Chapter 8.

Quantum theory:
Techniques and applications

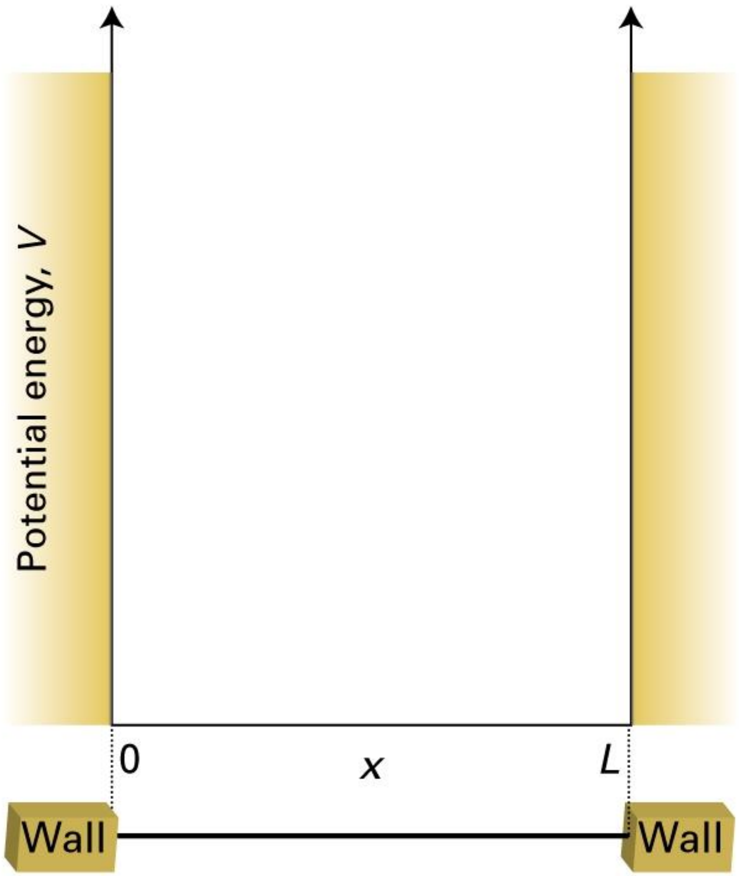
-Translational (V_k=0)
-Vibrational
-Rotational
-Techniques and approximation

Translational motion

8.1 A particle in a box
8.2 Motion in two and more dimensions
8.3 Tunnelling

8.1 A particle in a box

What is "a particle in a box"?

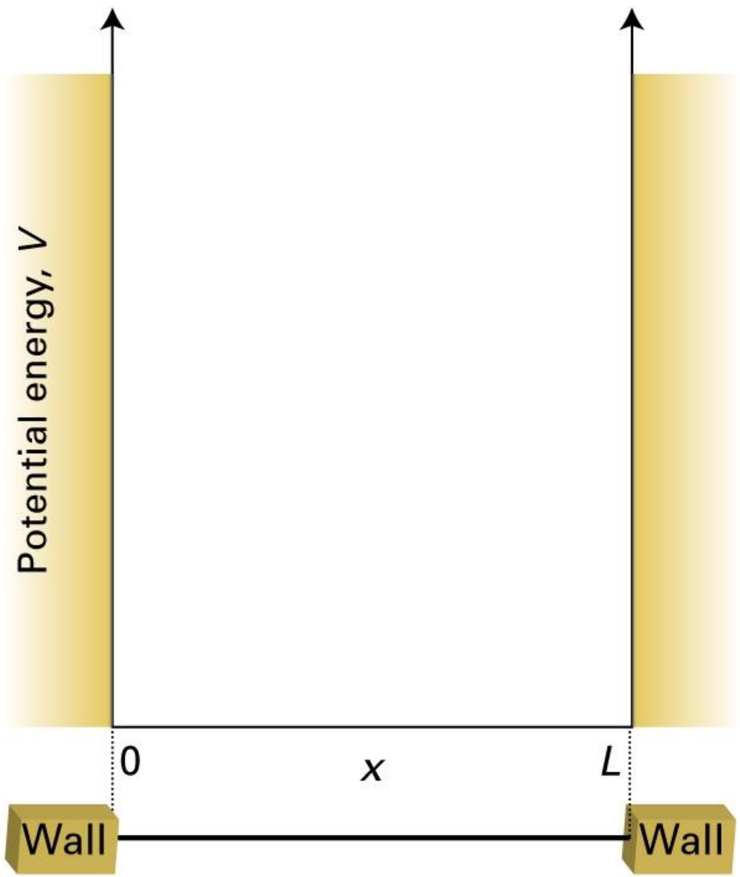


A particle (mass: m) is confined,

Outside the wall: infinite potential
Inside the wall: zero potential

Ex)
-a gas molecule in 1-d container
-Electronic structure of a metal or conjugated molecule

Energy and wavefunction of a particle in a box



$$\psi_k(x) = C\sin kx + D\cos kx$$

$$E_k = \frac{k^2\hbar^2}{2m}$$

With B.C.,

$$\psi_k(0) = \psi_k(L) = 0$$

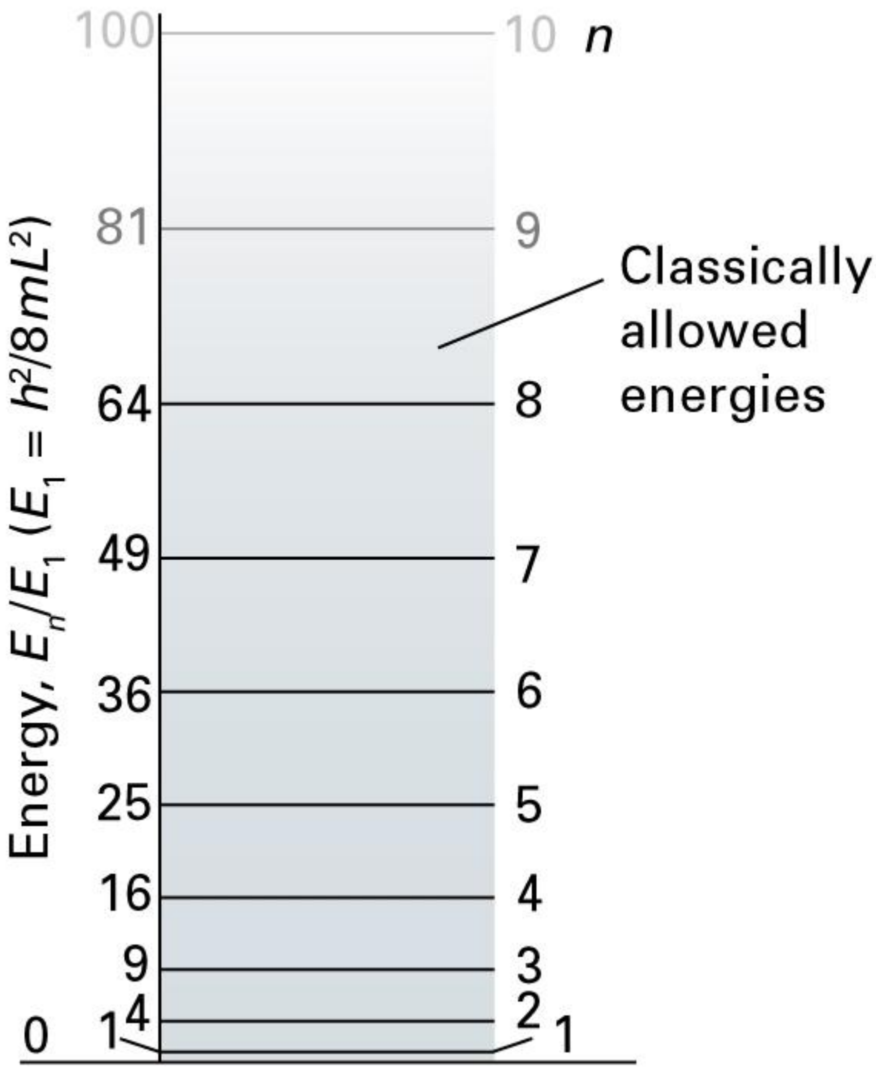
(quantized)

$$\psi_k(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$$

$$E_n = \frac{n^2h^2}{8mL^2}, n = 1, 2, \ldots$$

How about momentum?

Properties of the solutions (a particle in a box)



$$E_n = \frac{n^2 h^2}{8mL^2}, n = 1, 2, \ldots$$

Figure 8.2

$$L = n \times \tfrac{1}{2}\lambda \qquad n = 1, 2, \ldots$$

$$\lambda = \frac{2L}{n} \qquad \text{with } n = 1, 2, \ldots$$

$$p = \frac{h}{\lambda} = \frac{nh}{2L} \qquad E = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2} \qquad \text{with } n = 1, 2, \ldots$$

$$kL = n\pi \qquad n = 1, 2, \ldots$$

$$\psi_n(x) = C \sin(n\pi x/L) \qquad n = 1, 2, \ldots$$

$$\int_0^L \psi^2 \, \mathrm{d}x = C^2 \int_0^L \sin^2 \frac{n\pi x}{L} \, \mathrm{d}x$$

$$= C^2 \times \frac{L}{2} = 1, \qquad \text{so} \quad C = \left(\frac{2}{L}\right)^{1/2}$$

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L} = \frac{1}{2\mathrm{i}}\left(\frac{2}{L}\right)^{1/2}(\mathrm{e}^{\mathrm{i}kx} - \mathrm{e}^{-\mathrm{i}kx}) \qquad k = \frac{n\pi}{L}$$

The average value of the linear momentum of a particle in a box:
$\langle p \rangle = 0$

The average value of p^2 of a particle in a box:
$\langle p^2 \rangle = 0$

Existence of zero point E:
(for classical mechanics: lowest E is 0.)

$$E_1 = \frac{h^2}{8mL^2}$$

1. Location is not completely indefinite.

Momentum is non-zero.

KE is non-zero.

2. ψ is curved. -> non-zero KE
(0 at walls. But, smooth, continuous, and non-zero everywhere)

Separation E,

$$E_{n+1} - E_n = \frac{(n+1)^2h^2}{8mL^2} - \frac{n^2h^2}{8mL^2}$$

$$= (2n+1)\frac{h^2}{8mL^2}$$

For free particles, Translation E is not quantized any more.

-> the particles are not confined any more!

$$\psi^2(x) = \frac{2}{L}\sin^2\frac{n\pi x}{L}$$

When n becomes infinite,

-The particles are not bounded any more.
-the probability becomes more uniform.
-Classical mechanics emerges.

