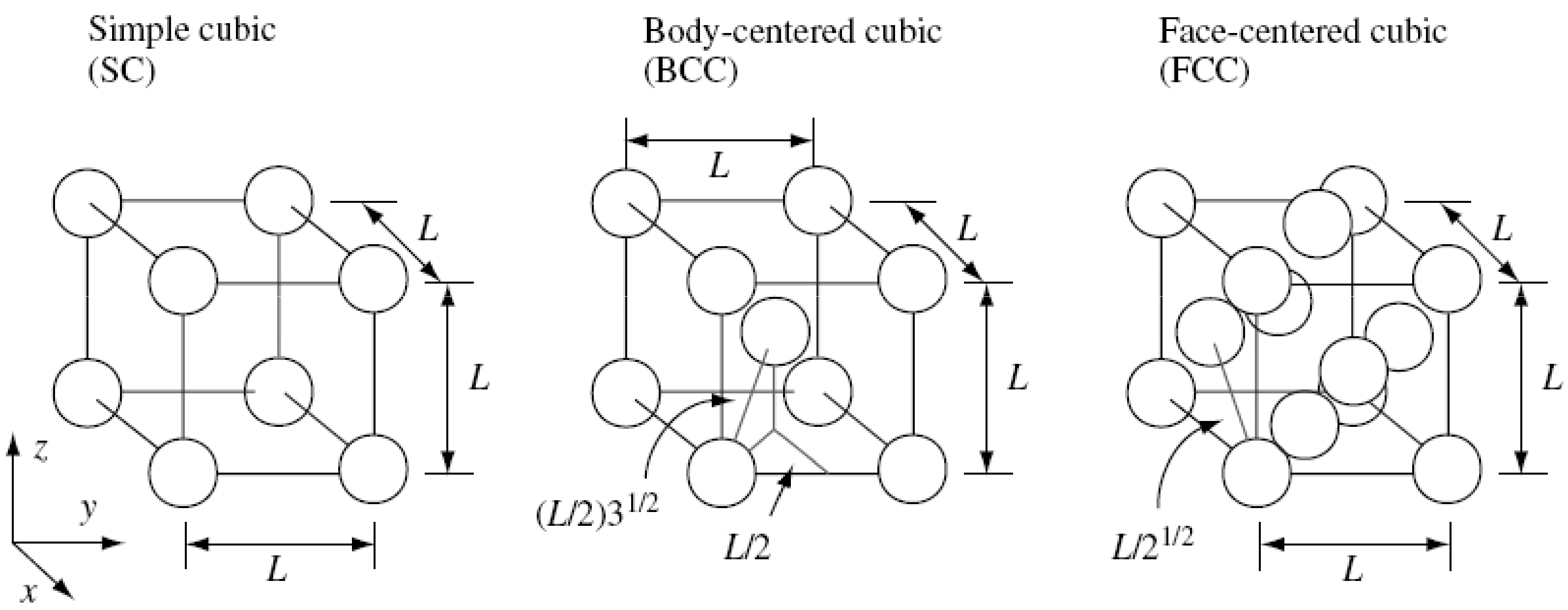
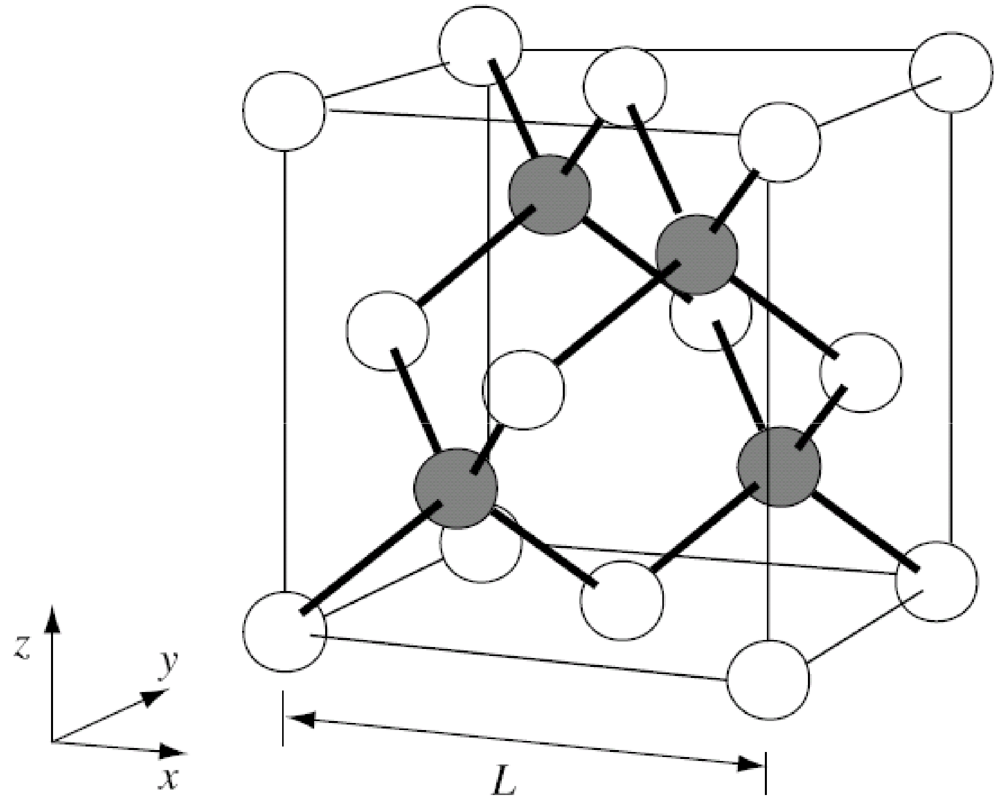


Fig. 2.20 Illustration of the indicated three-dimensional **cubic unit cells**, each of **lattice constant** L. In the figure, each **sphere** represents the **position of an atom**.

2.2.5 Crystal structure (5)

Fig. 2.21 Illustration of the diamond lattice cubic unit cell with lattice constant L. GaAs is an example of a III–V compound semiconductor with the zinc blende crystal structure. Ga (dark spheres) and As (white spheres).



2.2.5 Crystal structure

P.F.	Atom / unit cell	ساختار کریستالی	مواد
$\pi/6 = 0.52$	1	S.C	فسفر، منگنز
$\frac{\sqrt{3}.\pi}{8} = 0.68$	2	b.c.c	سدیم، لیتیم، پتاسیم، تنگستن، کروم،آهن، مولیبدینیم، باریم، سزیم
$\frac{\sqrt{2}.\pi}{6} = 0.74$	4	f.c.c	مس، نقره، طلا، آلومینیم، گالیم، پلاتین، سرب، نیکل
(b=a): 0.403 (2R=a)	2	hex.	کربن (گرافیت)، سلنیم، تلوریم
(b=a): 0.4275 $(2R=(a.2^{1/2})/2)$	6	c.p.h.	منیزیم، روی، کادمیم، تیلوریم، نیکل
$\frac{\sqrt{3}.\pi}{16} = 0.34$	8	diamond	کربن (الماس)، سیلیکون، ژرمانیوم، گالیم آرسناید، ایندیم فسفاید، . . .

