Ira N. Levine, Quantum Chemistry

Quantum Mechanics

- Chapter 2

Differential Equations

Ordinary differential equations

Partial differential equations

$$y''' + 2x(y')^2 + \sin x \cos y = 3e^x$$

Third order

Linear differential equation

$$A_n(x)y^{(n)} + A_{n-1}(x)y^{(n-1)} + \cdots + A_1(x)y' + A_0(x)y = g(x)$$

$g(x) = 0$ Homogeneous; otherwise it is inhomogeneous

Linear homogeneous differential equation

$$y'' + P(x)y' + Q(x)y = 0$$

Differential Equations

$$y'' + P(x)y' + Q(x)y = 0$$

y_1 , y_2 solutions

$y = c_1 y_1 + c_2 y_2$ General solution

$$\begin{aligned} &c_1 y_1'' + c_2 y_2'' + P(x)c_1 y_1' + P(x)c_2 y_2' + Q(x)c_1 y_1 + Q(x)c_2 y_2 \\ &= c_1[y_1'' + P(x)y_1' + Q(x)y_1] + c_2[y_2'' + P(x)y_2' + Q(x)y_2] \\ &= c_1 \cdot 0 + c_2 \cdot 0 = 0 \end{aligned}$$

Differential Equations

Linear homogeneous second order differential equation with constant coefficients

$$y'' + py' + qy = 0$$

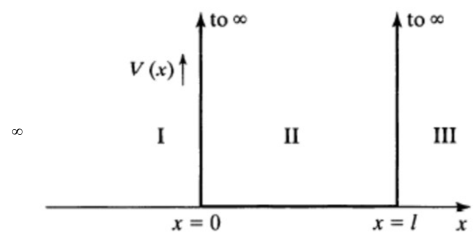
$y = e^{sx}$. $\longrightarrow$ $s^2 e^{sx} + pse^{sx} + qe^{sx} = 0$

$s^2 + ps + q = 0$ Auxiliary equation

$y_1 = e^{s1x}$ $y_2 = e^{s2x}$

$$y = c_1 e^{s_1 x} + c_2 e^{s_2 x}$$

particle in a one-dimensional box



Potential energy function V(x) for the particle in a one-dimensional box

boundary conditions

- $V(x) = 0$ when $0 < x < l$
- $V(x) = \infty$ elsewhere

particle in a one-dimensional box

Schrödinger equation for regions I and III: $V(x) = \infty$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + \infty\,\psi(x) = E\,\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar}(E - \infty)\psi(x) = 0$$

Neglecting E in comparison with ∞

$$\frac{\partial^2\psi(x)}{\partial x^2} = \infty\,\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2}\frac{1}{\infty} = \psi(x)$$

We conclude that $\psi(x)$ is zero outside the box:

$$\psi_I(x) = \psi_{III}(x) = 0$$

particle in a one-dimensional box

For region II (inside the box): V(x) = 0

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0$$

where, m = mass of the particle, and E is a total energy

a linear homogeneous second-order differential equation with constant coefficients

$$Y'' + py' + qy = 0 \longrightarrow s^2 + ps + q = 0$$

$y_1 = e^{s1x}$ $y_2 = e^{s2x}$

The general solution is: $y = C_1 e^{s1x} + C_2 e^{s2x}$

particle in a one-dimensional box

$$\left.\begin{array}{l} s^2 + q = 0 \\ q = \dfrac{2m}{\hbar^2} E \end{array}\right\} \quad s^2 + 2mE/\hbar^2 = 0 \qquad s^2 = (-2mE)/\hbar^2 \qquad s = \pm(-2mE)^{1/2}/\hbar$$

$$\psi_{II} = c_1 e^{i(2mE)^{1/2} x/\hbar} + c_2 e^{-i(2mE)^{1/2} x/\hbar}$$

Let: $\theta = (2mE)^{1/2} x/\hbar$

$$\psi(x) = c_1 e^{i\theta} + c_2 e^{-i\theta}$$

particle in a one-dimensional box

$$\psi_{II}(x) = c_1 e^{i\theta} + c_2 e^{-i\theta}$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{-i\theta} = \cos(-\theta) + i\sin(-\theta) = \cos\theta - i\sin\theta$$