Correspondence principle

Orthogonality and the bracket notation

<u>Wave functions corresponding to different energies are orthogonal</u>

$$\int \psi_n^* \psi_{n'} \, d\tau = 0$$

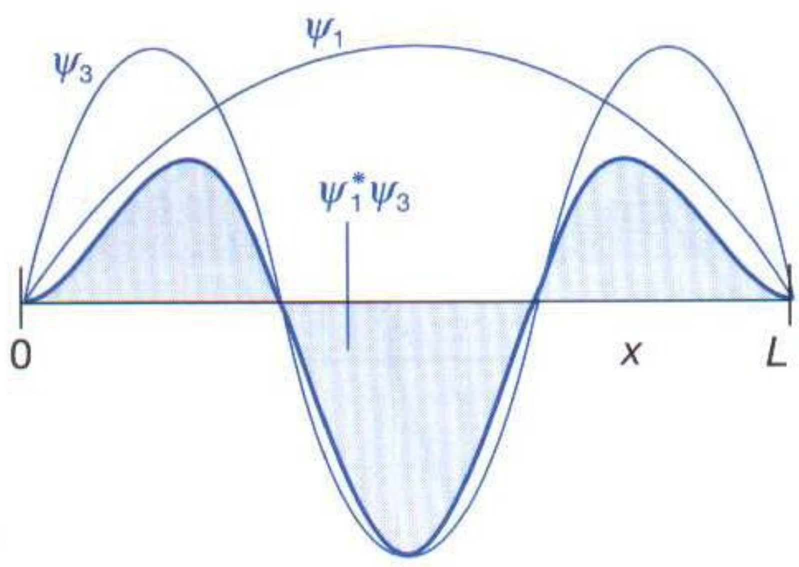
Dirac bracket notation

$$\langle n | n' \rangle = 0 \qquad (n' \neq n)$$

$$\langle n | n \rangle = 1$$

$$\langle n | n' \rangle = \delta_{nn'}$$

Kronecker delta
Orthonormal



The first five normalized wave function of a particle in a box

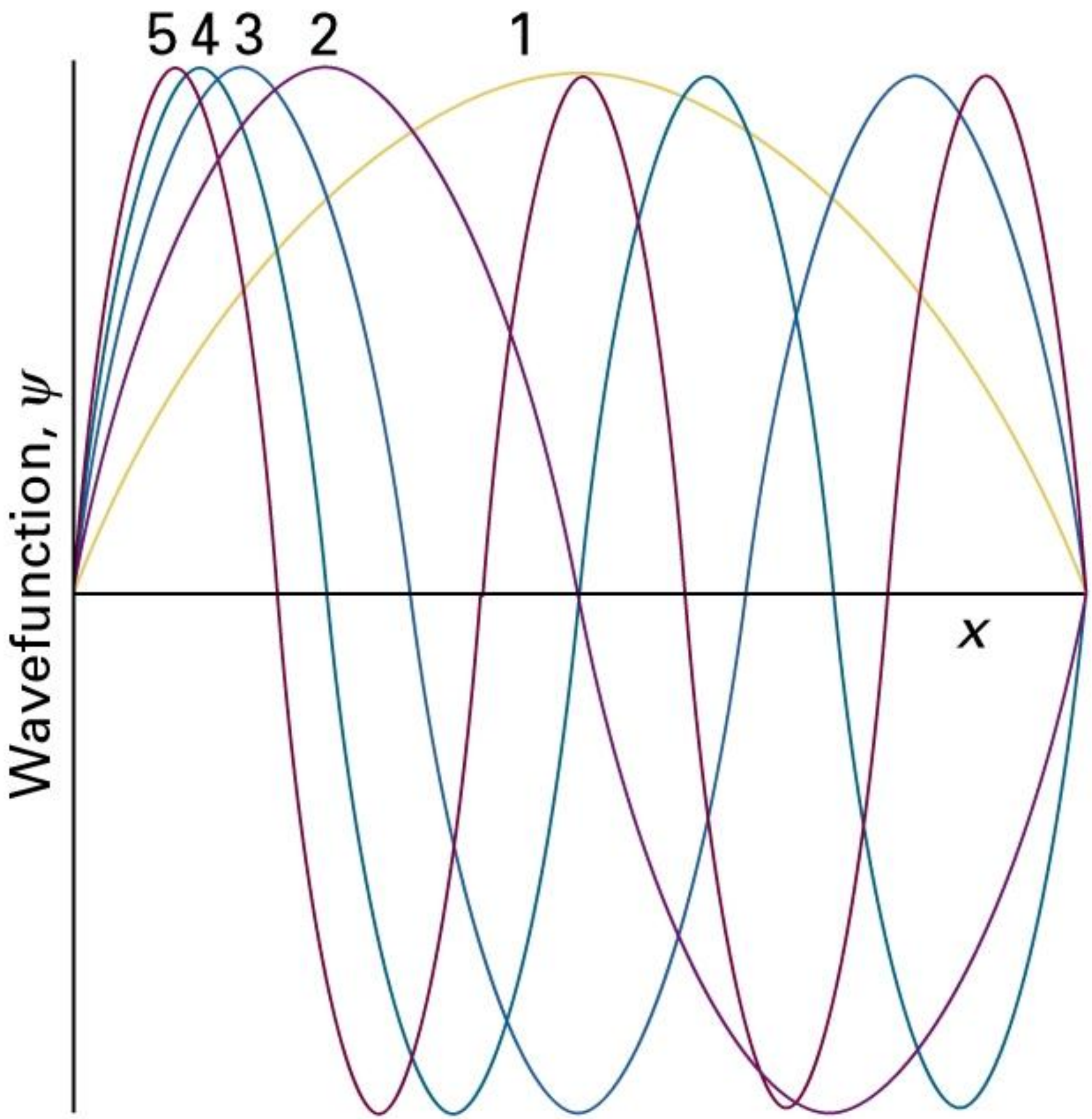
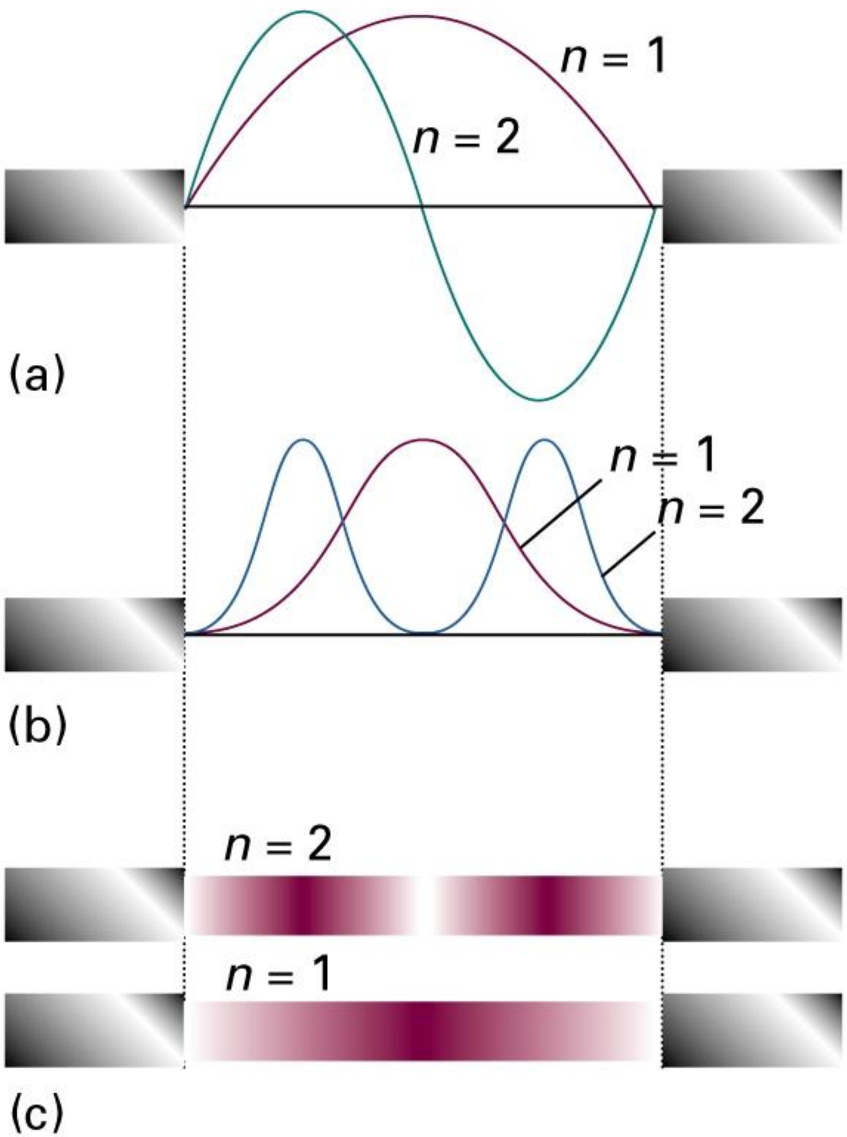


Figure 8.3



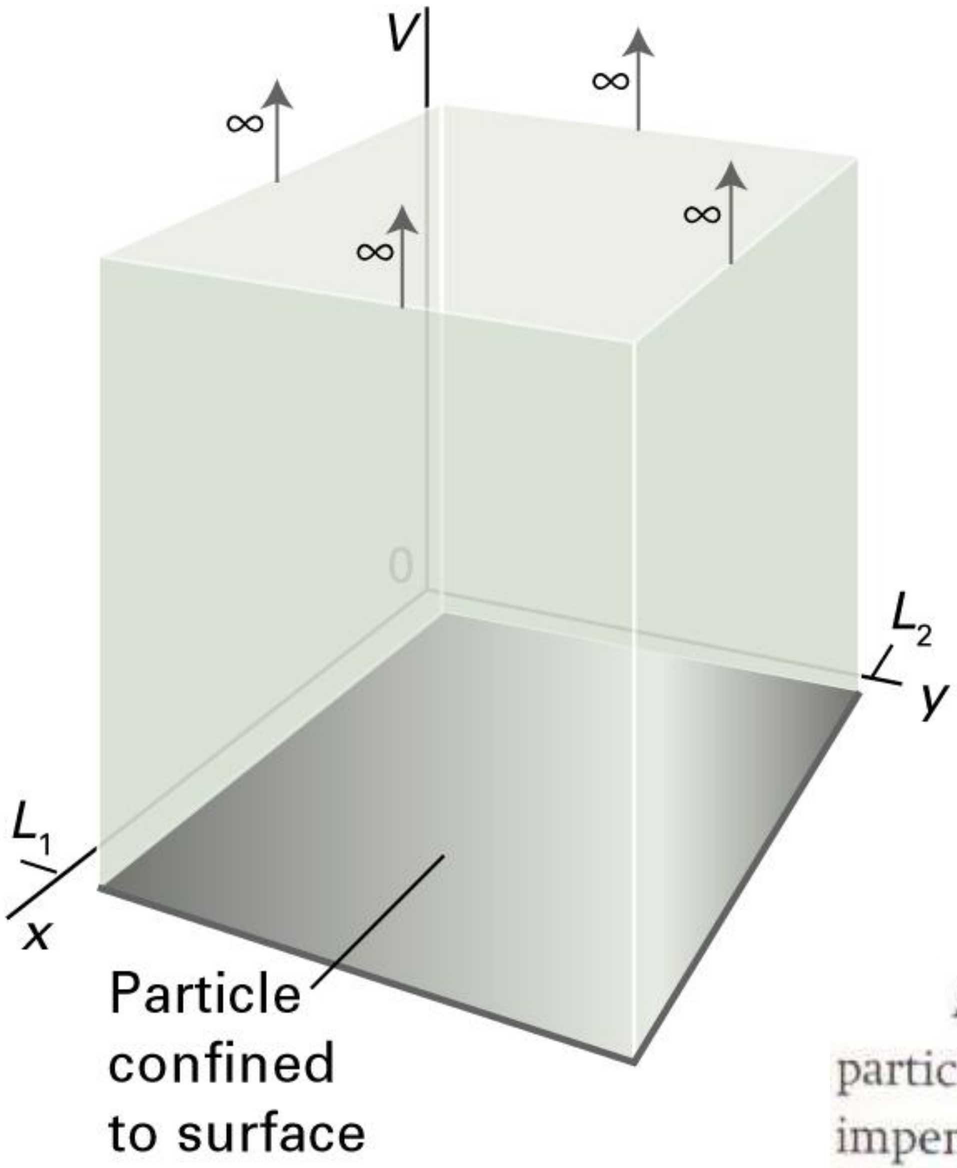
The first two normalized wave function of a particle in a box and the corresponding probability distribution

Figure 8.4

8.2 Motion in two and more dimensions

a particle in a 2-d box

Figure 8.5



A two-dimensional square well. The particle is confined to the plane bounded by impenetrable walls. As soon as it touches the walls, its potential energy rises to infinity.

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

$$\psi(x, y) = X(x)Y(y)$$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_X X \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}=E_Y Y \qquad E=E_X+E_Y$$

$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_1\pi x}{L_1} \qquad Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_2\pi y}{L_2}$$

Then, because $\psi = XY$ and $E = E_X + E_Y$, we obtain

$$\psi_{n_1,n_2}(x, y)=\frac{2}{(L_1L_2)^{1/2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2} \qquad 0\le x\le L_1,\quad 0\le y\le L_2$$

$$E_{n_1,n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m}$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi \qquad \psi(x,y)=X(x)Y(y)$$

$$\frac{\partial^2\psi}{\partial x^2}=\frac{\partial^2 XY}{\partial x^2}=Y\frac{d^2X}{dx^2} \qquad \frac{\partial^2\psi}{\partial y^2}=\frac{\partial^2 XY}{\partial y^2}=X\frac{d^2Y}{dy^2}$$

$$-\frac{\hbar^2}{2m}\left(Y\frac{d^2X}{dx^2}+X\frac{d^2Y}{dy^2}\right)=EXY$$

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}=-\frac{2mE}{\hbar^2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_XX \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}=E_YY \qquad E=E_X+E_Y$$

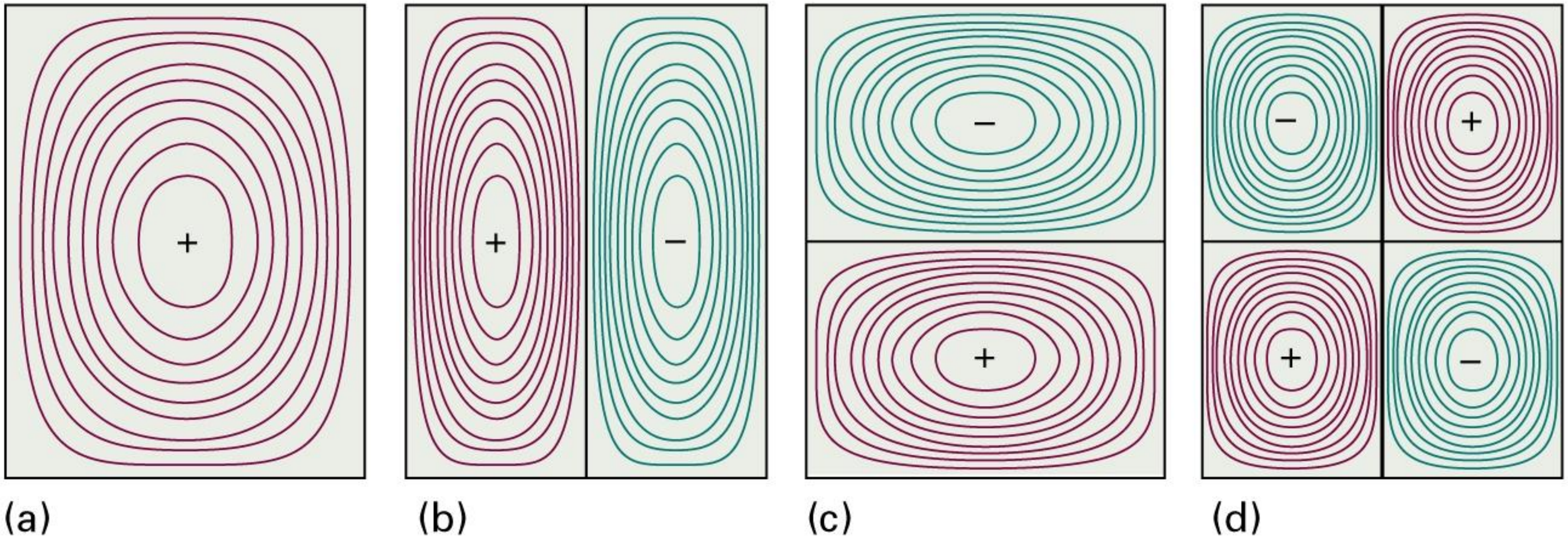
$$\frac{1}{X}\frac{d^2X}{dx^2}=-\frac{2mE_X}{\hbar^2} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2}=-\frac{2mE_Y}{\hbar^2}$$

a particle in a 3-d box

$$\psi_{n_1,n_2,n_3}(x, y, z) = \left(\frac{8}{L_1L_2L_3}\right)^{1/2} \sin\frac{n_1\pi x}{L_1} \sin\frac{n_2\pi y}{L_2} \sin\frac{n_3\pi z}{L_3}$$

$$0 \le x \le L_1, \quad 0 \le y \le L_2, \quad 0 \le z \le L_3$$

$$E_{n_1,n_2,n_3} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)\frac{h^2}{8m} \qquad (12.20)$$



The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1 = 1$, $n_2 = 1$, the state of lowest energy, (b) $n_1 = 1$, $n_2 = 2$, (c) $n_1 = 2$, $n_2 = 1$, and (d) $n_1 = 2$, $n_2 = 2$.