2.2.5.5 The reciprocal lattice

Because the properties of crystals are often studied using wave-scattering experiments, it is important to consider the reciprocal lattice which exists in **reciprocal space** (also known as **wave vector space** or **k space**).

Given the basic **unit cell** defined by the vectors a_1, a_2, and a_3 in real space, one may construct three fundamental reciprocal vectors, g_1, g_2, and g_3, in reciprocal space defined by $a_i \cdot g_j = 2\pi\delta_{ij}$.

So that $g_1 = 2\pi(a_2 \times a_3)/\Omega_{cell}$, $g_2 = 2\pi(a_3 \times a_1)/\Omega_{cell}$, and $g_3 = 2\pi(a_1 \times a_2)/\Omega_{cell}$.

Crystal structure may be defined as a reciprocal-space translation of basic points throughout the space, in which:

$$\mathbf{G} = n_1\mathbf{g}_1 + n_2\mathbf{g}_2 + n_3\mathbf{g}_3 \tag{84}$$

2.2.5.5 The reciprocal lattice

where n_1, n_2, and n_3 are integers. The complete space spanned by **G** is called the ***reciprocal lattice***. *The volume of the three-dimensional reciprocal-space unit cell is:*

$$\Omega_k = \mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3) = \frac{(2\pi)^3}{\Omega_{\text{cell}}} \quad \textbf{(85)}$$

The ***Brillouin zone*** *of the reciprocal lattice has the same definition as the Wigner–Seitz* cell in real space. The first Brillouin zone may be found by **bisecting** with perpendicular **planes** all **reciprocal-lattice** vectors. The smallest volume enclosed is the **first Brillouin zone**.

2.2.5.5 The reciprocal lattice

As an example, consider a **face-centered cubic** lattice in real space.

To find the basic **reciprocal lattice** vectors for a **face-centered cubic** lattice we note that the basic **unit cell vectors** in real space are:

$a_1 = (0, 1, 1)(L/2)$, $a_2 = (1, 0, 1)(L/2)$, and $a_3 = (1, 1, 0)(L/2)$,

so that $g_1 = 2\pi(-1, 1, 1)/L$, $g_2 = 2\pi(1, -1, 1)/L$, and $g_3 = 2\pi(1, 1, -1)/L$.

Hence, the reciprocal lattice of a **face-centered cubic** lattice in **real space** is a **body-centered cubic** lattice.

2.2.5.5 The reciprocal lattice

Fig. 2.22 Illustration of the **Brillouin zone** for the FCC lattice with lattice constant L.

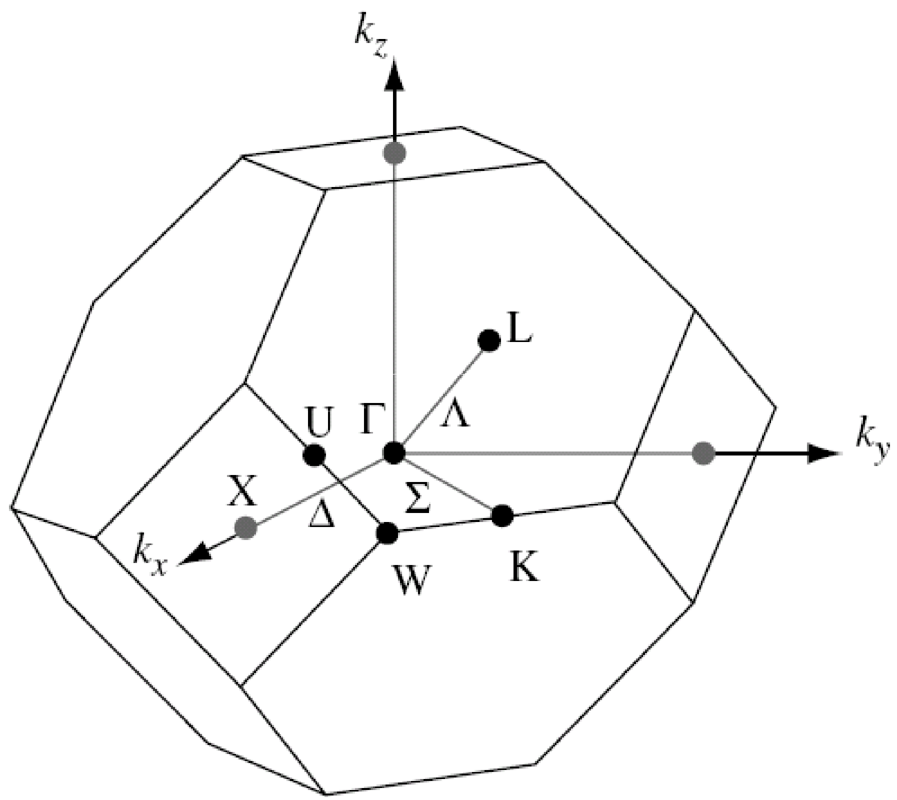
Some high-symmetry points are

Γ= (0, 0, 0), X = (2π/L)(1, 0, 0),

L = (2π/L)(0.5, 0.5, 0.5),

W = (2π/L)(1, 0.5, 0).

The high-symmetry line between the points Γ and X is labeled Δ, the line between the points Γ and L is Λ, and the line between Γ and K is Σ.



2.2.6 Electronic properties of bulk semiconductors and heterostructures

The **energy states** of an electron in a **hydrogen** atom are **quantized** and may only take on discrete values.

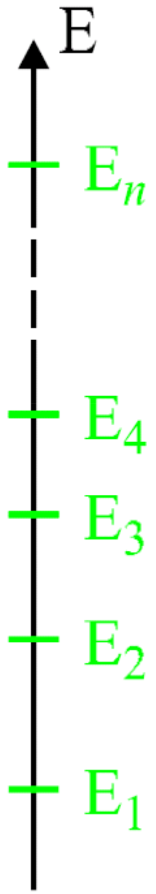
The same is true for electrons **in all atoms**.

In a **single-crystal solid**, electrons from the many atoms that make up the crystal can **interact** with **one another**.

Under these circumstances, the **discrete energy** levels of single atom electrons **disappear,** and instead there are **finite and continuous ranges** or **bands** of **energy states** with contributions from many individual atom electronic states.