$$\psi_{II}(x) = c_1\cos\theta + ic_1\sin\theta + c_2\cos\theta - ic_2\sin\theta$$

$$\psi_{II}(x) = (c_1 + c_2)\cos\theta + (ic_1 - ic_2)\sin\theta$$

$$\boxed{\psi_{II}(x) = A\cos\theta + B\sin\theta}$$

A and B are new arbitrary constants

particle in a one-dimensional box

$$\psi_{II}(x) = A\cos[\hbar^{-1}(2mE)^{1/2}x] + B\sin[\hbar^{-1}(2mE)^{1/2}x]$$

$$\psi_{II}(x) = A\cos\sqrt{\frac{2mE}{\hbar^2}}\,x + B\sin\sqrt{\frac{2mE}{\hbar^2}}\,x$$

Now we determine A and B by applying boundary conditions.

particle in a one-dimensional box

It seems reasonable to **postulate** that the wave function will be continuous.

If Ψ(x) is to be continuous at the point x=0

$$\lim_{x-0}\psi(x)=0$$

$$\lim_{x-0}[A\cos\sqrt{\frac{2mE}{\hbar^2}}x+B\sin\sqrt{\frac{2mE}{\hbar^2}}x]=0$$

$$A\cos\sqrt{\frac{2mE}{\hbar^2}}(0)+B\sin\sqrt{\frac{2mE}{\hbar^2}}(0)=0$$

$$A\cos\sqrt{\frac{2mE}{\hbar^2}}(0)=0$$

$$A=0$$

particle in a one-dimensional box

$$\psi(x)=B\sin\sqrt{\frac{2mE}{\hbar^2}}x$$

If Ψ(x) is to be continuous at the point x=l

$$\lim_{x\to l}\psi(x)=0$$

$$\lim_{x\to l}[B\sin\sqrt{\frac{2mE}{\hbar^2}}x]=0$$

$$B\sin\sqrt{\frac{2mE}{\hbar^2}}(l)=0$$

B cannot be zero because this would make the wave function zero everywhere.

particle in a one-dimensional box

$$\sin\sqrt{\frac{2mE}{\hbar^2}}\,l = 0$$

$$\sqrt{\frac{2mE}{\hbar^2}}\,l = \pm n\pi \quad , \quad n = 1, 2, \ldots$$

We must reject the value zero for n, which makes E = 0. why?

$$E = n^2 \frac{h^2}{8ml^2} \quad , \quad n = 1, 2, \ldots$$

Ground state n = 1

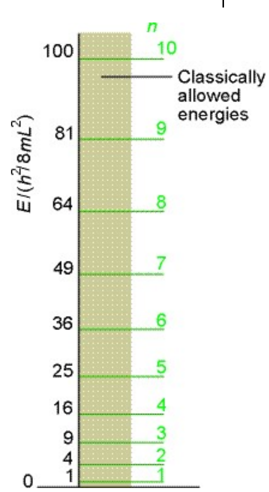
Exited state n > 1

Application of boundary conditions has forced us to the conclusion that the values of the energy are quantized.

particle in a one-dimensional box

$$E = n^2 \frac{h^2}{8ml^2} \quad , \quad n = 1, 2, \ldots$$

$$\frac{E}{\frac{h^2}{8ml^2}} = n^2$$



Example:

A particle of mass 2.00 X 10^{-26} g is in a one-dimensional box of length 4.00 nm. Find the frequency and wavelength of the photon emitted when this particle goes from the n = 3 to the n = 2 level.