Figure 8.6

Degeneracy in a 2-d box

Degenerate: the same

Ex) for 2-d: square box ($\psi_{1,2} = \psi_{2,1}$)

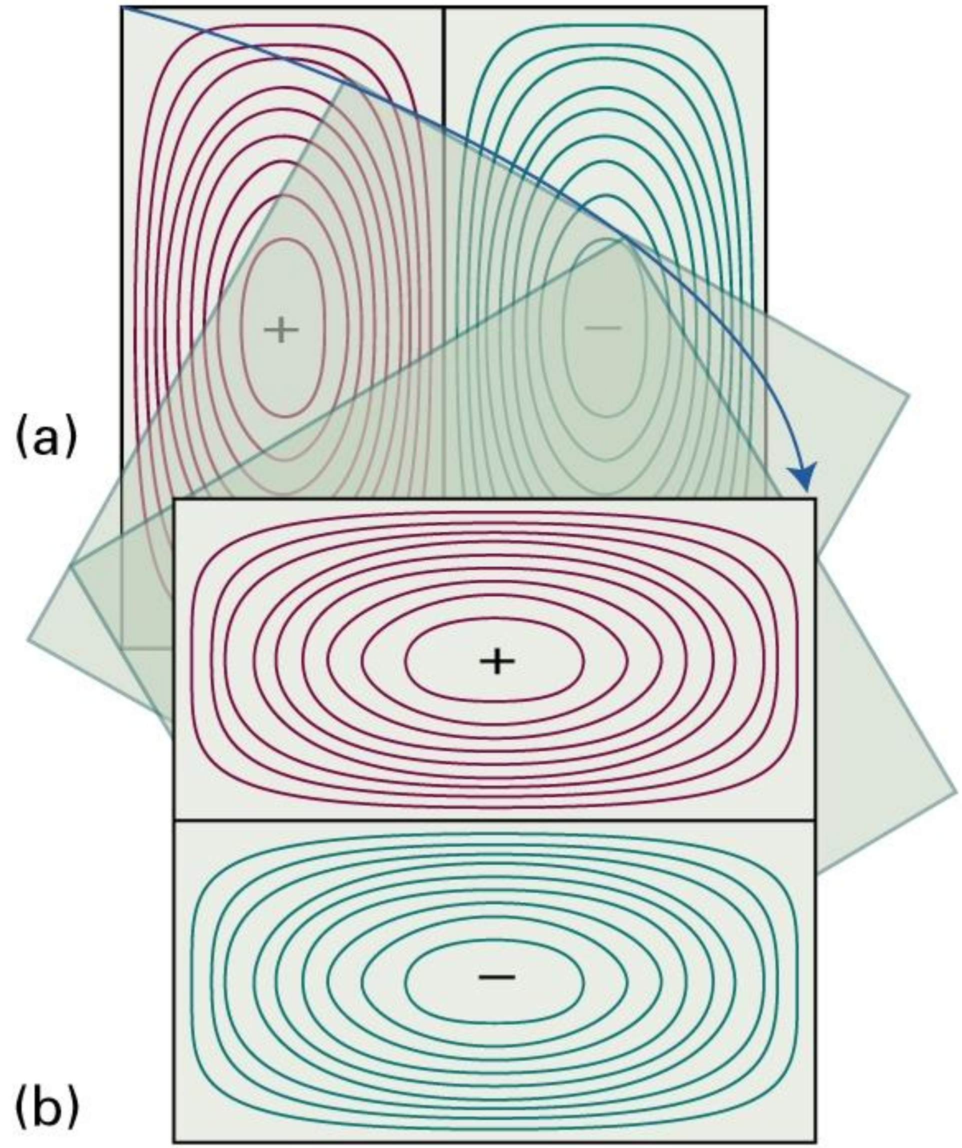


Figure 8.7

8.3 Tunnelling

Very important for light particles
: electrons, muons, and moderate for protons

Ex. Isotope dep. Rxn rate
p. 336

STM (p. 337)

When E<V, the wave function does not decay to '0' abruptly!

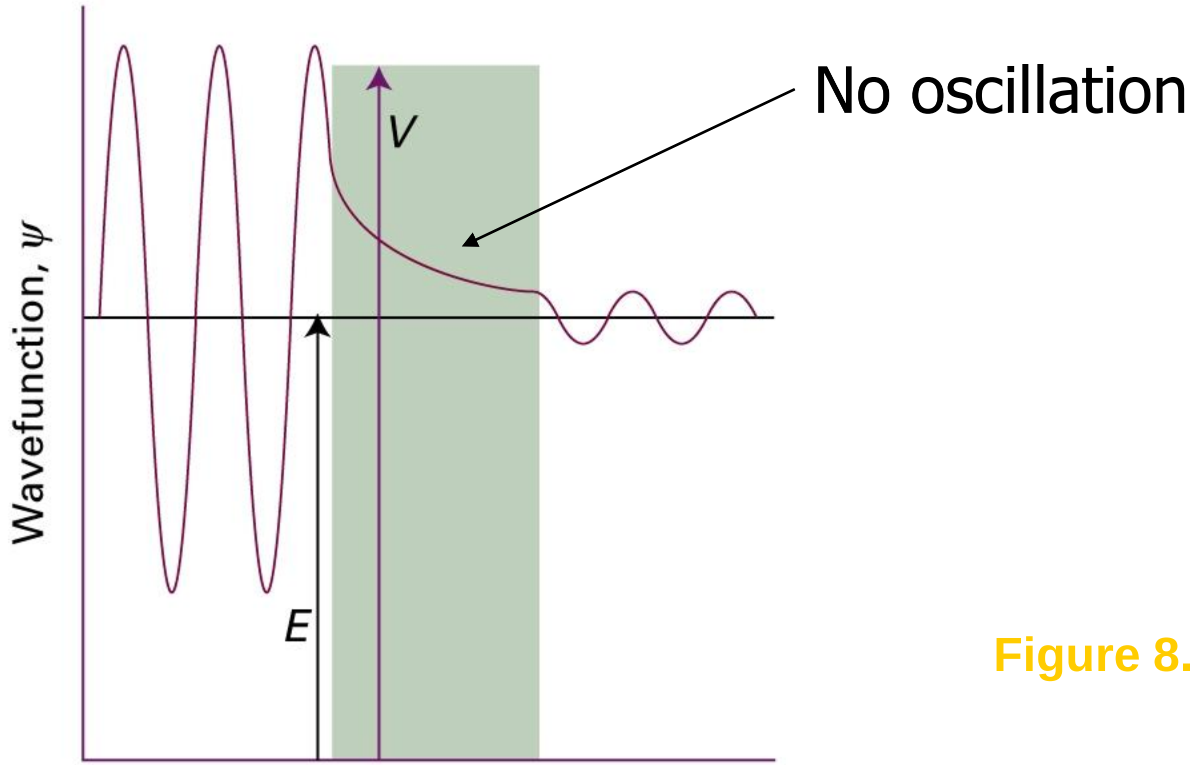


Figure 8.8

A particle incident on a barrier from the left has an oscillating wavefunction, but inside the barrier there are no oscillations (for $E < V$). If the barrier is not too thick, the wavefunction is nonzero at its opposite face, and so oscillations begin again there. (Only the real component of the wavefunction is shown.)

For, x<0, V=0

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad k\hbar = (2mE)^{1/2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$ (0<x<L, E<V)

$$\psi = Ce^{\kappa x} + De^{-\kappa x} \qquad \kappa\hbar = \{2m(V-E)\}^{1/2}$$ (since V-E>0…)

To the right of the barrier, x>L

$$\psi = A'e^{ikx} + B'e^{-ikx} \qquad k\hbar = (2mE)^{1/2}$$ (for x>L, V=0)

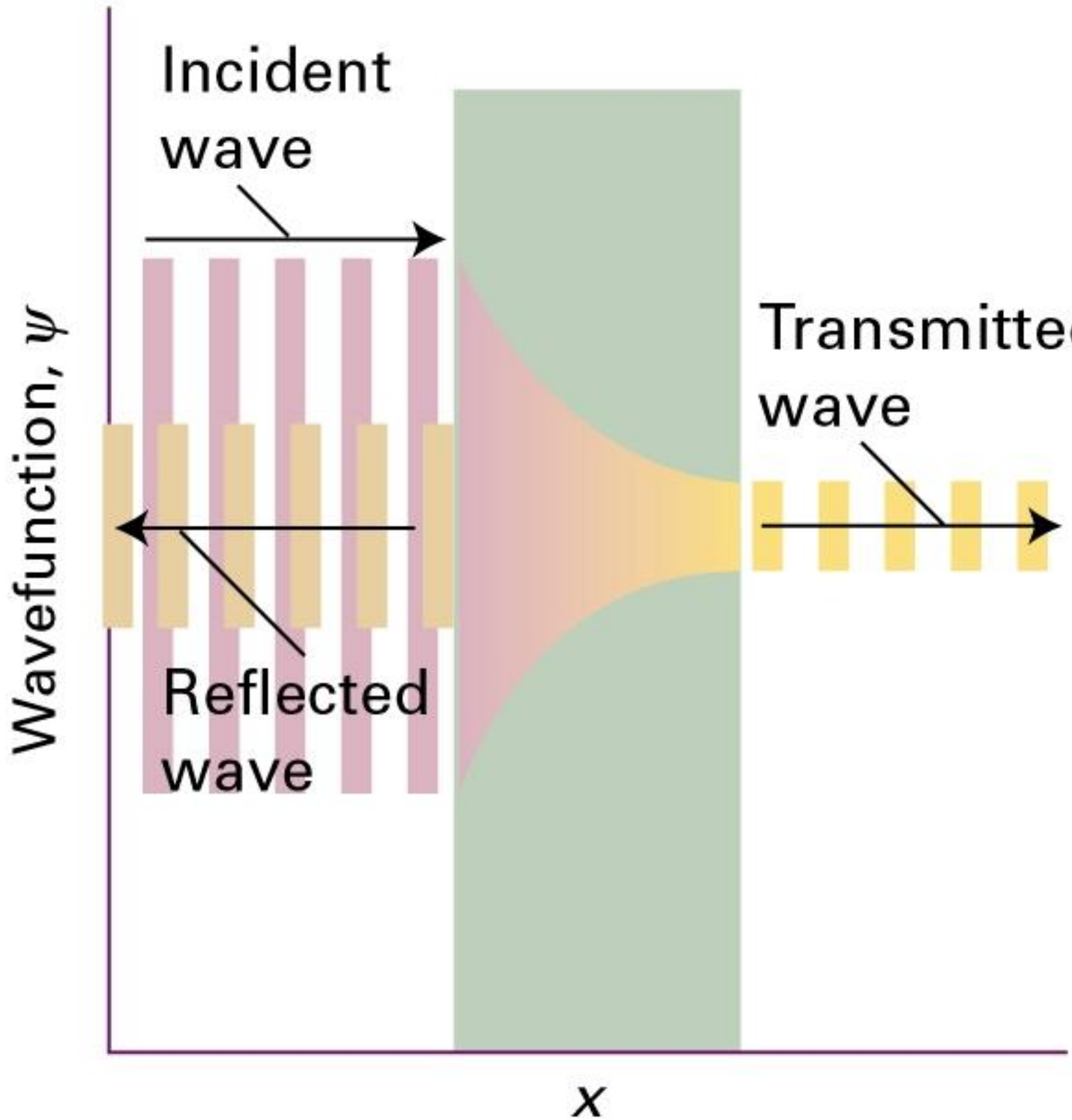

Incident
wave
Transmitted
wave
Wavefunction, ψ
Reflected
wave
x

Figure 8.9

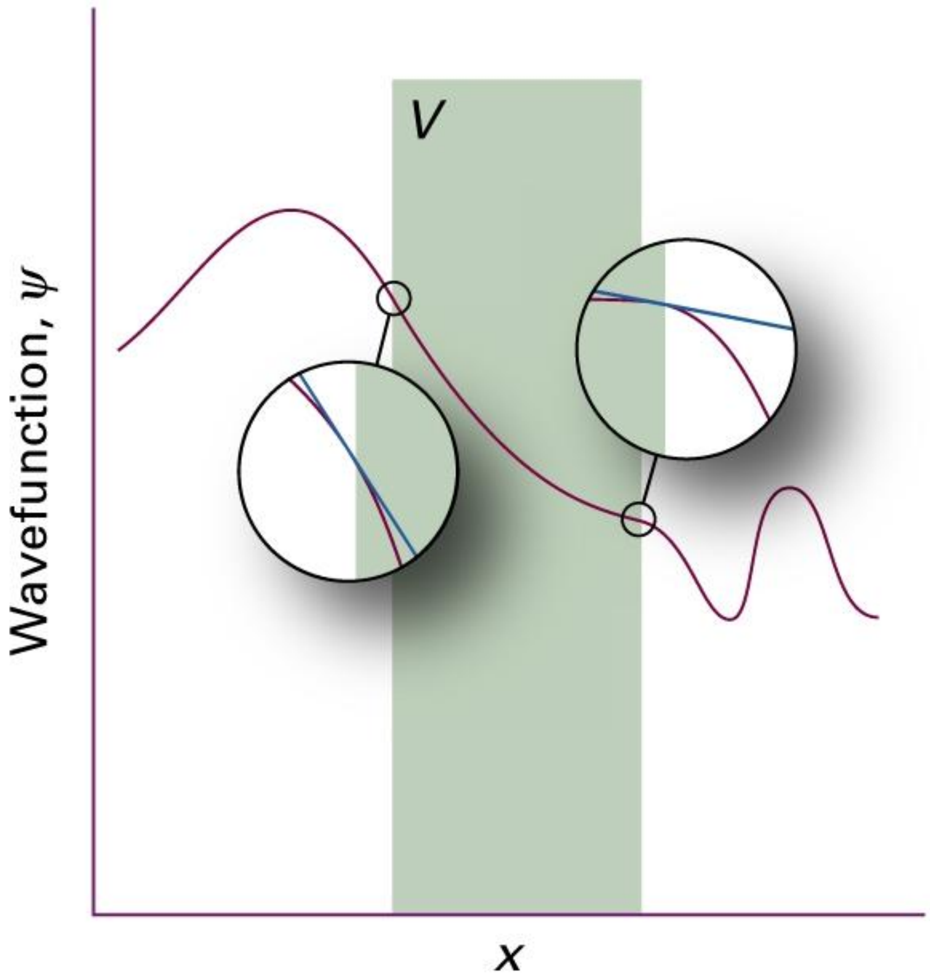


Figure 8.10

Continuity of Wavefunction and its slope at the boundary

The wavefunction and its slope should be continuous,

$$A + B = C + D \qquad Ce^{\kappa L} + De^{-\kappa L} = A'e^{ikL} + B'e^{-ikL}$$

(at x=0) (at x=L)

$$ikA - ikB = \kappa C - \kappa D \qquad \kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA'e^{ikL} - ikB'e^{-ikL}$$

(at x=0) (at x=L)

- B′=0

after the barrier no particles travelling to the left

Note. We cannot say B≠0.