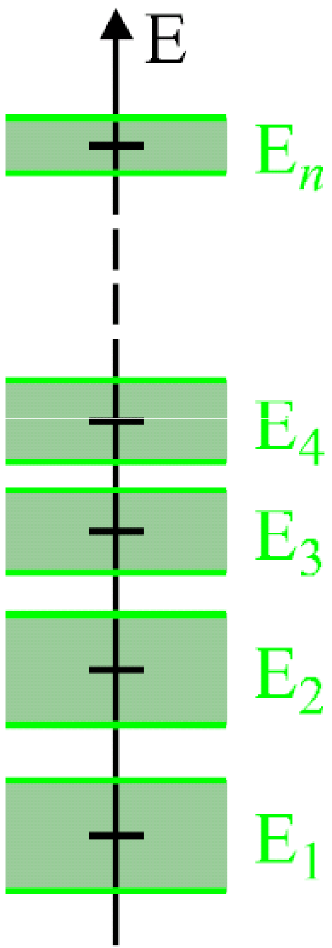
2.2.6 Electronic properties of bulk semiconductors and heterostructures

- A free electron can assume any energy level (continuous).
- Quantum mechanics predicts a **bound** electron can only assume discrete energy levels.
- This is a result of the **interaction** between the electron and the nuclear proton(s)



2.2.6 Electronic properties of bulk semiconductors and heterostructures

- Crystal is composed of a large number of atoms (≈10^{22} /cm^3 for silicon)
- Interaction between the electrons of each atom and the protons of other atoms
- Result is a perturbation of each electron's discrete energy level to form **continua** at the previous energy levels



2.2.6 Electronic properties of bulk semiconductors and heterostructures

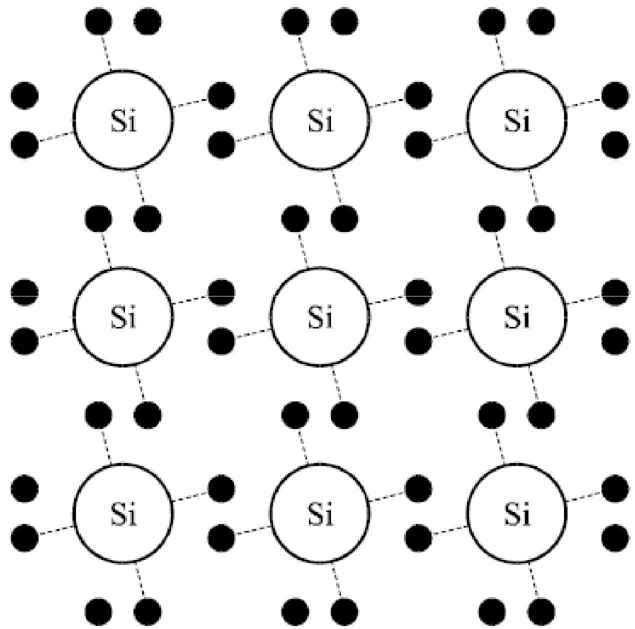
• Silicon crystal formed by covalent bonds

• **Covalent bonds** share electrons between atoms in lattice so each thinks its orbitals are full

• Most important bands are

– **valence band:** band which would be filled at 0K

– **conduction band:** next band above in energy

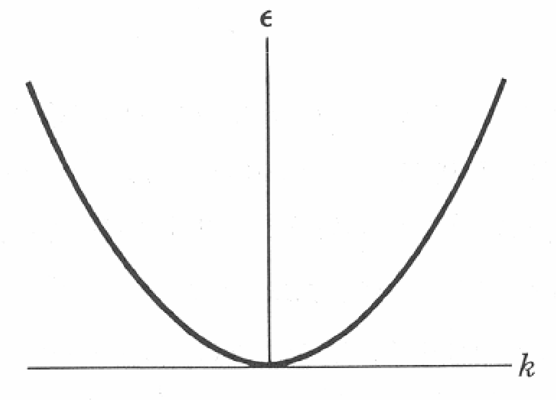


2.2.6 Electronic properties of bulk semiconductors and heterostructures

If an **electron is free** to move in the **material**, its motion is influenced by the presence of the **periodic potential**.

Typically, electrons with **energy near** the **conduction-band minimum** or energy near the **valence-band maximum** have an electron **dispersion relation** that may be characterized by a parabola, $\omega(k) \propto k^2$

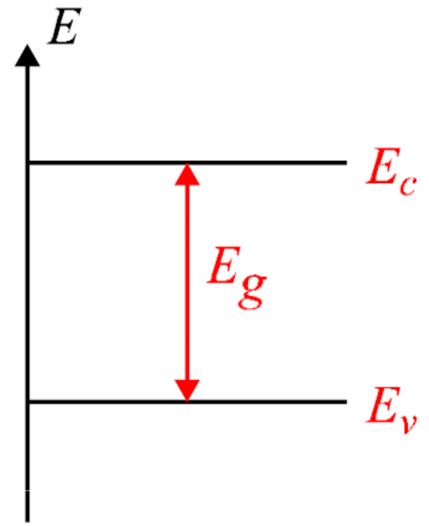
The kinetic energy of the electron in the crystal may therefore be written as $E_k = \hbar\omega = \hbar^2 k^2/2m^*$, where m^* is called the ***effective electron mass***. The value of m^* can be **greater** or **less** than the mass of a "**bare**" electron moving in free space.

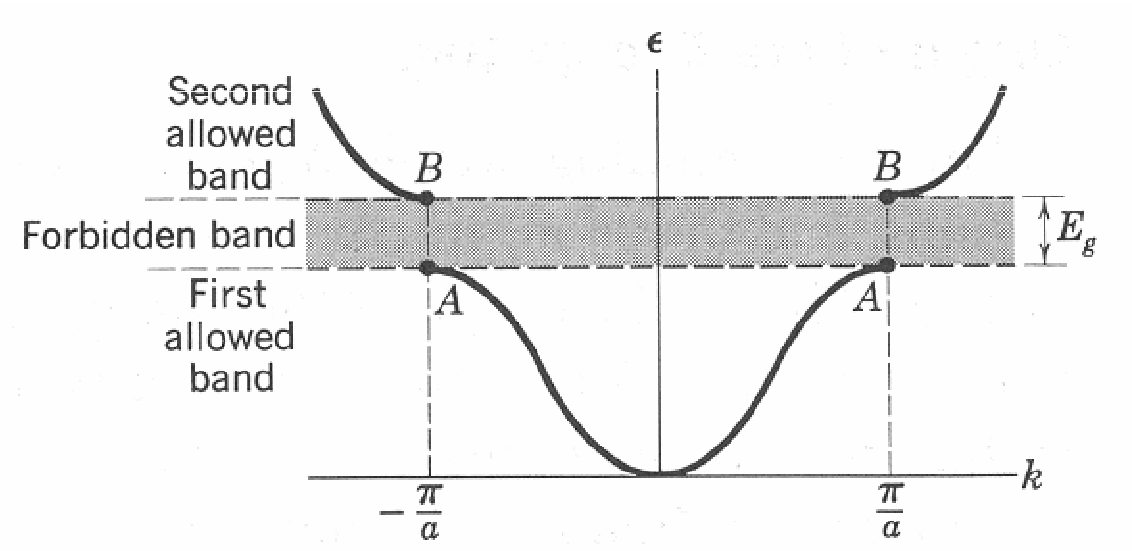


For GaAs $m^* = 0.07m_0$, and InAs $m^* = 0.02m_0$, where m_0 is the **bare electron mass**.