By conservation of energy,

$$h\nu = E_{\text{upper}} - E_{\text{lower}} = n_u^2 h^2/8ml^2 - n_l^2 h^2/8ml^2$$

$$\nu = \frac{(n_u^2 - n_l^2)h}{8ml^2} = \frac{(3^2 - 2^2)(6.626 \times 10^{-34}\ \text{J s})}{8(2.00 \times 10^{-29}\ \text{kg})(4.00 \times 10^{-9}\ \text{m})^2} = 1.29 \times 10^{12}\ \text{s}^{-1}$$

$$\lambda = 2.32 \times 10^{-4}\ \text{m.}$$

particle in a one-dimensional box

$$\psi(x) = B \sin \sqrt{\frac{2mE}{\hbar^2}}\, x$$

$$\sqrt{\frac{2mE}{\hbar^2}}\, l = \pm n\pi$$

?

$$\psi(x) = B \sin\left(\frac{n\pi x}{l}\right)$$

n = 1, 2, 3, …

The constant B is still arbitrary. To fix its value, we use the normalization requirement:

particle in a one-dimensional box

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \partial x = 1$$

$$\int_{-\infty}^{a} |\psi(x)|^2 dx + \int_{0}^{l} |\psi(x)|^2 dx + \int_{l}^{\infty} |\psi(x)|^2 dx = 1$$

$$|B|^2 \int_0^l \sin^2\left(\frac{n\pi x}{l}\right) dx = 1 = |B|^2\, l/2$$

$$|B| = \sqrt{\frac{2}{l}}$$

$(2/l)^{1/2} e^{i\alpha}$

Note that we have determined only the absolute value of B.

$$\boxed{\psi_{II}(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)}$$

particle in a one-dimensional box

To explain this:

$$\cos^2\theta + \sin^2\theta = 1$$

$$\cos^2\theta - \sin^2\theta = \cos 2\theta$$

By summation

$$2\cos^2\theta = \cos 2\theta + 1$$

By subtraction

$$2\sin^2\theta = 1 - \cos 2\theta \qquad \sin^2\theta = (1 - \cos 2\theta)/2$$

particle in a one-dimensional box

$$\int_0^l \sin^2\left(\frac{n\pi x}{l}\right)dx = \frac{1}{2}\int_0^l 2\sin^2\left(\frac{n\pi x}{l}\right)dx$$

$$= \frac{1}{2}\int_0^l \left(1-\cos\frac{2n\pi x}{l}\right)dx$$

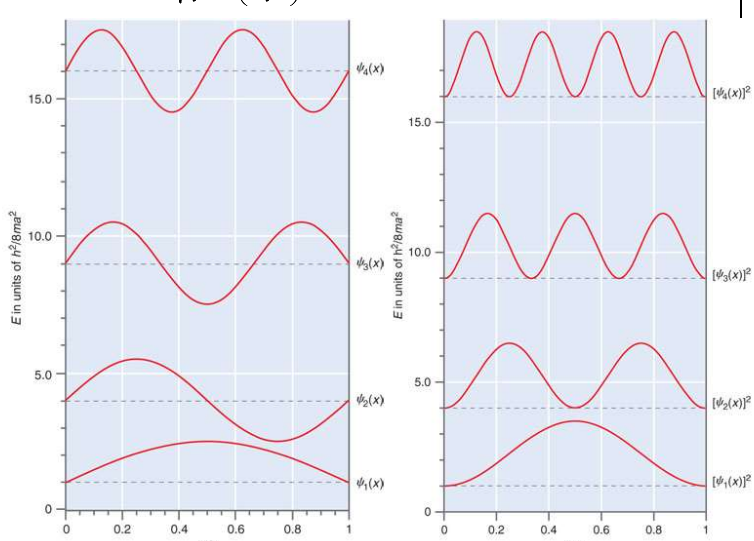
$$= \frac{1}{2}\int_0^l dx - \frac{1}{2}\int_0^l \cos\frac{2n\pi x}{l}dx$$

$$= \frac{1}{2}x\Big|_0^l - \frac{l}{4n\pi}\int_0^l \cos\frac{2n\pi x}{l}\, d\frac{2n\pi x}{l}$$

$$= \frac{1}{2}l - \frac{l}{4n\pi}\sin\frac{2n\pi x}{l}\Big|_0^l \qquad = \frac{1}{2}l - \frac{l}{4n\pi}\left[\sin 2n\pi - \sin 0\right] = \frac{1}{2}l$$