Transmission probability

$$T = \frac{|A'|^2}{|A|^2}$$

$$T = \left\{1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1} \qquad \varepsilon = E/V$$

For high wide barriers, $\kappa L >> 1$

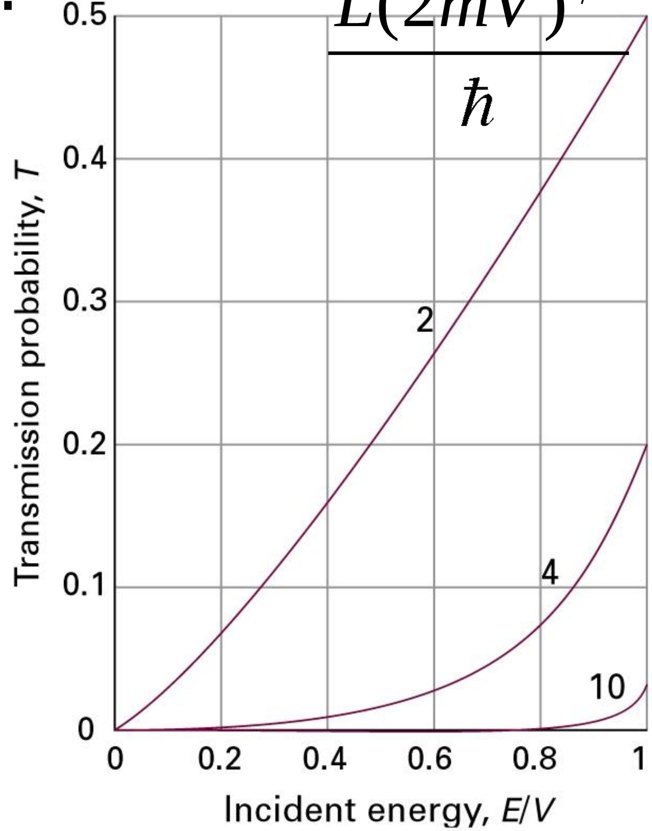
$$T \approx 16\varepsilon(1-\varepsilon)e^{-2\kappa L}$$

Classically T=0

Classically T=1

E<V:

$$\frac{L(2mV)^{1/2}}{\hbar}$$



E>V

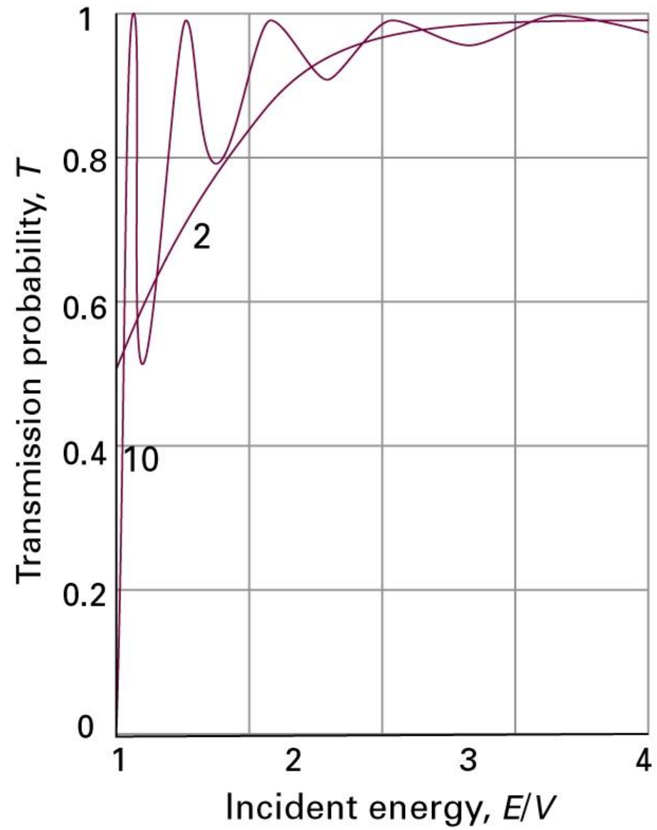
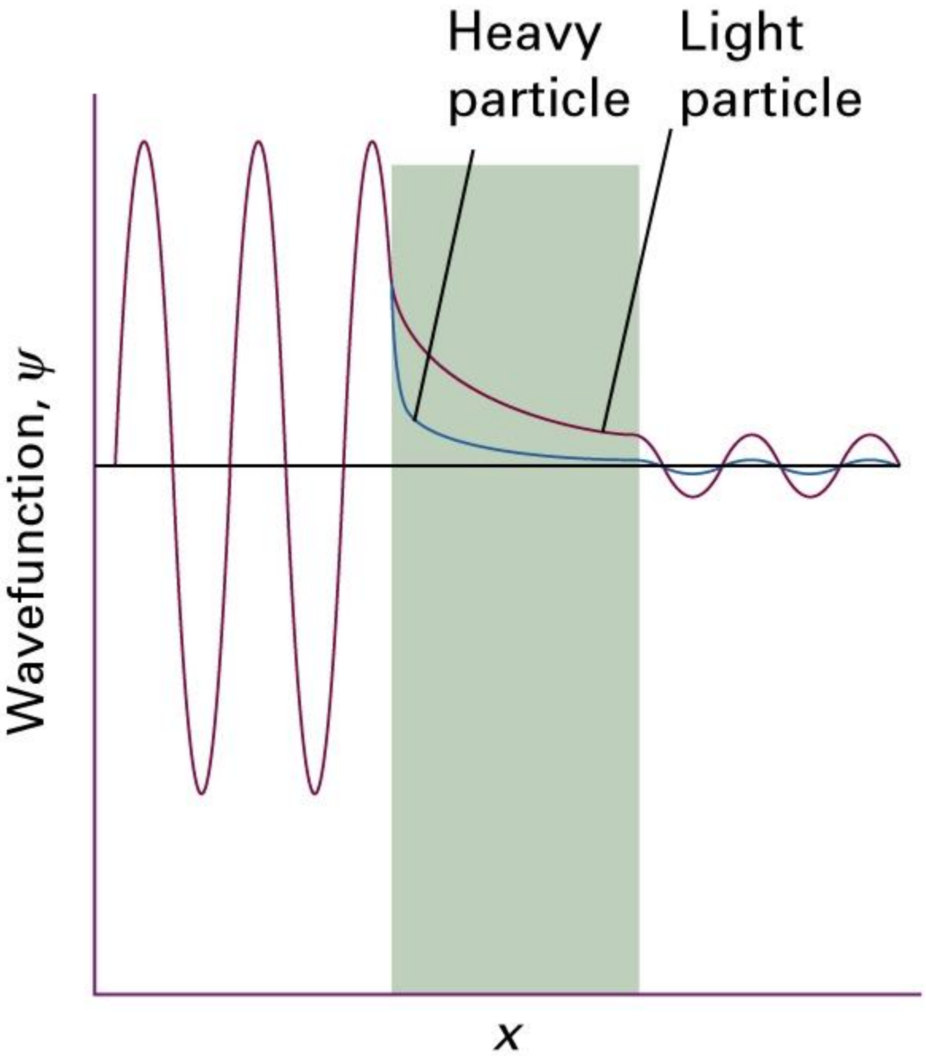


Figure 8.11

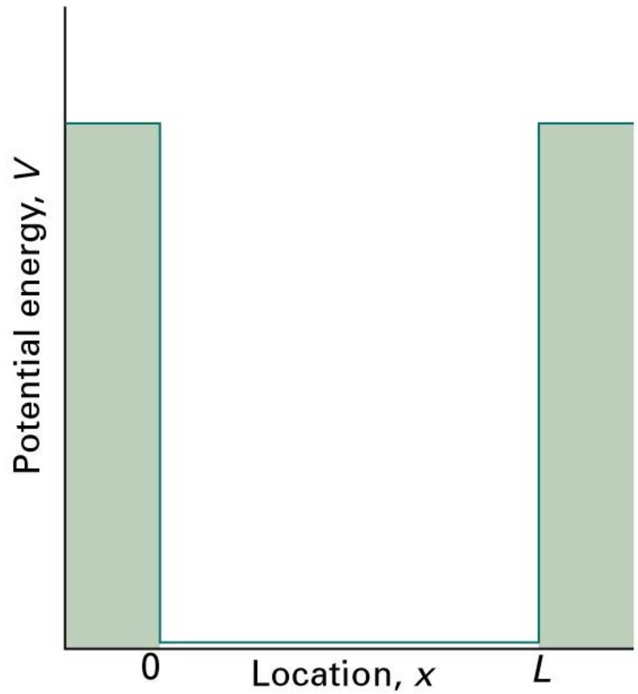
T exponentially decreases with L and $m^{1/2}$



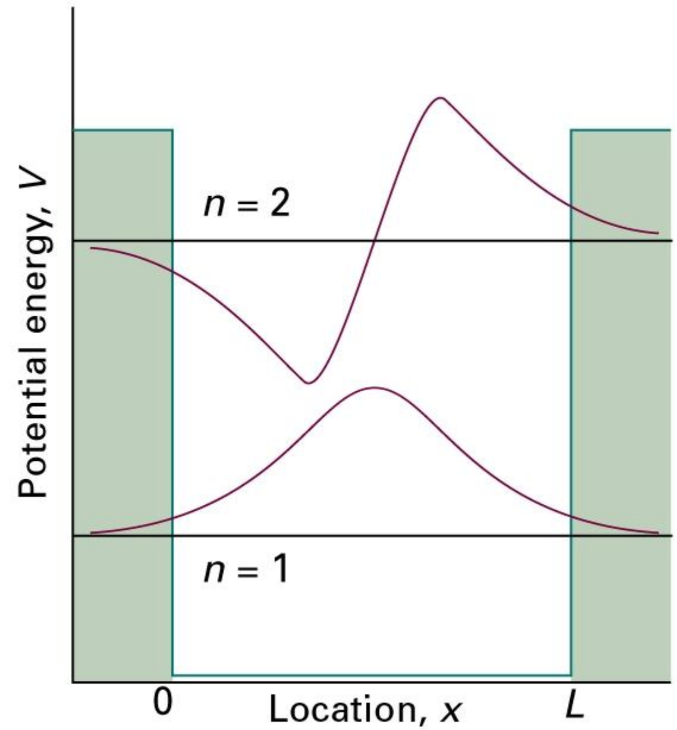
The wavefunction of a heavy particle decays more rapidly inside a barrier than that of a light particle. Consequently, a light particle has a greater probability of tunnelling through the barrier.

A particle in a square well potential of finite depth

a potential well of finite depth



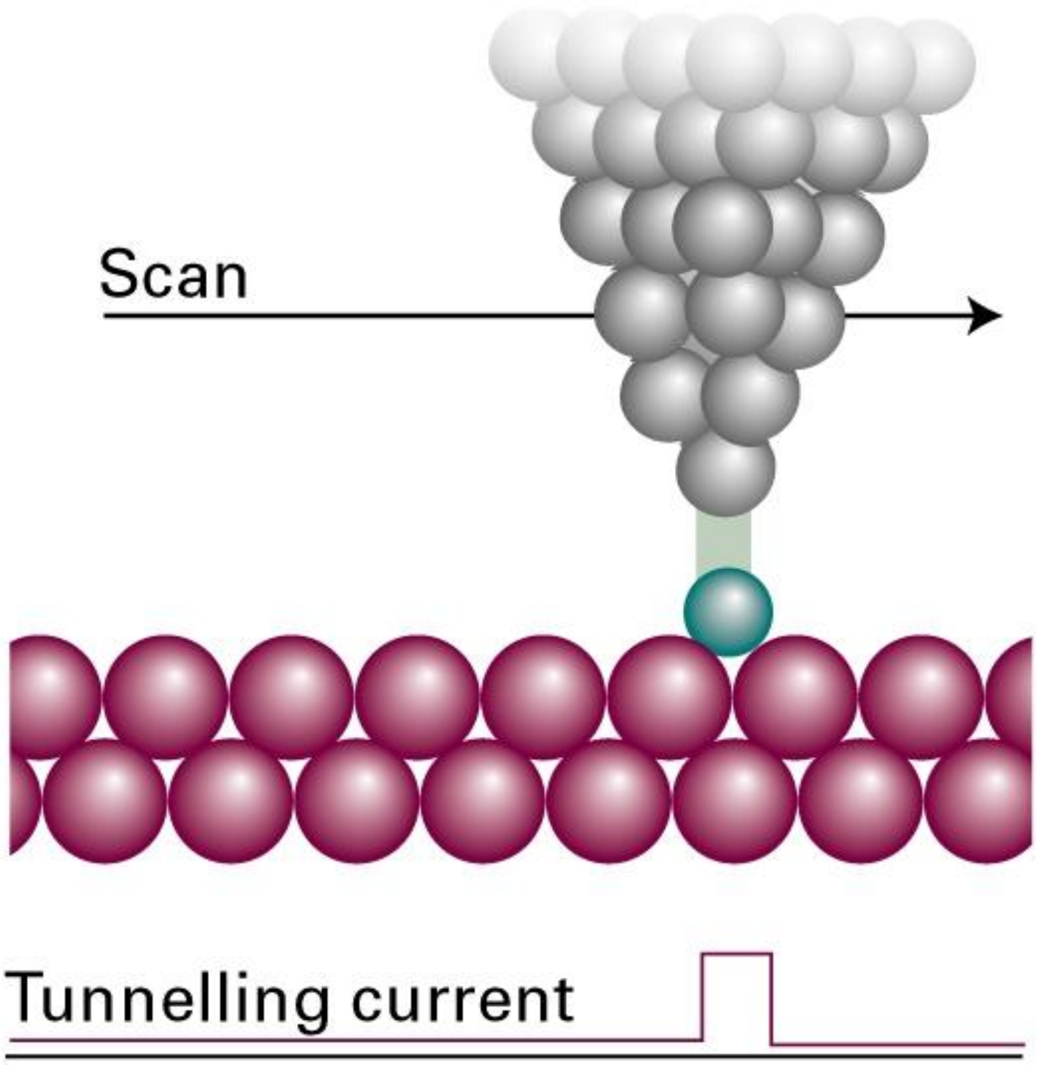
Two lowest bound-state of wavefunctions for a particle in a potential well of finite depth



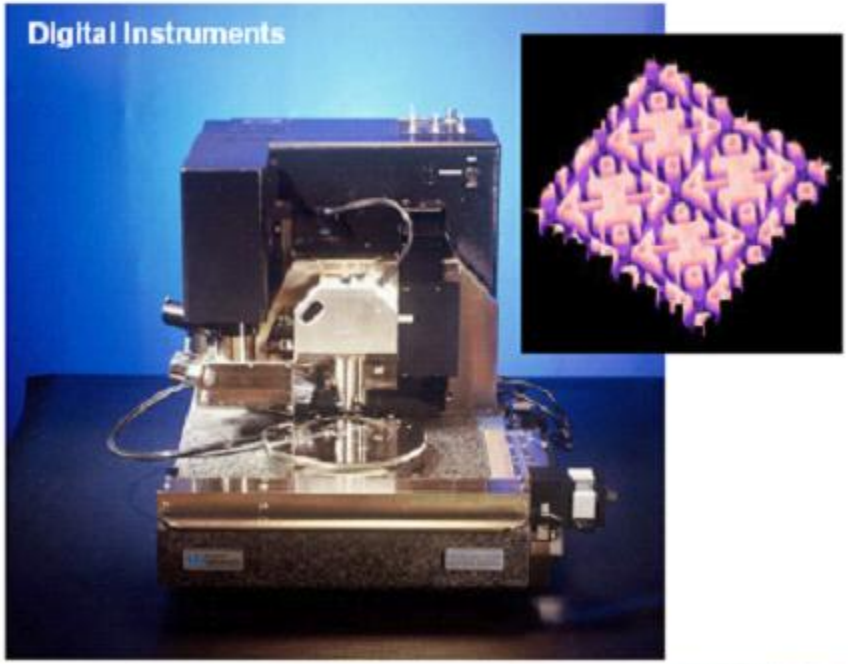
•Difference from an infinitely deep well case: finite number of bound states