2.2.6 Electronic properties of bulk semiconductors and heterostructures

- top of valence band (E_v)
- bottom of conduction band (E_c)
- difference in energy between E_c and E_v, ***energy gap*** E_g

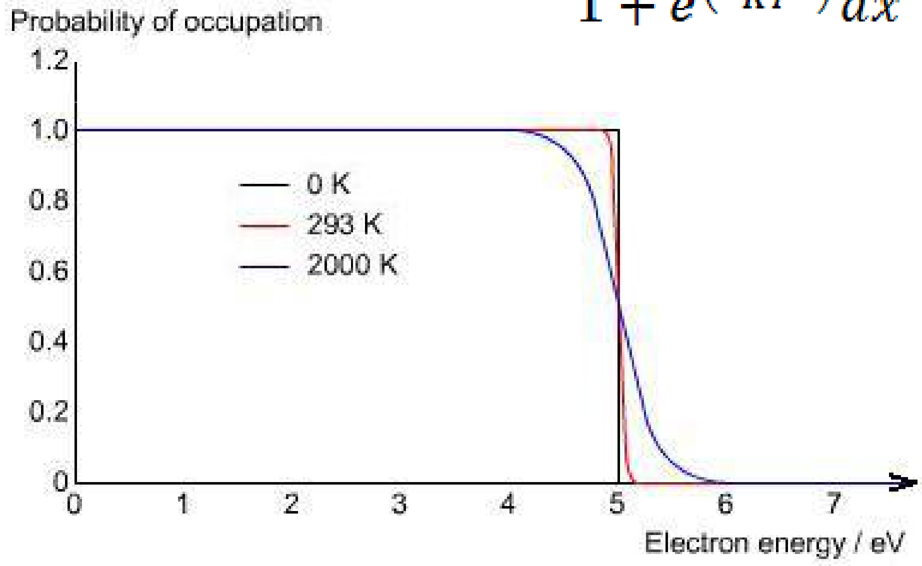




The statistical energy distribution of electrons in thermal equilibrium at absolute temperature T is typically described by the Fermi–Dirac distribution function:

$$f_{\mathrm{k}}(E_{\mathbf{k}}) = \frac{1}{e^{(E_{\mathbf{k}}-\mu)/k_{\mathrm{B}}T} + 1}$$

$$f(E) = \frac{1}{1 + e^{\left(\frac{E-E_f}{KT}\right)}dx}$$



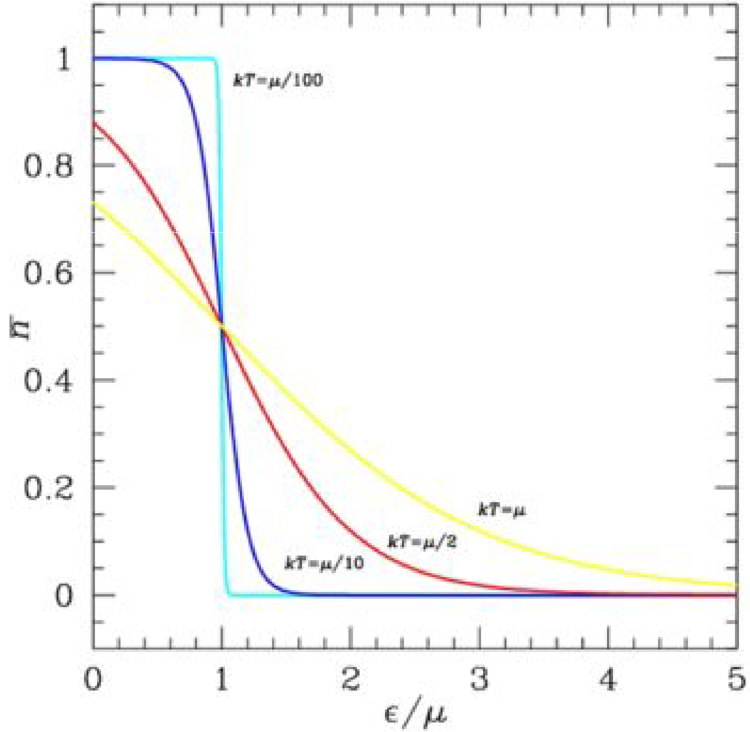
Fermi-Dirac distribution for several temperatures

μ: chemical potential

$f_k(E_k)$: probability of occupancy of a given electron state of energy E_k.

The Fermi–Dirac distribution is driven by the **Pauli exclusion principle** which states that ***identical indistinguishable half-odd-integer spin particles cannot occupy the same state.***

For electrons with effective mass m^*, $E_F = \hbar^2 k_F^2 / 2m^*$, where k_F is called the Fermi wave vector.



At **finite temperatures**, and in the limit of electron energies that are **large** compared with the **chemical potential**, the **distribution function** takes on the Boltzmann form $f_k(E) \rightarrow\ = e^{-E/kT}$.