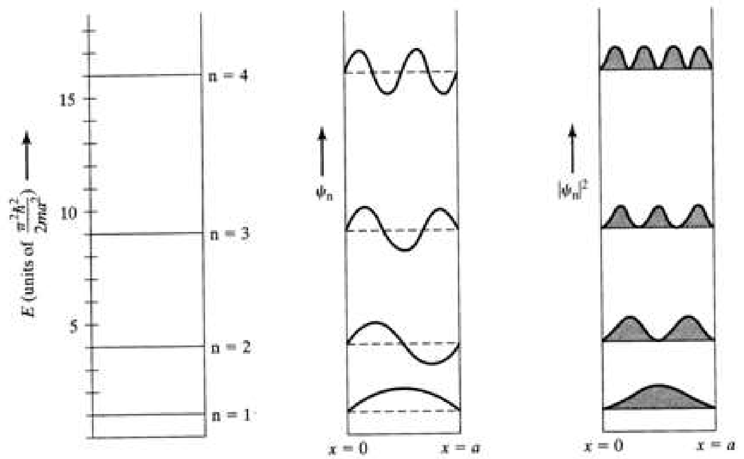
particle in a one-dimensional box

$$\psi_{II}(x) = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right) \qquad \left|\psi_{II}(x)\right|^2 = \psi_{II}\psi_{II}^* = \frac{2}{l}\left(\sin(\frac{n\pi x}{l})\right)^2$$



node

particle in a one-dimensional box



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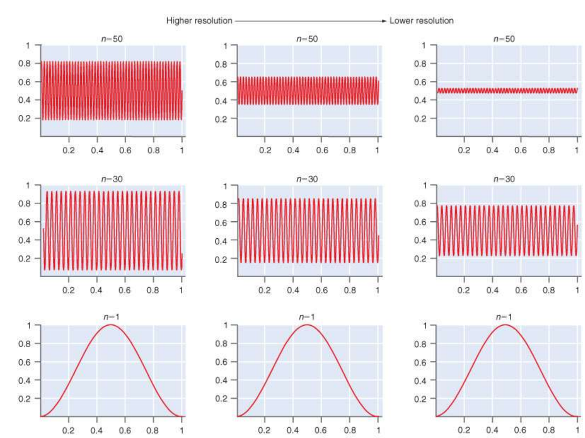
Graph of $\psi_n^2(x)$ / $[\psi_1^2(x)]_{max}$



Bohr correspondence principle
Result of Q.M 'approach' to the C.M when classical limit

Exercise:

- For particle in a box show:

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = 1 \qquad \text{if } i = j$$

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = 0, \qquad i \neq j$$

Example:
Find the probability of finding the particle in the first tenth (from 0 to L/10) of the box for n = 1, 2, and 3 states.

Solution: The wavefunction is given by:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

To find the probability in a region, the probability density must be integrated over that region of space.

$$P_n = \int_0^{L/10} \left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right]\left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right] dx = \frac{2}{L}\int_0^{L/10} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\int \sin^2(cx)\,dx = \frac{x}{2} - \left(\frac{1}{4c}\right)\sin(2cx)$$

$$P_n = \frac{2}{L}\left[\frac{L}{20} - \left(\frac{L}{4n\pi}\right)\sin\left(\frac{2n\pi}{10}\right)\right] = \left[\frac{1}{10} - \left(\frac{1}{2n\pi}\right)\sin\left(\frac{n\pi}{5}\right)\right]$$

$$\text{For n} = 1:\ P_1 = \frac{1}{10} - \frac{1}{2\pi}\sin\left(\frac{\pi}{5}\right) \cong 0.0064$$

$$\text{For n} = 2:\ P_2 = \frac{1}{10} - \frac{1}{4\pi}\sin\left(\frac{2\pi}{5}\right) \cong 0.024$$

$$\text{For n} = 3:\ P_3 = \frac{1}{10} - \frac{1}{6\pi}\sin\left(\frac{3\pi}{5}\right) \cong 0.050$$

Exercise:
For the particle in a one-dimensional box of length l, we could have put the coordinate origin at the center of the box. Find the wave functions and energy levels for this choice of origin.