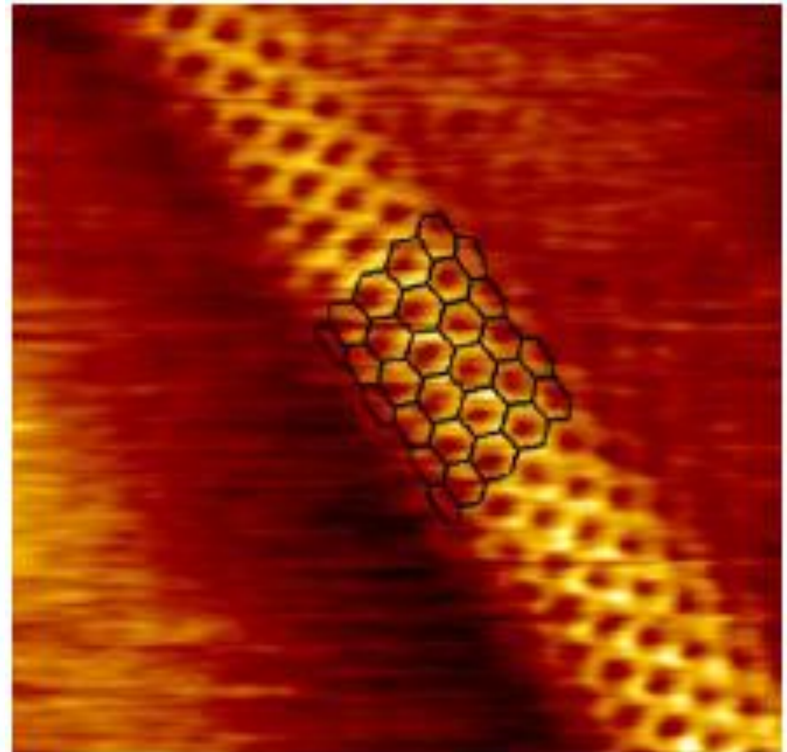
$$N - 1 < \frac{(8mVL)^{1/2}}{h} < N$$

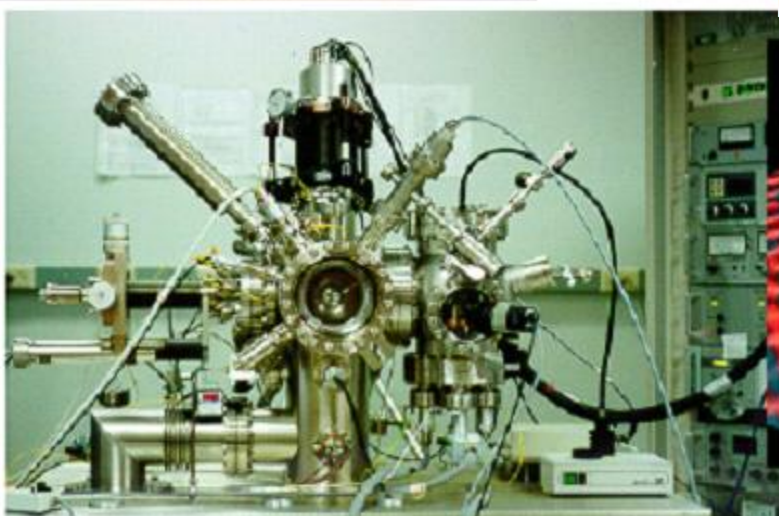
Deeper and wider: greater the # of the states

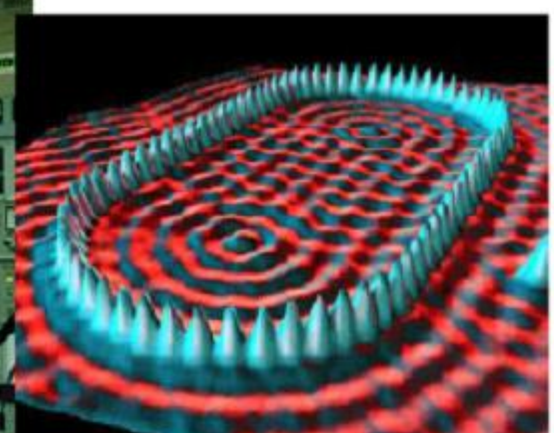

Scan
Tunnelling current

Scanning Probe Microscopy



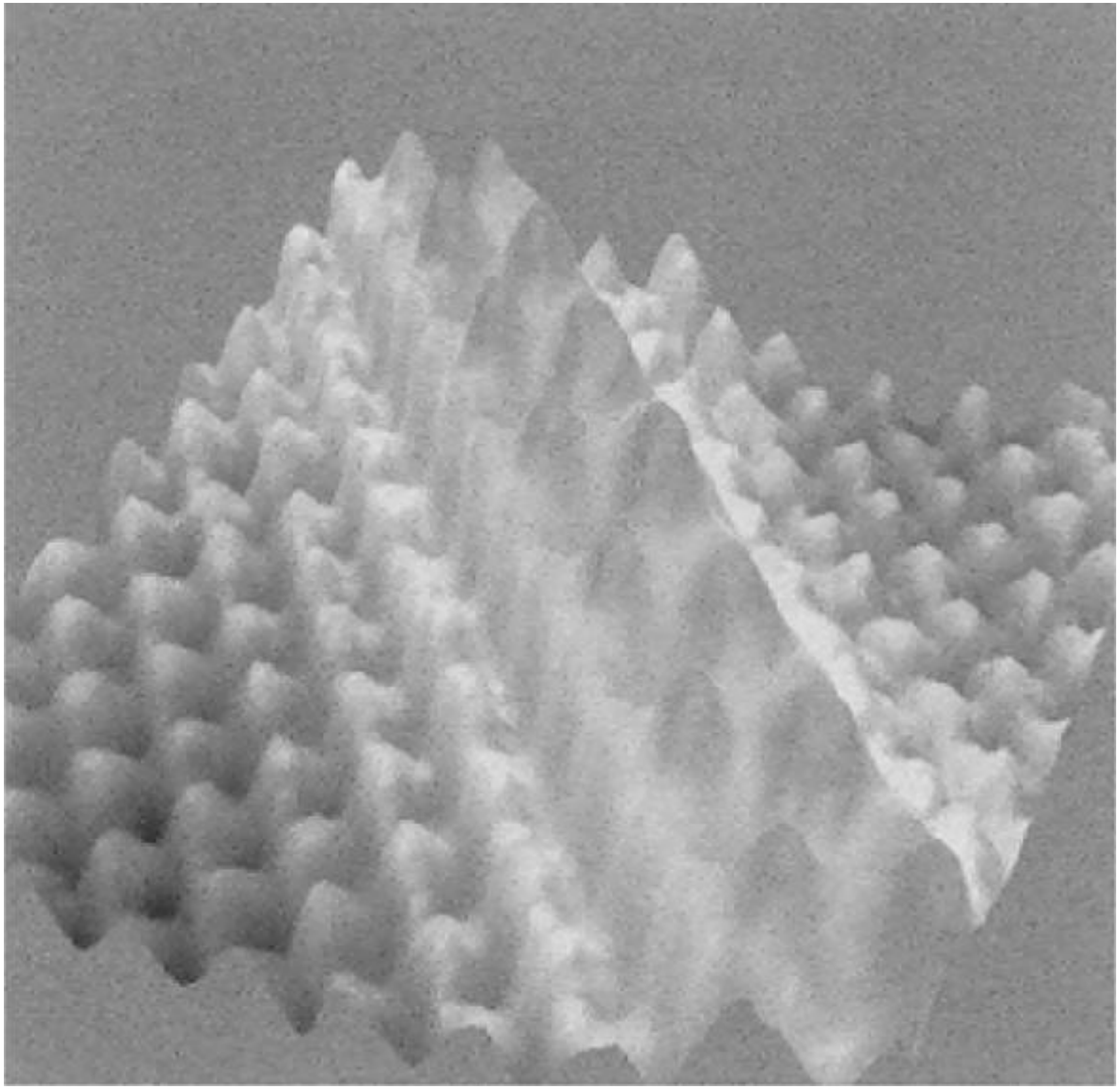






Eigler *et al.*, IBM Research

Figure 8.16



Vibrational motion

8.4 The energy levels
8.5 The wavefunctions

8.4 The energy levels

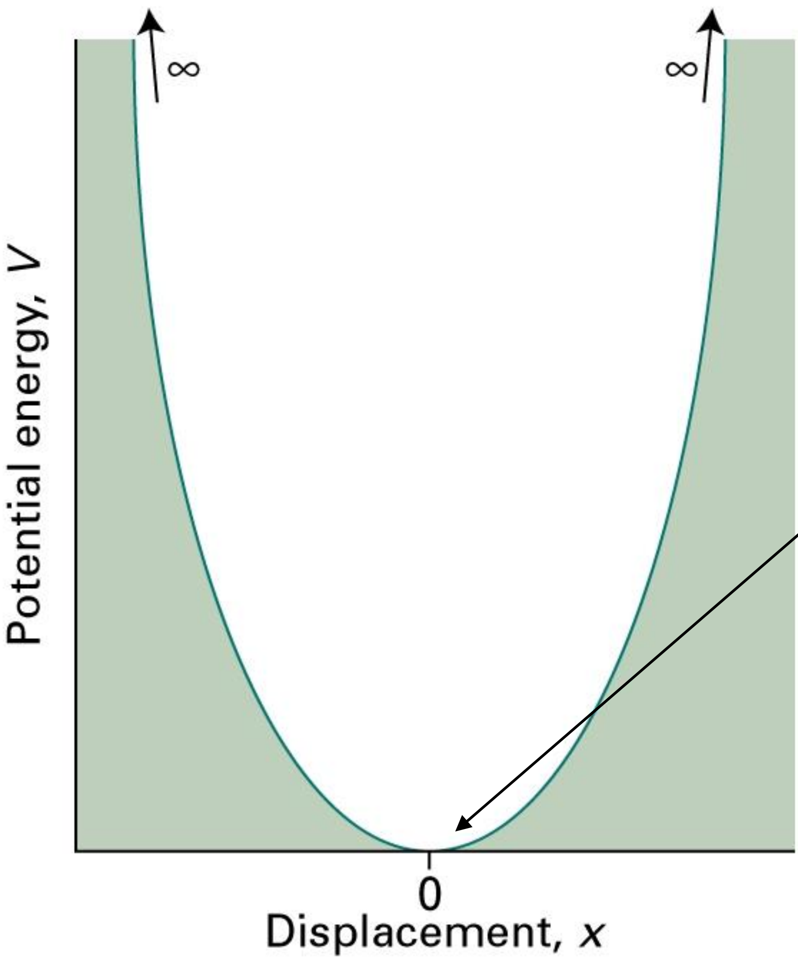
Harmonic motion of a particle
(w/ restoring force)

$$F = -kx = -\nabla V = -\frac{dV}{dx}$$

$$V = \frac{kx^2}{2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$$

Parabolic Potential E of a harmonic oscillator



$$V = \frac{kx^2}{2}$$

- Displacement at equilibrium

- Narrowness dep. on k:

larger k, narrower the wall
-> stronger confinement

Figure 8.17

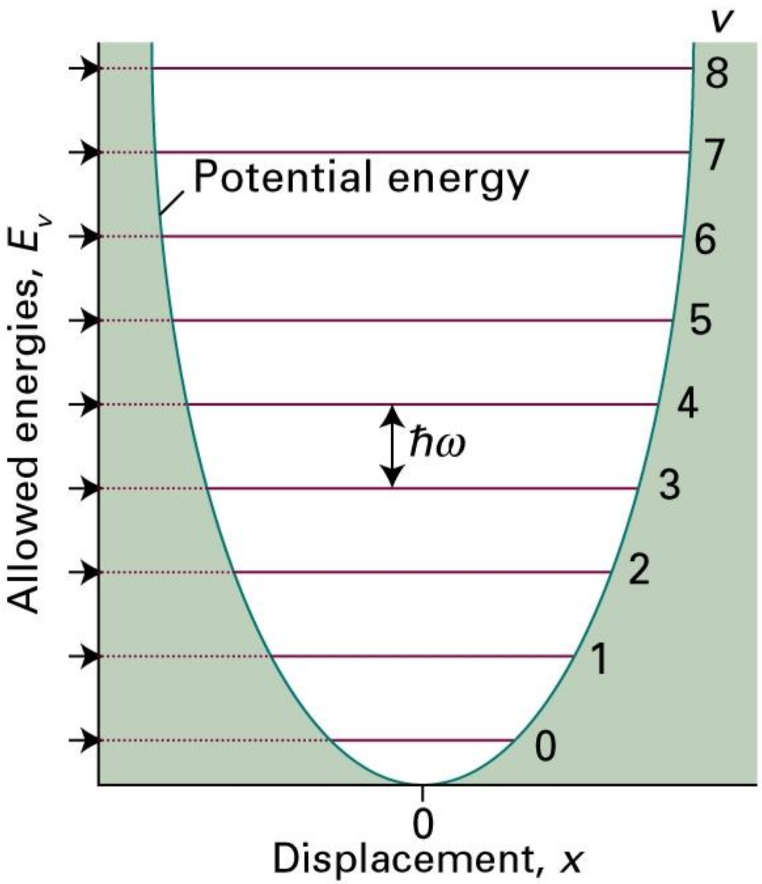


Figure 8.18

$$E_{v+1} - E_v = \hbar\omega$$

$$E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \qquad v = 0, 1, 2, \ldots$$

$$E_0 = \tfrac{1}{2}\hbar\omega$$

- For the typical molecular oscillator: E_0~30 zJ (10^{-21}J)

- Zero point E is non-zero.
  -position is not completely uncertain
  -momentum and KE is non-zero
  -particle fluctuates around eq. position

Note) Classical Mechanics allows the particle to be perfectly still.

8.5 The wavefunctions

Difference betw. Particle in a box and Harmonic motion of a particle

1. In the oscillator, $\psi \rightarrow 0$ more slowly at large x.

(P.E. is proportional to x^2.)

2. K.E. of the oscillator and curvature of the wave function depends on x in a more complex way

The form of the wavefunctions

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \qquad y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

$$\psi_0(x) = N_0 e^{-y^2/2} = N_0 e^{-x^2/2\alpha^2}$$

$$\psi_0^2(x) = N_0^2 e^{-x^2/\alpha^2}$$ (Fig 19 and 20)

$$\psi_1(x) = N_1 \times 2y\, e^{-y^2/2}$$ (Fig 21)

Hermite polynomial

The Hermite polynomials are solutions of the differential equation

$$H_v'' - 2yH_v' + 2vH_v = 0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{v+1} + 2yH_v - 2vH_{v-1} = 0$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'}H_v e^{-y^2}\,dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2}2^v v! & \text{if } v' = v \end{cases}$$

(orthogonal!!!
Not normalized yet.)