2.2.6 Electronic properties of bulk semiconductors and heterostructures

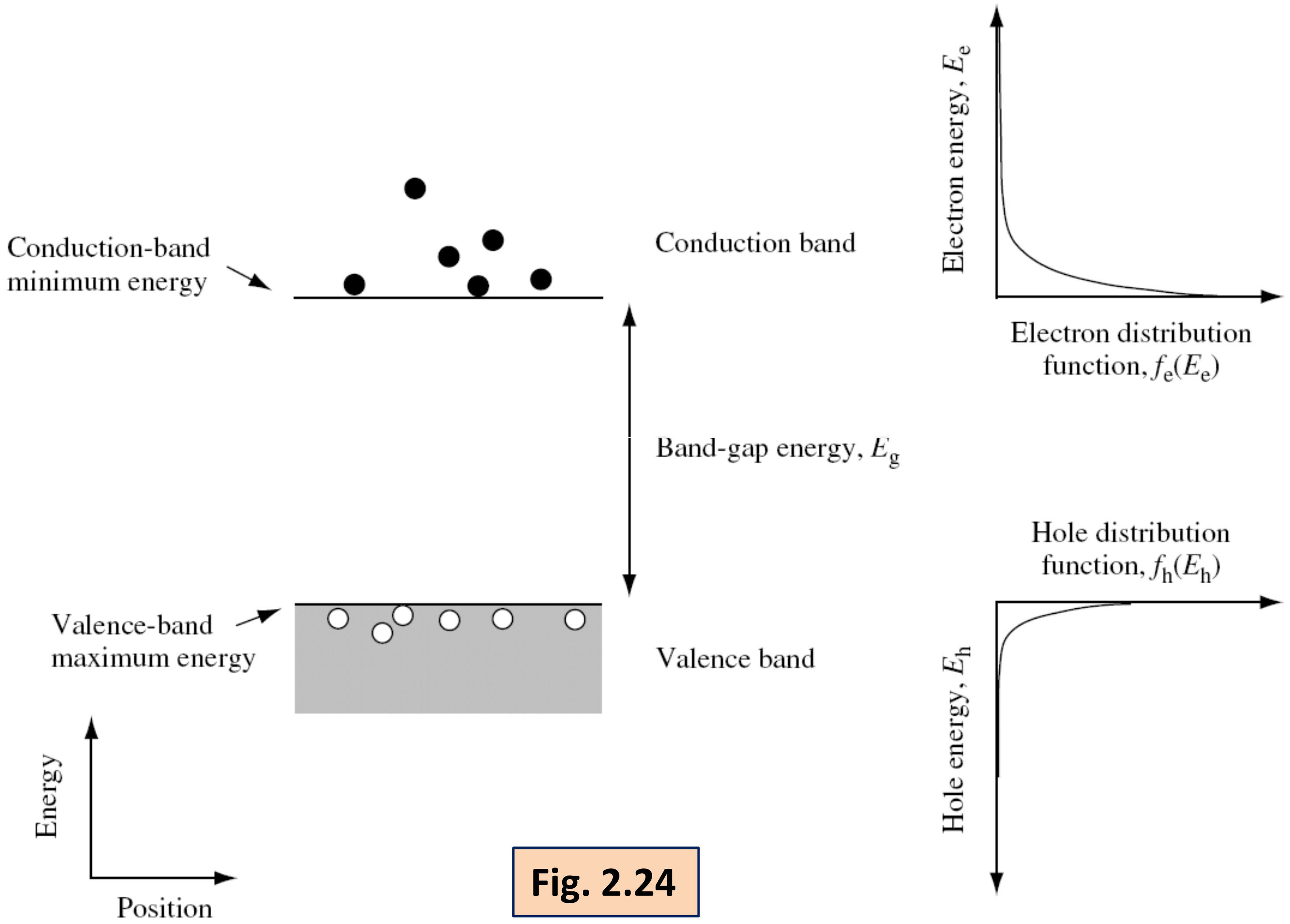
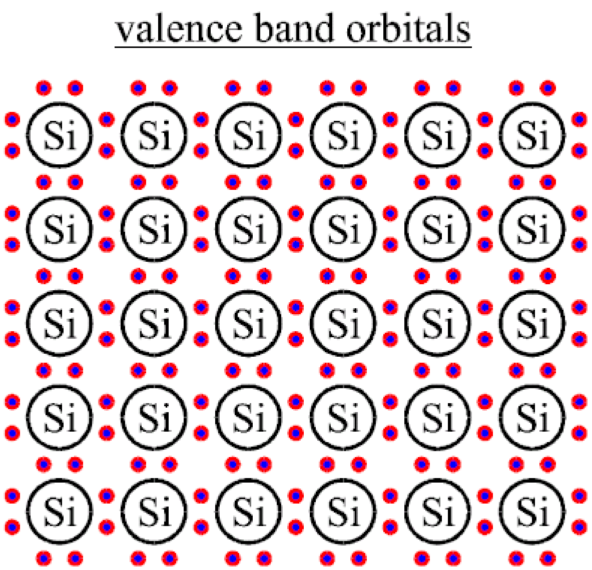
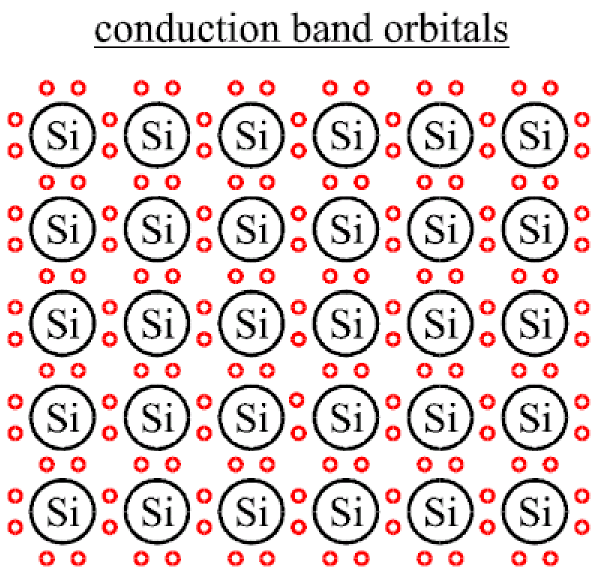


Fig. 2.24

A **pure crystalline** semiconductor is an electrical insulator at **low temperature**. In the lowest energy state, or ***ground state***, *of a* ***pure semiconductor***, *all electron states are occupied in* the ***valence band*** *and there are* ***no electrons*** *in the* ***conduction band***.