The free particle in one dimension

F = 0 → V = cte

V(x) = 0

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

$$\psi = c_1 e^{i(2mE)^{1/2}x/\hbar} + c_2 e^{-i(2mE)^{1/2}x/\hbar}$$

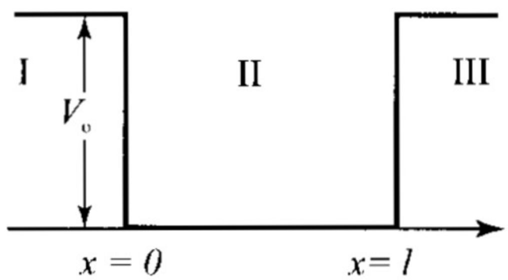
It seems reasonable to postulate that ψ will remain finite as x goes to ±∞.

For E < 0:

$$i(2mE)^{1/2} = i(-2m|E|)^{1/2} = i \cdot i \cdot (2m|E|)^{1/2} = -(2m|E|)^{1/2}$$

$$\boxed{E \geq 0}$$

Particle in a rectangular well



V = V_0 for x < 0,,

V = 0 for 0 ≤ x ≤ l

V = V_0 for x > l

Particle in a rectangular well

$E < V_0$

$$d^2\psi/dx^2 + (2m/\hbar^2)(E - V_0)\psi = 0$$

$$s^2 + (2m/\hbar^2)(E - V_0) = 0$$

$$s = \pm(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}$$

$$\psi_{\mathrm{I}} = C \exp\,[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x] + D \exp\,[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x]$$

$$\psi_{\mathrm{III}} = F \exp\,[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x] + G \exp\,[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x]$$

$x \to -\infty$ $\quad D = 0$

$x \to +\infty$ $\quad F = 0$

Particle in a rectangular well

$$\psi_{\mathrm{I}} = C \exp\left[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x\right]$$

$$\psi_{\mathrm{III}} = G \exp\left[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x\right]$$

In region II, $V = 0$.

$$\psi_{\mathrm{II}} = A \cos\left[(2m/\hbar^2)^{1/2}E^{1/2}x\right] + B \sin\left[(2m/\hbar^2)^{1/2}E^{1/2}x\right]$$

Particle in a rectangular well

$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$ $\quad x = 0$

$\psi_{\mathrm{II}}(l) = \psi_{\mathrm{III}}(l)$ $\quad x = l$

$d\psi_{\mathrm{I}}/dx = d\psi_{\mathrm{II}}/dx$ $\quad x = 0$

$d\psi_{\mathrm{II}}/dx = d\psi_{\mathrm{III}}/dx$ $\quad x = l$

if d/dx changed discontinuously
at a point then its derivative
$d^2\psi/dx^2$ would become
infinite at that point.
$d^2\psi/dx^2 = (2m/\hbar^2)(V - E)\psi$
does not contain anything
infinite on the right

$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$ $\quad C = A$

$\psi'_{\mathrm{I}}(0) = \psi'_{\mathrm{II}}(0)$ $\quad B = (V_0 - E)^{1/2}A/E^{1/2}$

$\psi_{\mathrm{II}}(l) = \psi_{\mathrm{III}}(l)$ $\quad$ G as a function of A

Particle in a rectangular well

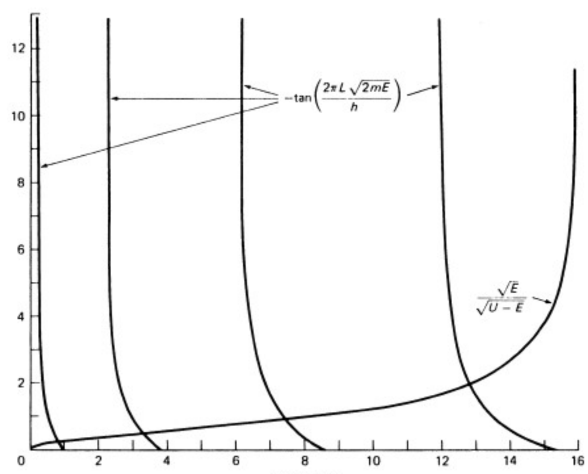
$$\psi'_{\mathrm{II}}(l) = \psi'_{\mathrm{III}}(l)$$