Table 8.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

The Hermite polynomials are solutions of the differential equation

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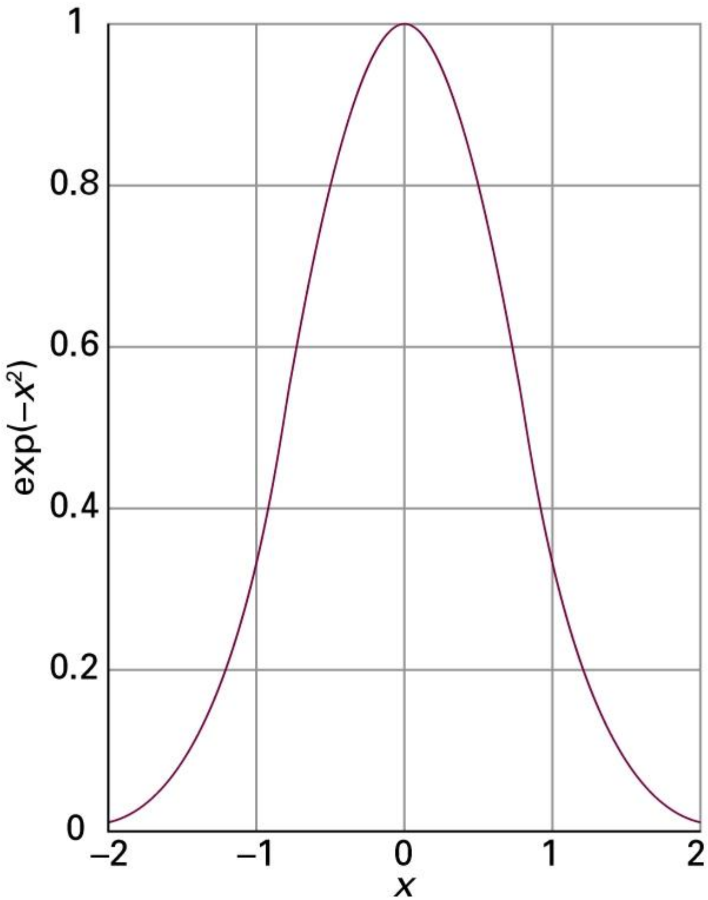
$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0$$

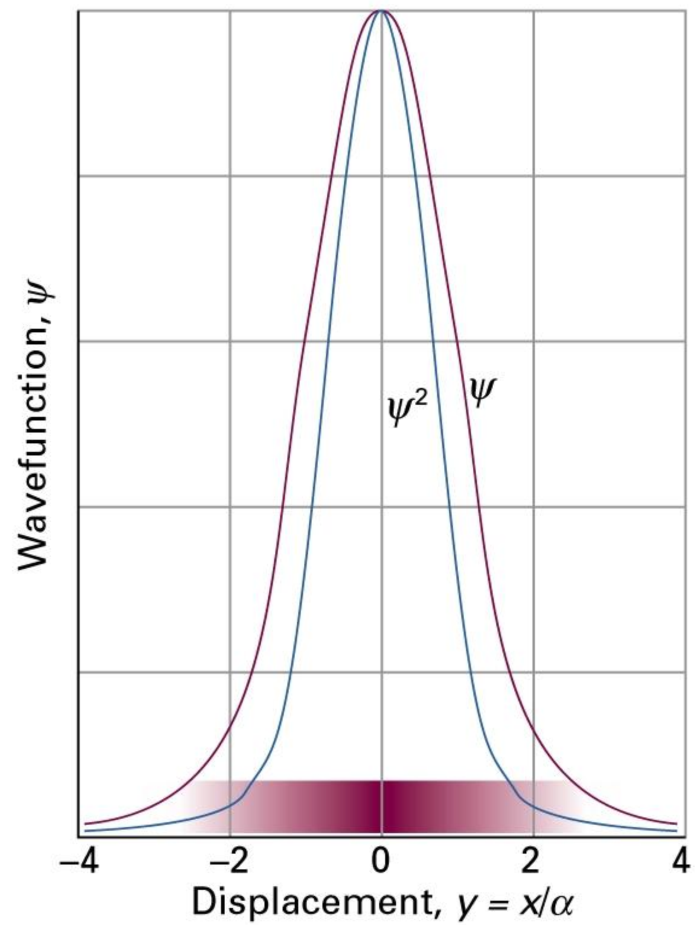
An important integral is

$$\int_{-\infty}^{\infty} H_{v'}H_v e^{-y^2}dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2}2^v v! & \text{if } v' = v \end{cases}$$

$$\psi_0^2(x) = N_0^2 e^{-x^2/\alpha^2}$$ (largest probability at eq)

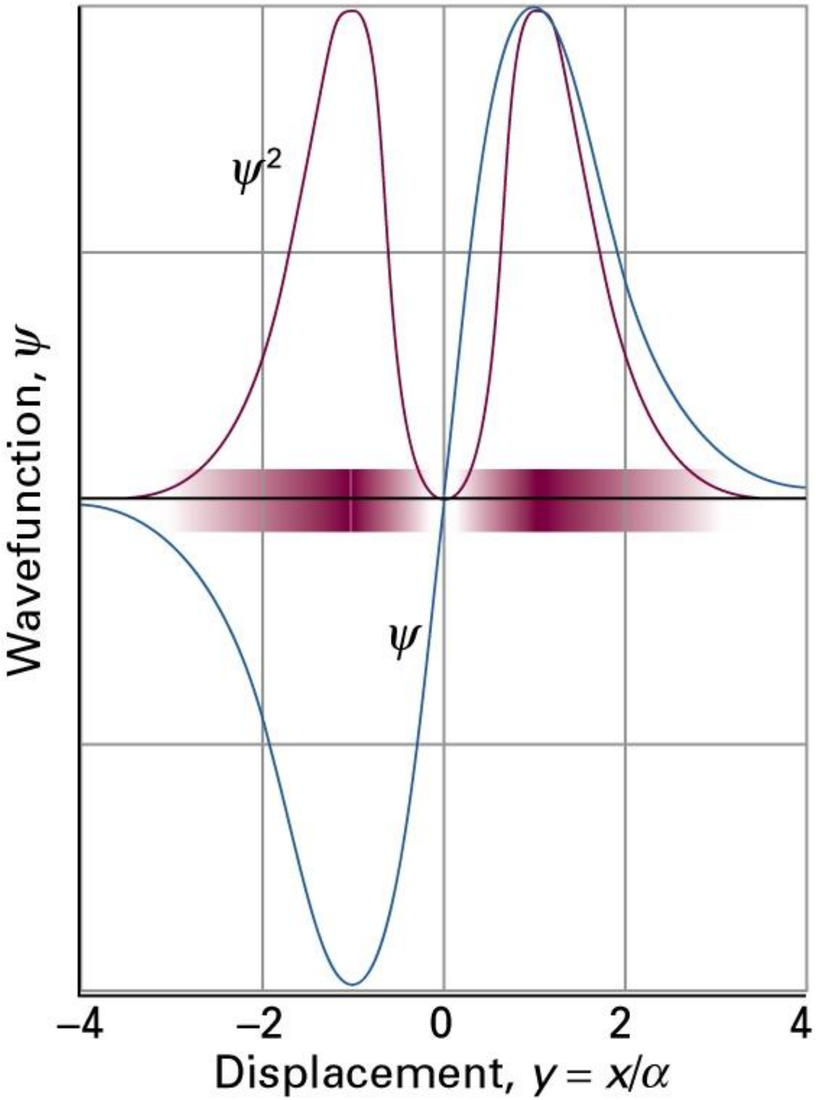


Graph of Gaussian curve



Waveftn and probability distribution for lowest E of a harmonic oscillaotr

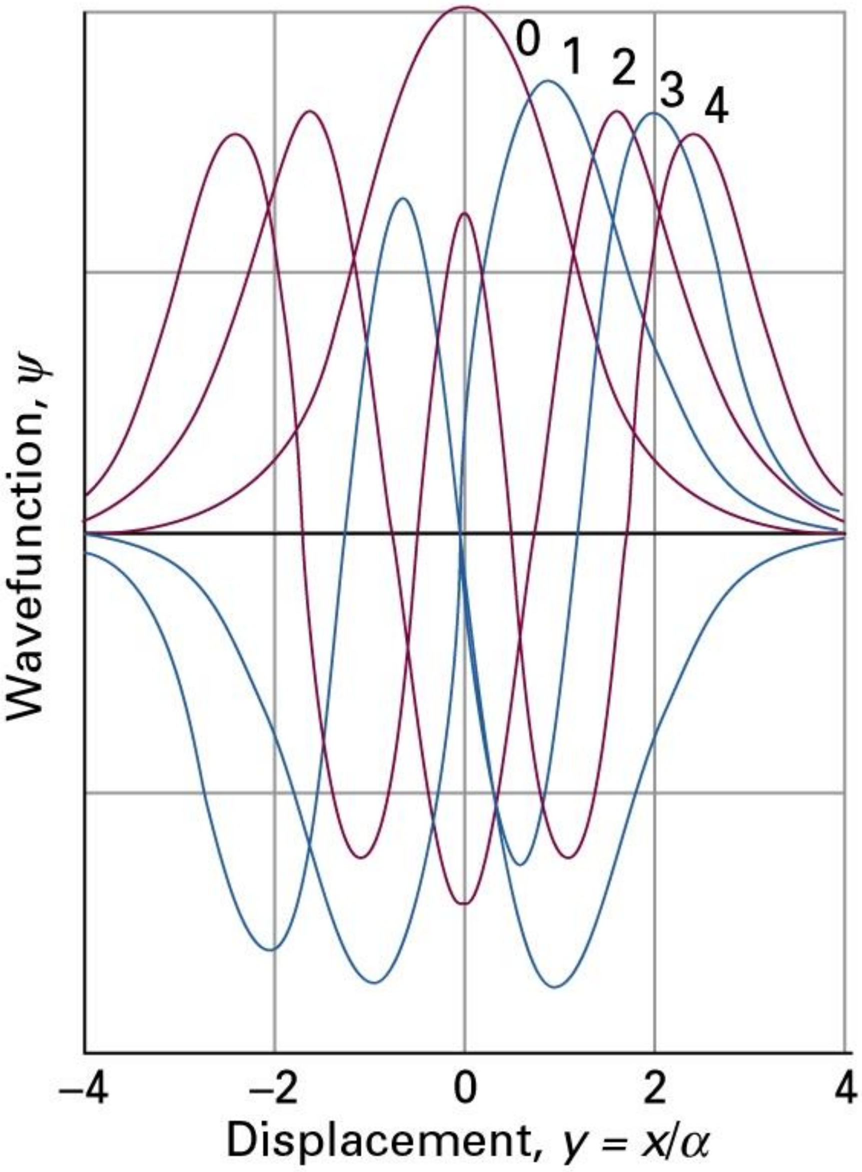
$$\psi_1(x) = N_1 \times 2y\,e^{-y^2/2}$$ (Fig 21)



Waveftn and probability distribution for the first excited state of a harmonic oscillaotr

Figure 8.21

The first 5 wavefunction



- The number of nodes are equal to v.

- Even v : symmetrical
- Odd v : antisymmetrical

Figure 8.22

The first 5 probability distribution

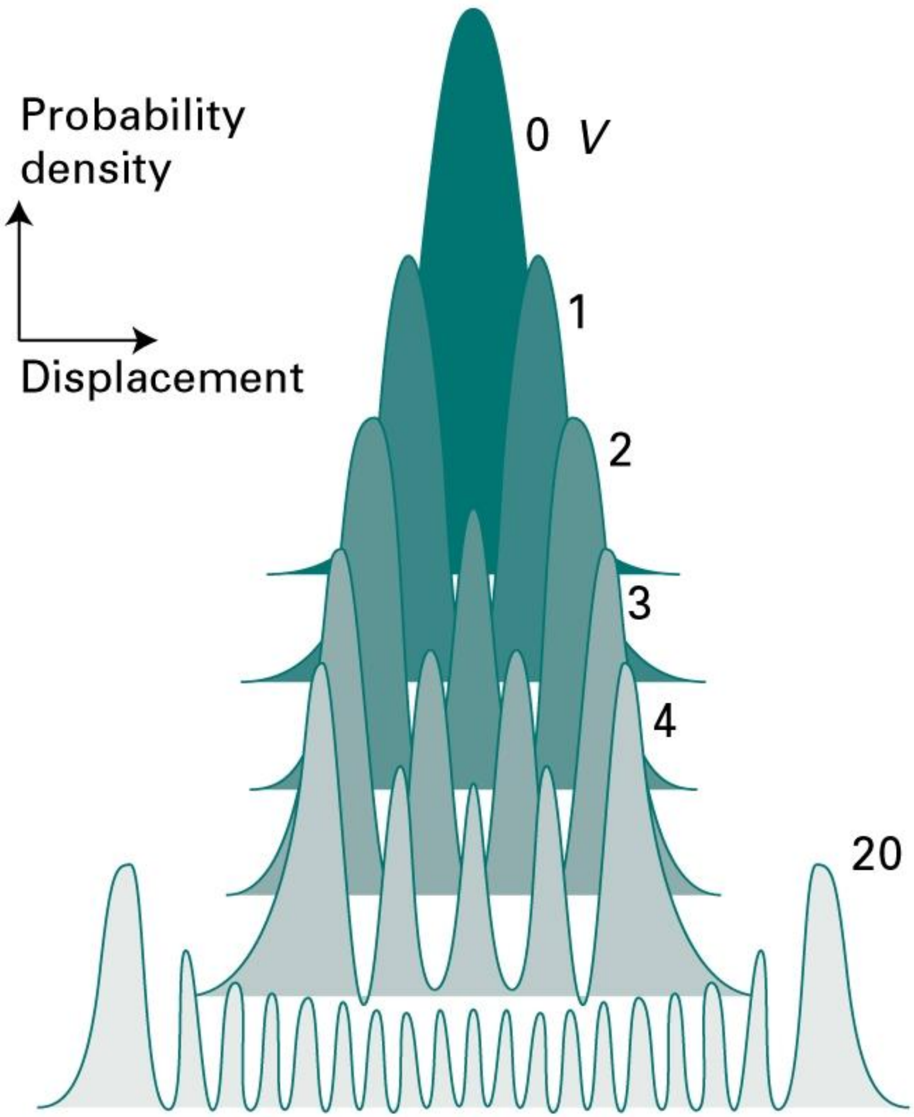


Figure 8.23

- Largest amplitude at high quantum numbers (see 20),

  near the turning point of CM motion (E_k=0 or V=E).

  In Classical Mechanics, the particle becomes slowest.

- At x=0, the particle is least likely to be found

(it travels most rapidly)

The properties of the oscillators

Expectation value $$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx$$

Dirac's braket notation $$\langle v' | \hat{\Omega} | v \rangle = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\Omega} \psi_v \, dx$$

Or Matrix element $\Omega_{\upsilon'\upsilon}$

the same states $$\langle \Omega \rangle = \langle v | \hat{\Omega} | v \rangle$$

Ex. for harmonic oscillator,

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = (v + \tfrac{1}{2}) \frac{\hbar}{(mk)^{1/2}}$$

The mean potential E

$$\langle V\rangle = \langle \tfrac{1}{2}kx^2\rangle = \tfrac{1}{2}(\upsilon + \tfrac{1}{2})\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}(\upsilon + \tfrac{1}{2})\hbar\omega$$

Since total E is $\left(\upsilon+\frac{1}{2}\right)\hbar\varpi$

$$\langle V\rangle = \tfrac{1}{2}E_\upsilon$$

$$\langle E_K\rangle = \tfrac{1}{2}E_\upsilon$$

KE and PE is equal… Special case of virial theorem

Virial theorem: if $V=ax^b$, then

$$2\langle E_K\rangle = b\langle V\rangle$$

An oscillator can be found even at V>E!!!