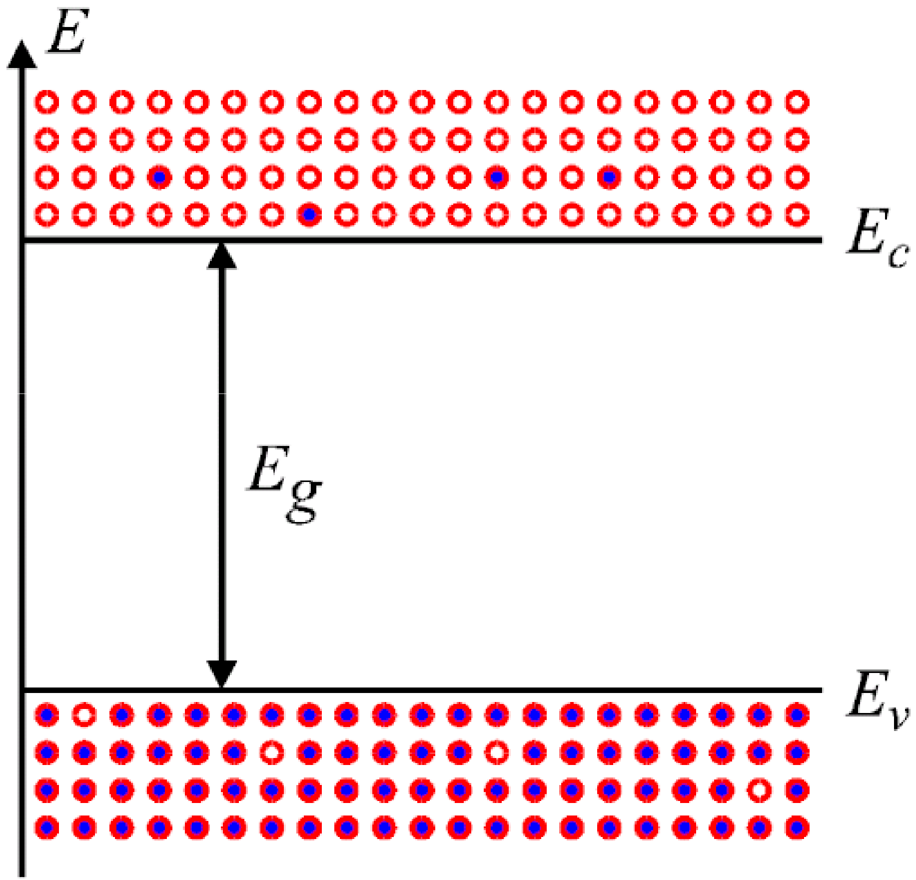




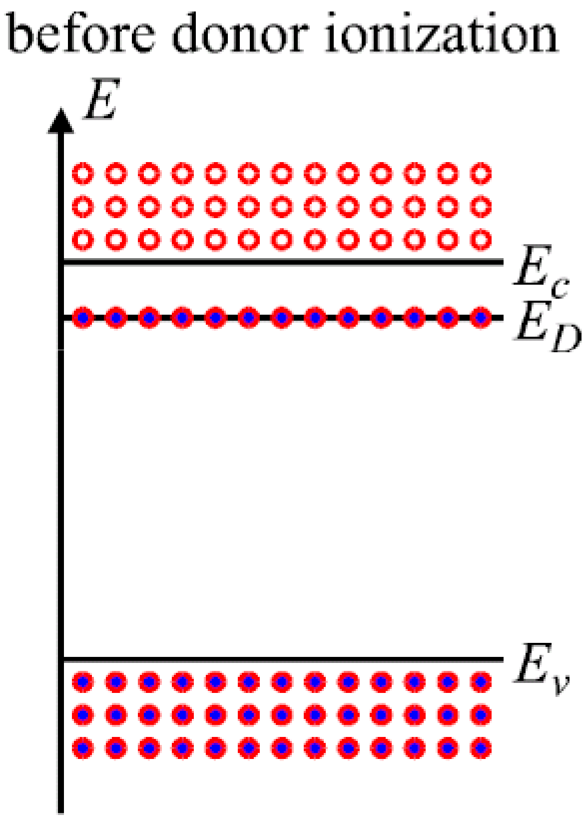
2.2.6 Electronic properties of bulk semiconductors and heterostructures