$$\psi_{\mathrm{II}}(l) = \psi_{\mathrm{III}}(l)$$

$$(2E - V_0)\sin\left[(2mE)^{1/2}l/\hbar\right] = 2(V_0E - E^2)^{1/2}\cos\left[(2mE)^{1/2}l/\hbar\right]$$

$$\varepsilon \equiv E/V_0 \qquad b \equiv (2mV_0)^{1/2}l/\hbar$$

$$(2\varepsilon - 1)\sin(b\varepsilon^{1/2}) - 2(\varepsilon - \varepsilon^2)^{1/2}\cos(b\varepsilon^{1/2}) = 0$$



Graphical solution of the equation tan(2πL√2mE/h) =√E/√U −E. Here L = 2.50 nm, m = 9.11 × 10−31 kg, U = 1 eV = 16.02 × 10−20 J. Intersections occur at E = 0.828×10−20 J, 3.30×10−20 J, 7.36×10−20 J and 12.8×10−20 J.

Particle in a rectangular well

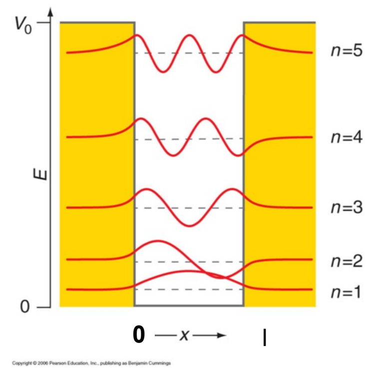
$$N - 1 < b/\pi \leq N$$

$$b \equiv (2mV_0)^{1/2} l/\hbar$$

$$V_0 = h^2/ml^2$$

$$b/\pi = 2(2^{1/2}) = 2.83$$

$$N = 3$$

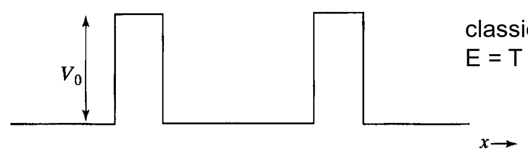


bound states when E < V_0 **unbound states when E > V_0**

- ✓ For E > V_0, $(V_0 - E)^{1/2}$ is imaginary → all energies above V_0 are allowed.
- ✓ A state in which $\psi \to 0$ as $x \to \infty$ and as $x \to -\infty$ is called a bound state.
- ✓ For an unbound state, ψ does not go to zero as $x \to \pm\infty$ and is not normalizable.
- ✓ For the particle in a rectangular well, states with E < V_0 are bound and states with E > V_0 are unbound.
- ✓ For the particle in a box with infinitely high walls, all states are bound.
- ✓ For the free particle, all states are unbound.

Tunneling

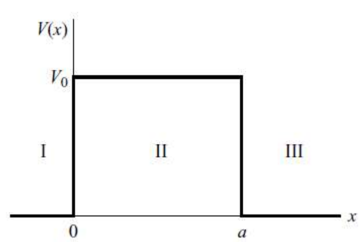
Tunneling: the penetration of a particle into a classically forbidden region or the passage of a particle through a potential-energy barrier whose height exceeds the particle's energy.



classical equations
E = T + V

- ✓ The emission of alpha particles from a radioactive nucleus
- ✓ The inversion of the NH_3 pyramidal molecule
- ✓ Internal rotation in CH_3CH_3
- ✓ Tunneling of electrons in oxidation-reduction reactions
- ✓ The scanning tunneling microscope (STM)

Tunneling



Potential energy barrier of height V_0 and width a.

$$\begin{aligned} V(x) &= V_0, \qquad 0 \leqslant x \leqslant a \\ &= 0, \qquad x < 0, \quad x > a \end{aligned}$$

Tunneling

$$T = 16\varepsilon(1-\varepsilon)e^{-2l/D}$$ The transmission coefficient

$$\varepsilon = \frac{E}{V_0}$$

$$D = \frac{\hbar}{\{2m(V_0 - E)\}^{1/2}}$$