Beyond its classical limit, p~0.079

(these tunnelling probabilities are indep. of mass and force const.

Macroscopic oscillator (such as pendulum) are in state with very high quantum number -> p(V>E)~0

But, for molecules are normally in their vib gnd state: p(V>E)~significant

In classical mechanics,

the turning point, x_{tp}, $(E=V=kx^2/2,\ E_k=0)$

$$x_{tp}^2 = \frac{2E}{k}, \qquad \text{or} \quad x_{tp} = \pm\left(\frac{2E}{k}\right)^{1/2}$$

Probability that an oscillator is stretched beyond its CM turning point,

$$P = \int_{x_{tp}}^{\infty} \psi_v^2\,dx$$

$$\alpha = (\hbar^2/mk)^{1/2}$$

$$y_{tp} = \frac{x_{tp}}{\alpha} = \left\{\frac{2(v+\frac{1}{2})\hbar\omega}{\alpha^2 k}\right\}^{1/2} = (2v+1)^{1/2}$$

For the state of lowest energy $(v=0)$, $y_{tp}=1$

$$P = \int_{x_{tp}}^{\infty} \psi_0^2\,dx = \alpha N_0^2\int_1^{\infty} e^{-y^2}\,dy \qquad \operatorname{erf} z = 1 - \frac{2}{\pi^{1/2}}\int_z^{\infty} e^{-y^2}\,dy$$

$$P = \tfrac{1}{2}(1-\operatorname{erf} 1) = \tfrac{1}{2}(1-0.843) = 0.079$$

Rotational motion

8.6 Rotation in 2-d: the particle on a ring
8.7 Rotation in 3-d: the particle on a sphere
8.8 Spin

8.6 Rotation in 2-d:

the particle on a ring

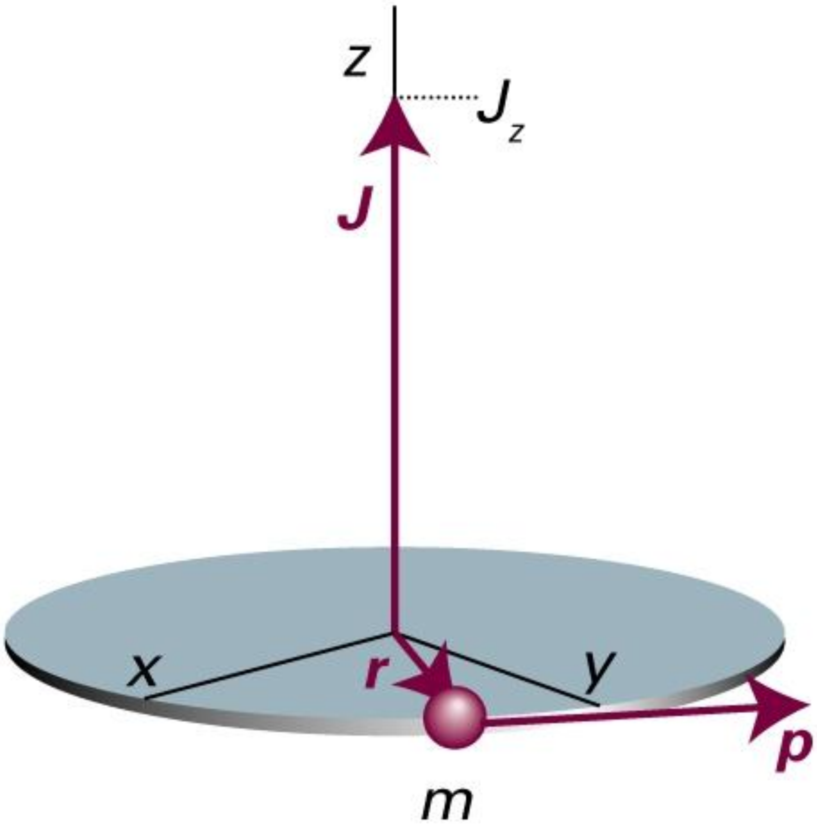


Figure 8.24

$$V = 0,\ E = E_k$$

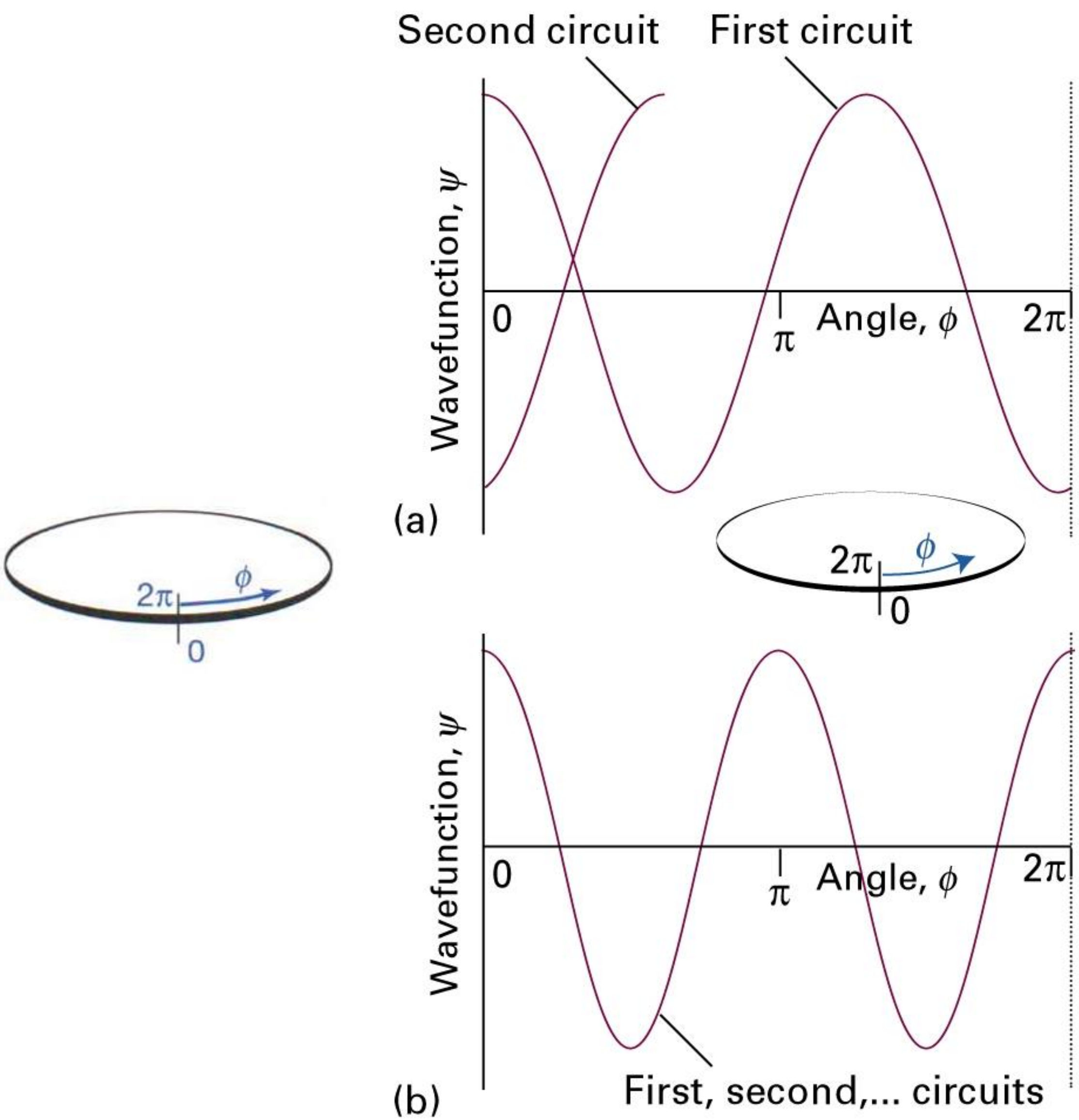
Jz : angular momentum

$$J_z = \pm pr = \pm \frac{hr}{\lambda}$$

$I = mr^2$: moment of inertia

$$E = \frac{p^2}{2m} = \frac{J_z^2}{2mr^2} = \frac{J_z^2}{2I}$$

Qualitative origin of quantized rotation



Not acceptable
: not single valued
and destructive

Acceptable
:constructive

Figure 8.25

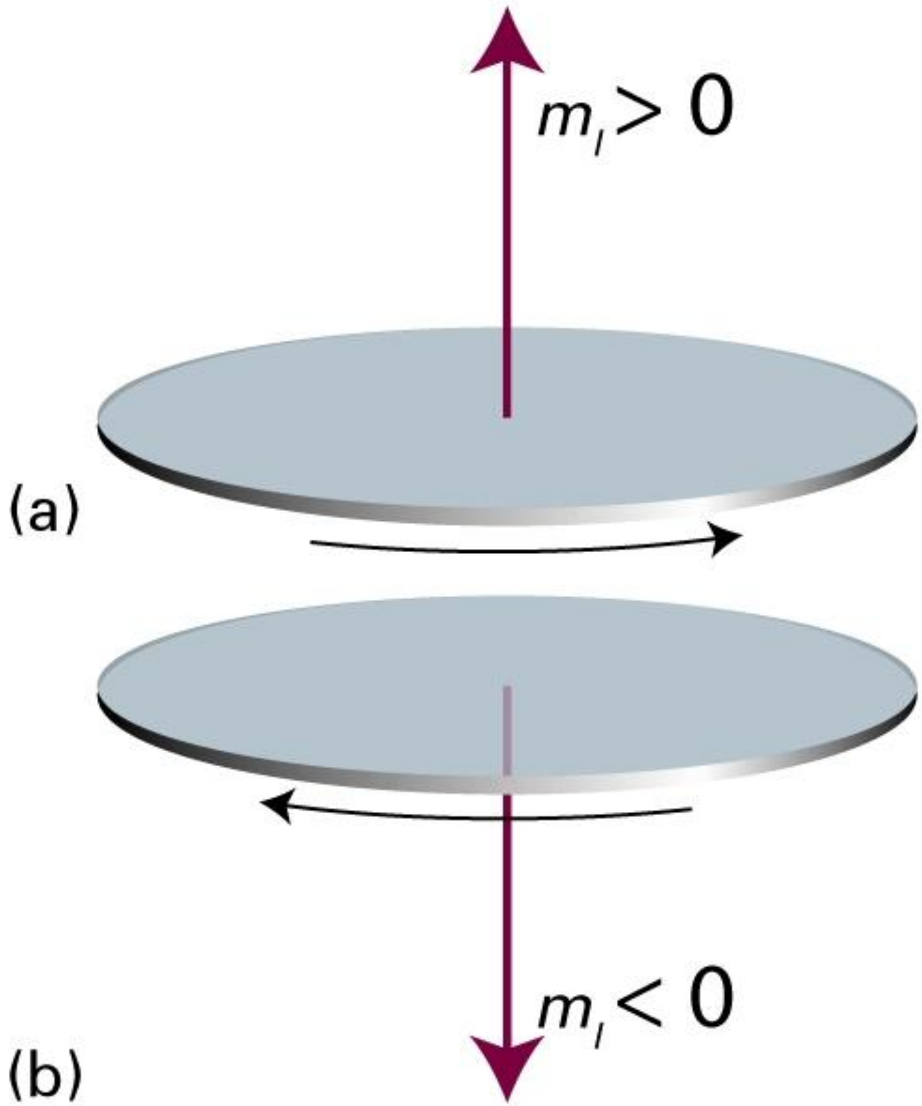


Figure 8.26

$$J_z = \pm\frac{hr}{\lambda}$$

$$\lambda = \frac{2\pi r}{m_l}$$

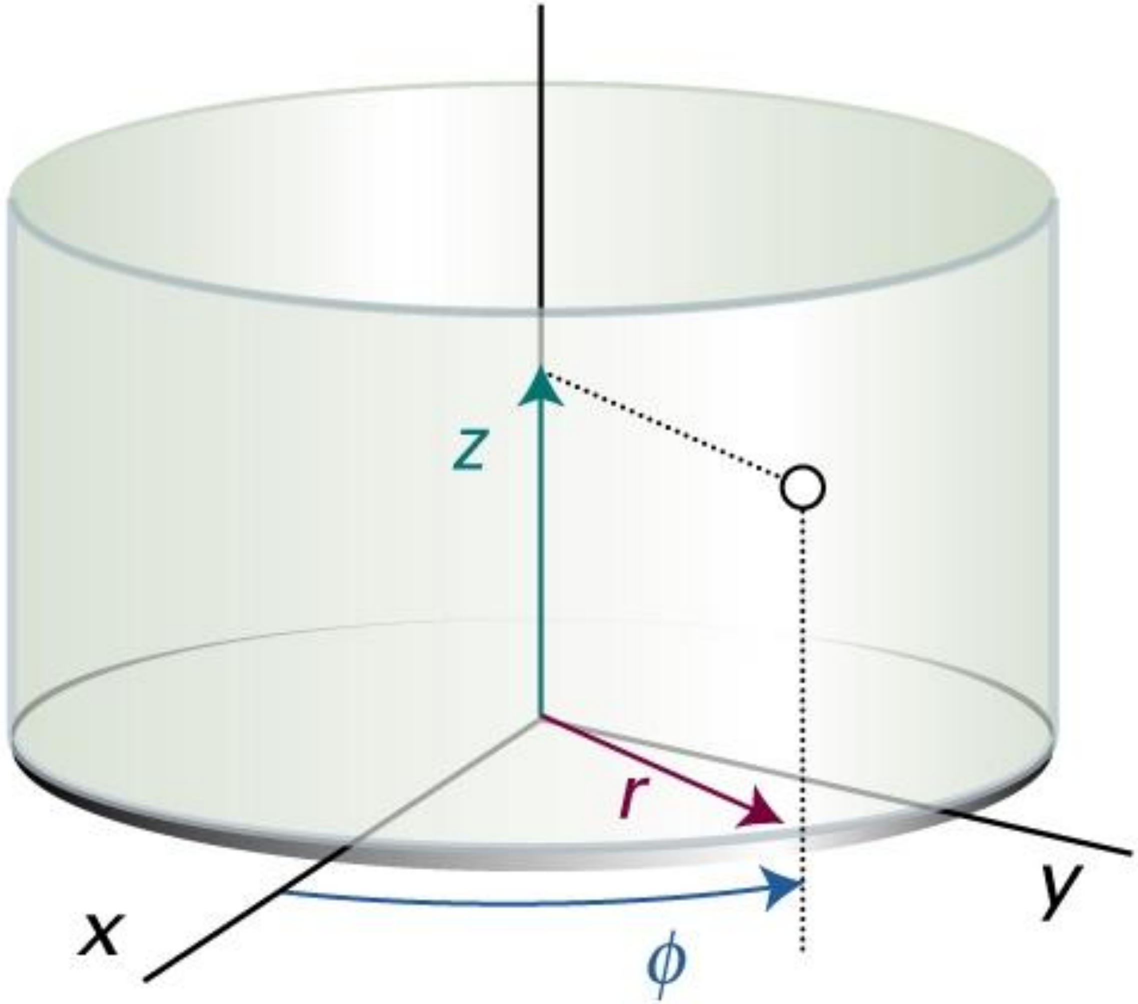
$$J_z = m_l\hbar \qquad m_l = 0, \pm1, \pm2, \ldots$$

$$J_z = \pm\frac{hr}{\lambda} = \frac{m_l hr}{2\pi r} = \frac{m_l h}{2\pi}$$

$$E = \frac{J_z^2}{2I} = \frac{m_l^2\hbar^2}{2I}$$

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}}$$

Cylindrical coordinate



$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

$$H = -\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$$

$$H = -\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\phi^2} = -\frac{2IE}{\hbar^2}\psi$$