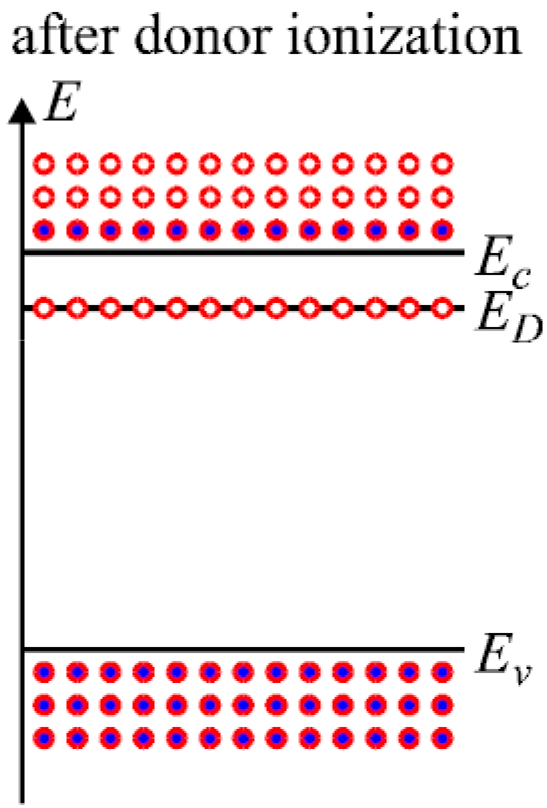
$$n = p = n_i$$

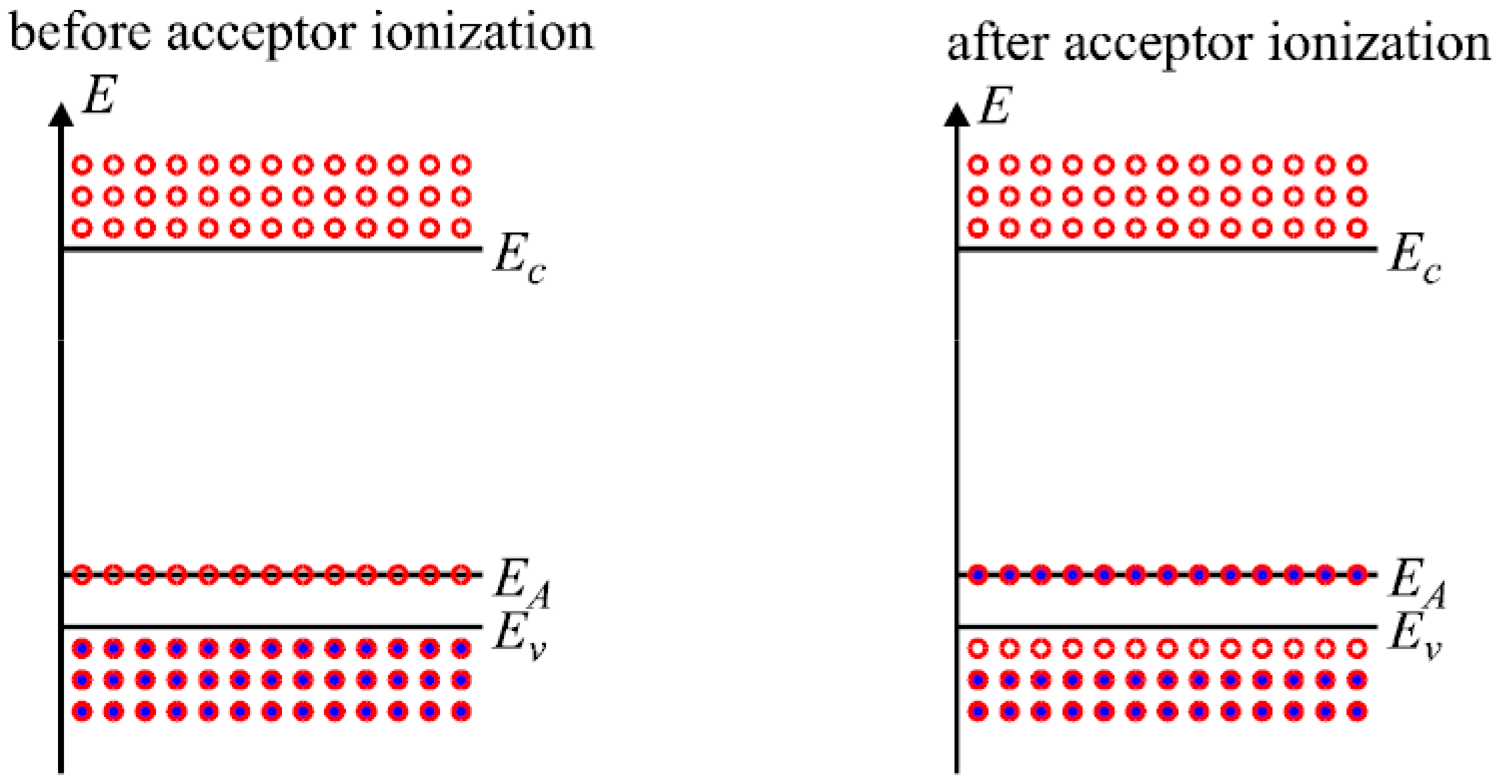
$$np = n_i^2$$



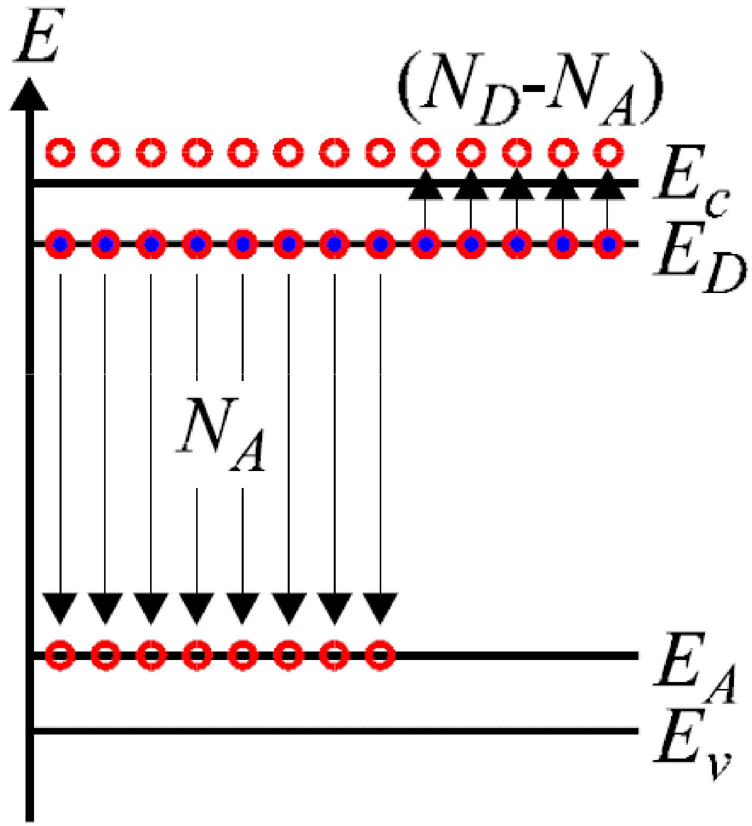
2.2.6 Electronic properties of **bulk** semiconductors and heterostructures






before acceptor ionization
after acceptor ionization
E
E
E_c
E_c
E_A
E_A
E_v
E_v

Compensated doping



2.2.6 Electronic properties of bulk semiconductors and heterostructures

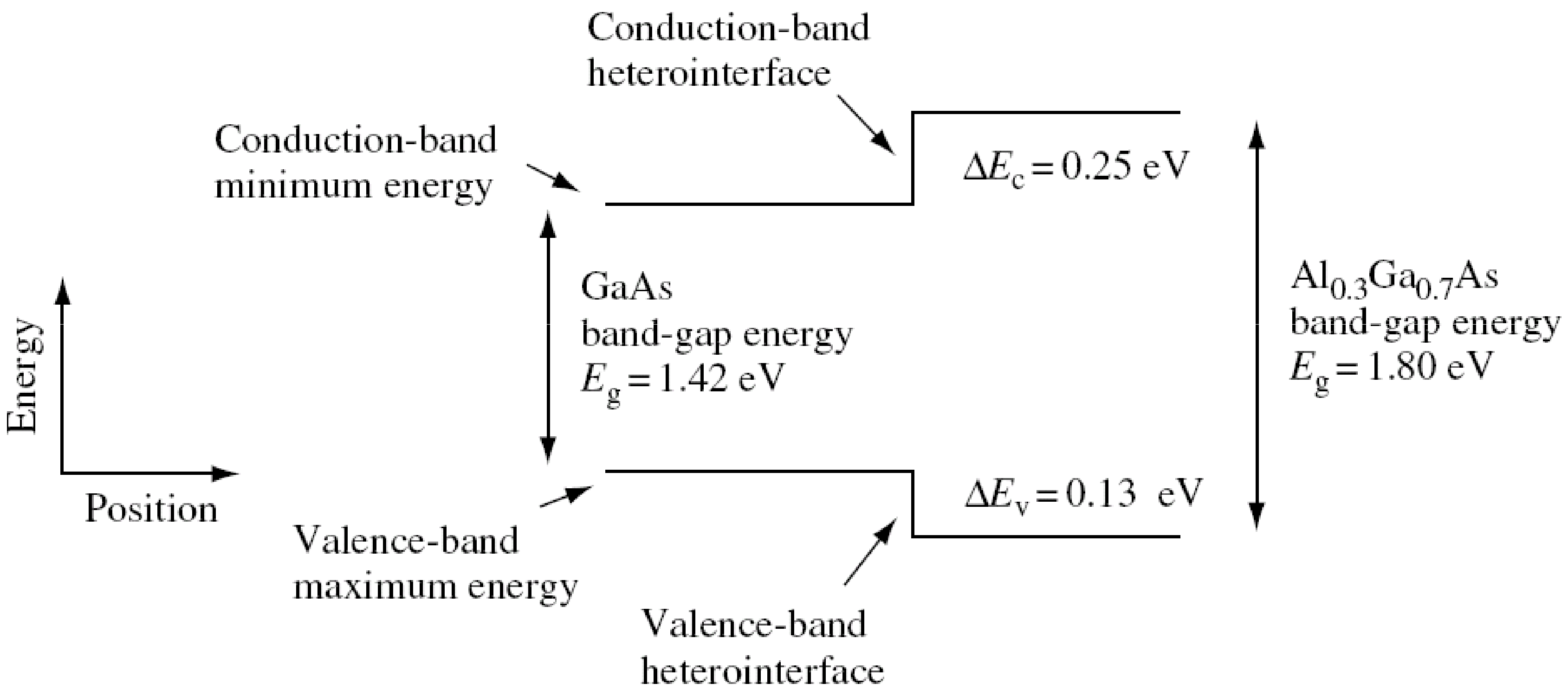
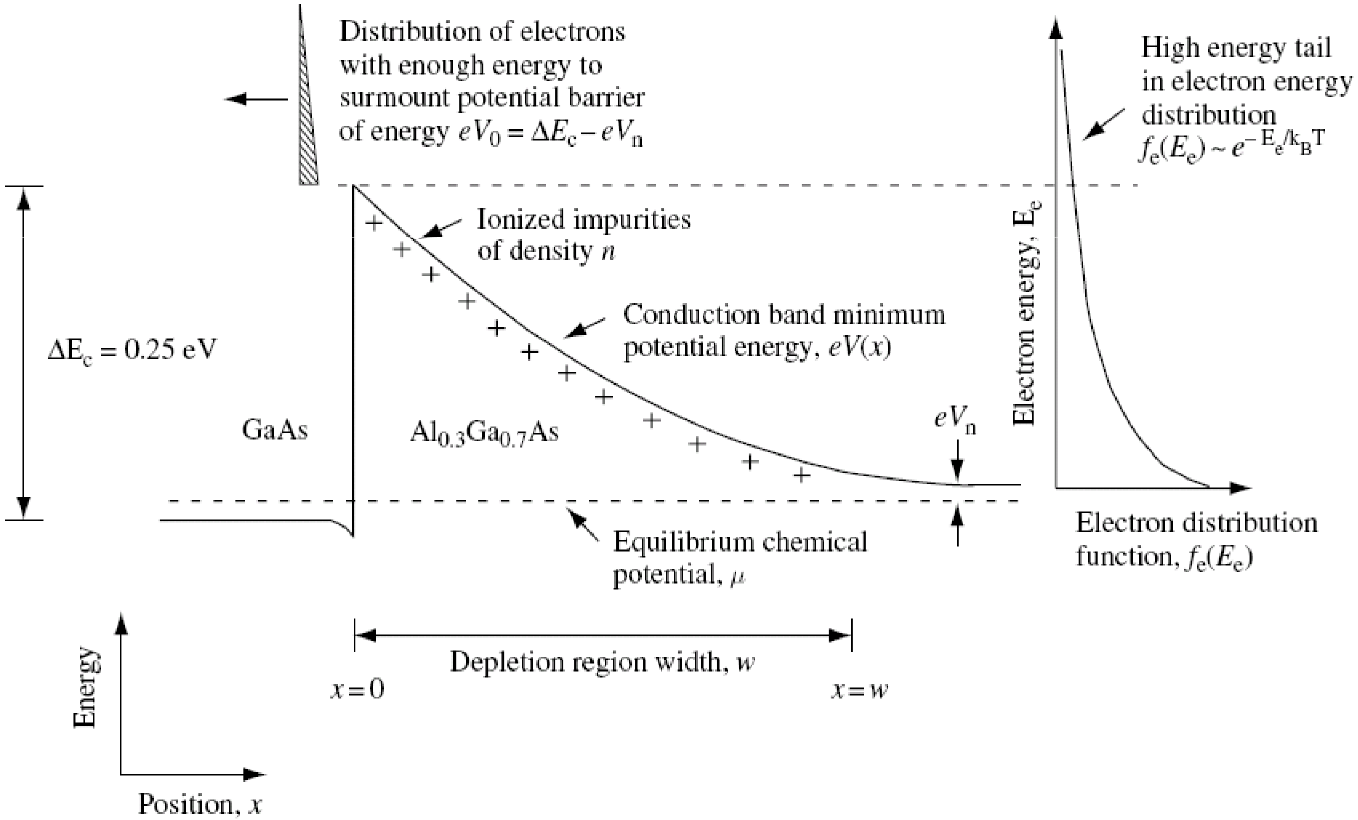


Fig. 2.25

2.2.6.1 The heterostructure diode

Fig. 2.27 Diagram of the **conduction band minimum** of a **unipolar n-type** **$GaAs/Al_{0.3}Ga_{0.7}As$ heterostructure diode**. The GaAs is **heavily** doped, and the $Al_{0.3}Ga_{0.7}As$ is lightly doped.



2.2.6.1 The heterostructure diode

by solving Poisson's equation: $\nabla \cdot \mathbf{E} = \rho / \varepsilon_0 \varepsilon_r$ $\rho = en,$

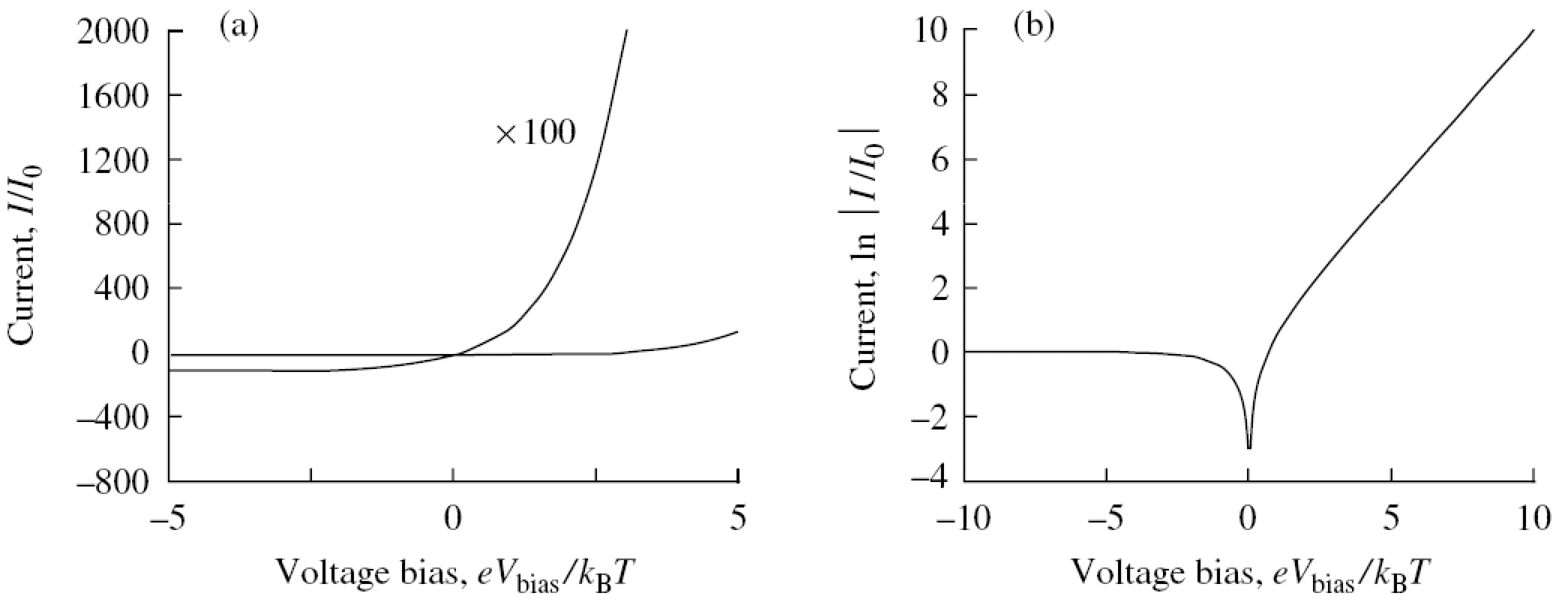
$$\frac{\partial \mathrm{E}_x}{\partial x} = \frac{en}{\varepsilon_0 \varepsilon_r} = -\frac{\partial^2}{\partial x} V(x) \quad (87)$$

$$w = \left(\frac{2\varepsilon_0 \varepsilon_r}{en} V_0 \right)^{1/2} \quad (88)$$

$$w = \left(\frac{2\varepsilon_0 \varepsilon_r}{en} (V_0 - V_{\mathrm{bias}}) \right)^{1/2} \quad (89)$$

2.2.6.1 The heterostructure diode

Fig. 2.28 **(a)** Current–voltage characteristics of an ideal diode plotted on a linear scale. (b) Current–voltage characteristics of an ideal diode. The natural logarithm of normalized current is plotted on the vertical axis.



$$I = I_0(e^{eV_{bias}/n_{id}k_BT} - 1) \quad (90)$$

2.3 Example exercises