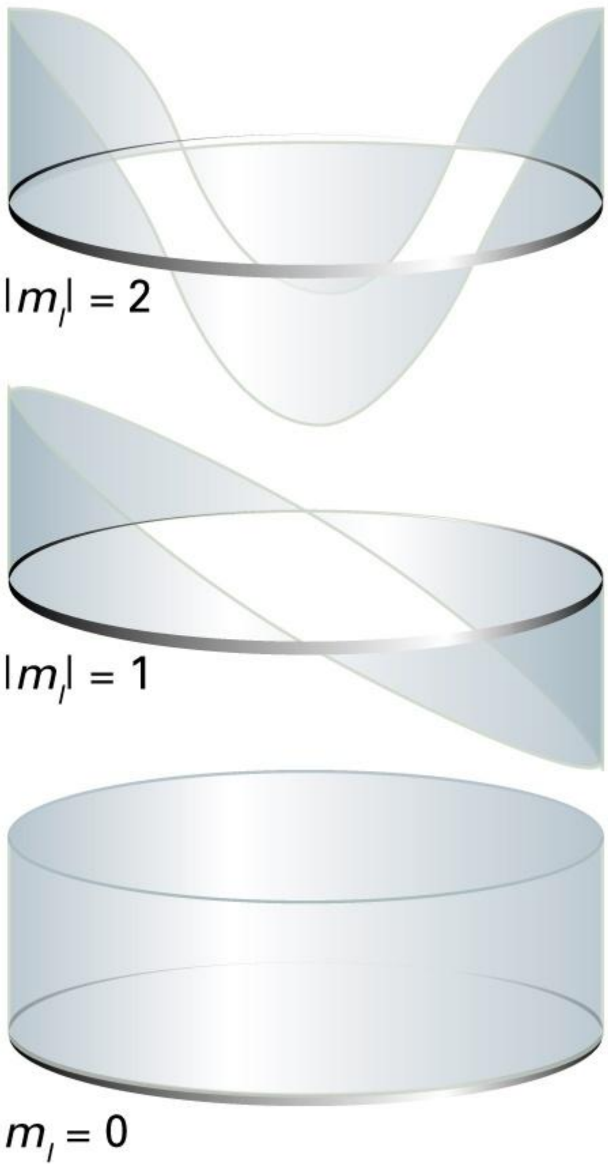
$$\psi_{m_l}(\phi) = \frac{\mathrm{e}^{im_l\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm\frac{(2IE)^{1/2}}{\hbar}$$

$$\psi_{m_l}(\phi + 2\pi) = \frac{\mathrm{e}^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{\mathrm{e}^{im_l\phi}\mathrm{e}^{2\pi im_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi)\mathrm{e}^{2\pi im_l}$$

Cyclic boundary condition $\psi(\phi + 2\pi) = \psi(\phi).$

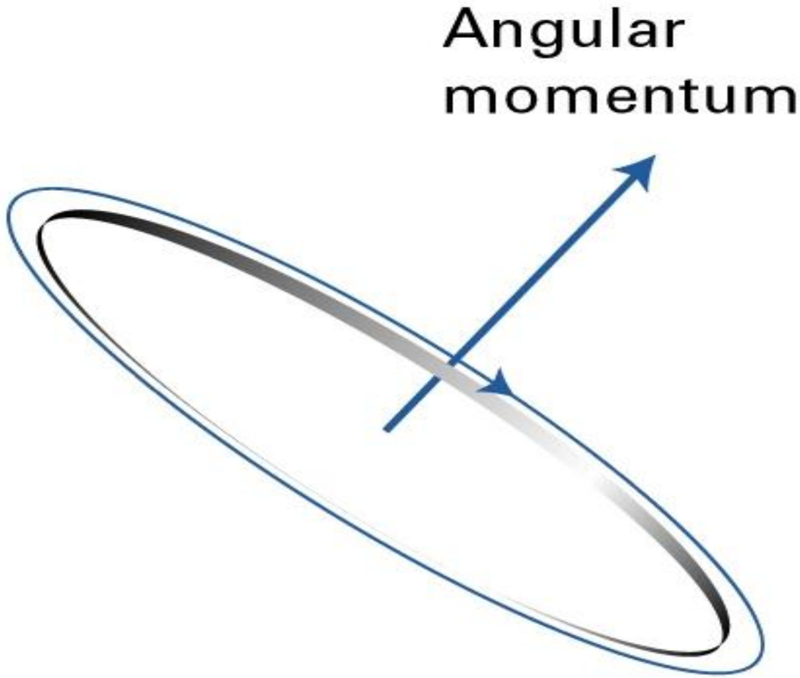
$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l}\psi(\phi)$$

Figure 8.28



Real parts of the waveftns of a particle on a ring

Shorter the wavelength, Angular momentum (z-axis) the larger in steps of h/2π



The basic ideas of the vector representation of angular momentum: the magnitude of the angular momentum is represented by the length of the vector, and the orientation of the motion in space by the orientation of the vector (using the right-hand screw rule).

Definition of angular momentum

$$l_z = xp_y - yp_x$$

Angular momentum operator

$$l_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

in cylindrical coordinate,

$$l_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

$$l_z\psi_{m_l} = \frac{\hbar}{i}\frac{d\psi_{m_l}}{d\phi} = im_l\frac{\hbar}{i}e^{im_l\phi} = m_l\hbar\psi_{m_l}$$

Probability density of a particle in a definite state of angular momentum~uniform

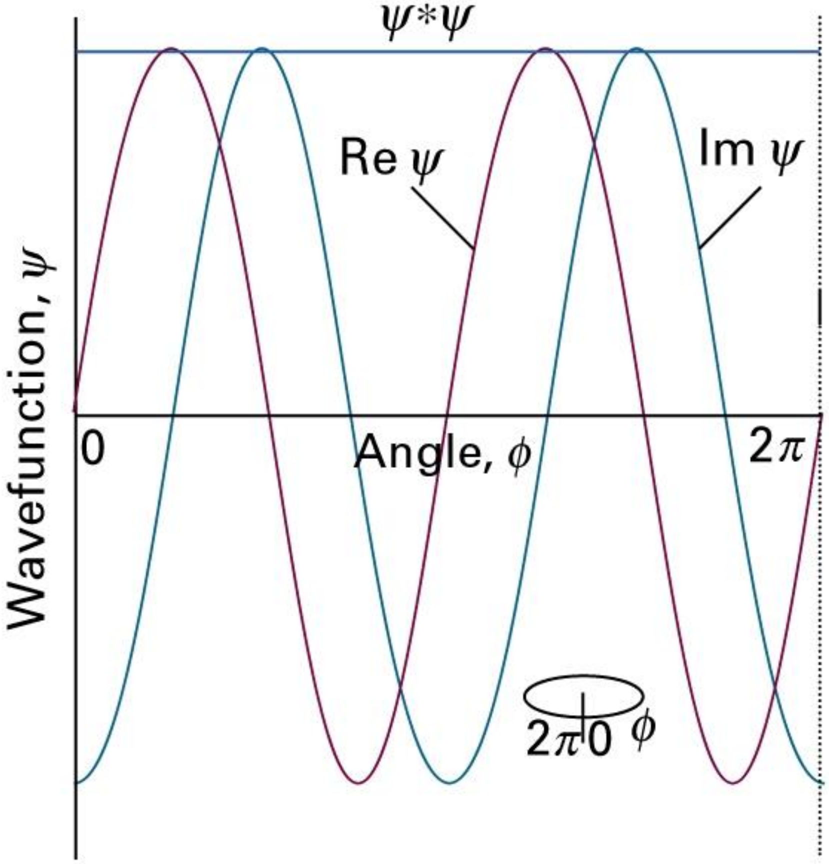


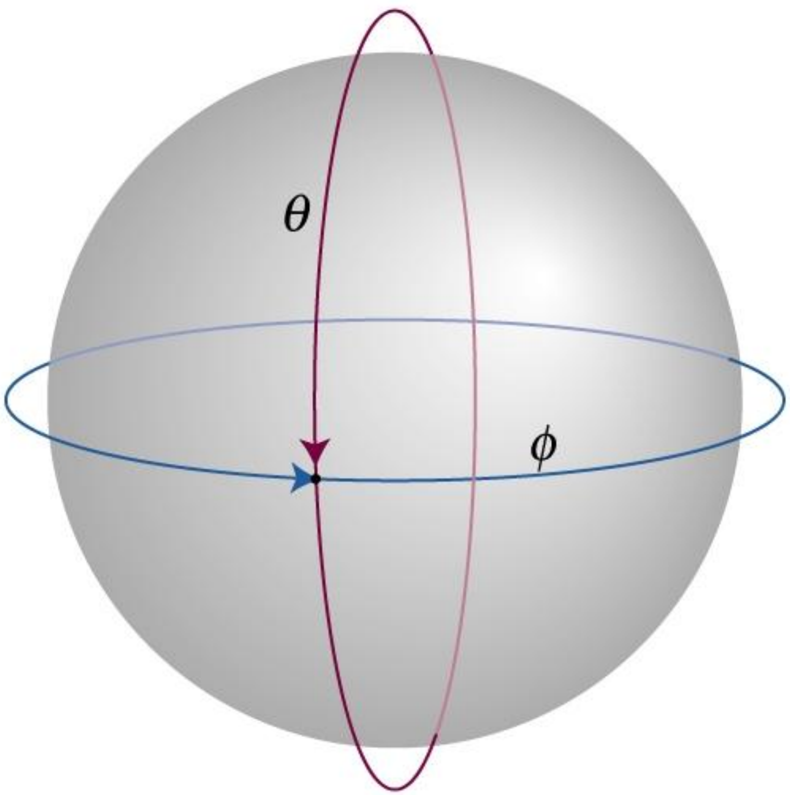
Figure 8.30

$$\psi^*_{m_l}\psi_{m_l} = \left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)^*\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right) = \left(\frac{e^{-im_l\phi}}{(2\pi)^{1/2}}\right)\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right) = \frac{1}{2\pi}$$

8.7 Rotation in 3-d

: e^- in atoms
Rotating molecules

Waveftn of a particle on a surface



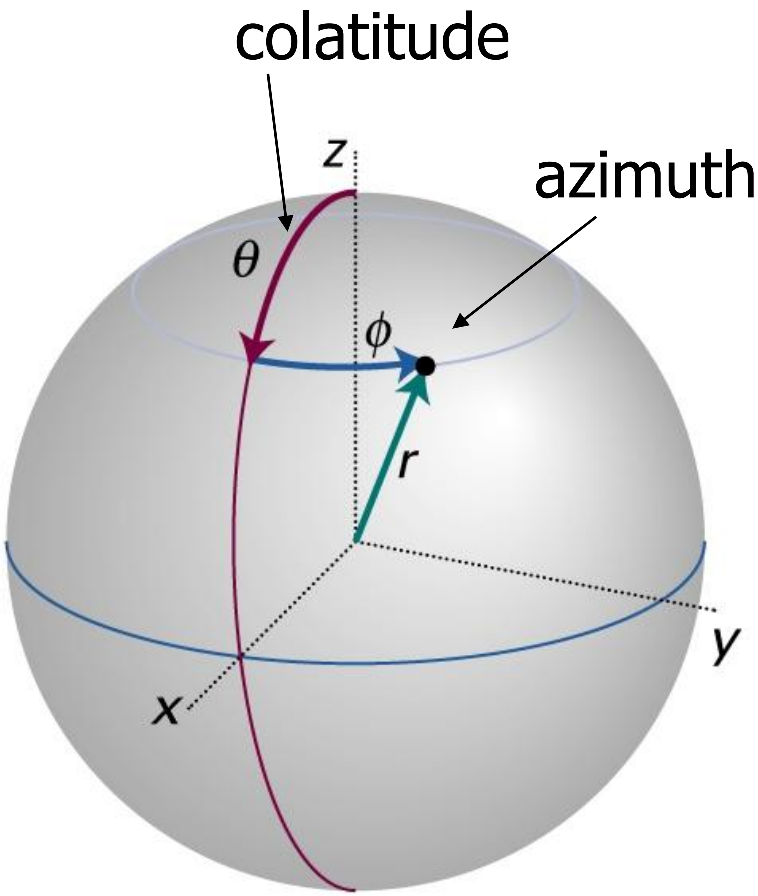
- Two cyclic BC

  ⇩

- Two quantum numbers

- V=0
- r: constant

The Schrodinger equation



Laplacian
or del squared
or nabla squared

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

Justification 8.6

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{2}{r^2}\Lambda^2$$

legendrian, Λ^2, $\quad \Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$

Since r is constant,

$$\frac{1}{r^2}\Lambda^2\psi = -\frac{2mE}{\hbar^2}\psi$$

because $I = mr^2$, as

$$\Lambda^2\psi = -\varepsilon\psi \qquad \varepsilon = \frac{2IE}{\hbar^2}$$

$$\psi = \Theta\Phi$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2(\Theta\Phi)}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial(\Phi\Theta)}{\partial\theta}=-\varepsilon\Theta\Phi$$

$$\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{\Phi}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}=-\varepsilon\Theta\Phi$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+\varepsilon\sin^2\theta=0$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+\varepsilon\sin^2\theta=m_l^2$$

Same as 8.4

Associated Legendre ftn

w/ cyclic BC: l (quantum number) appears
m_l is restricted by l

Orbital angular momentum quantum number
l : 0,1,2,3…

Magnetic quantum number
m_l: l, l-1, …,-l

Spherical harmonics

$$Y_{l,m_l}$$

Table 8.2 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\,e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\,e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\,e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\,e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\,e^{\pm 3i\phi}$

The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^{\pi}\int_0^{2\pi} Y_{l',m_l'}(\theta,\phi)^* Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi = \delta_{l'l}\delta_{m_l'm_l}$$

An important 'triple integral' is

$$\int_0^{\pi}\int_0^{2\pi} Y_{l'',m_l''}(\theta,\phi)^* Y_{l',m_l'}(\theta,\phi) Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi$$

$$=0 \quad \text{unless} \quad m_l''=m_l'+m_l$$

and we can form a triangle with sides of lengths l'', l', and l (such as 1, 2, and 3 or 1, 1, and 1, but not 1, 2, and 4).

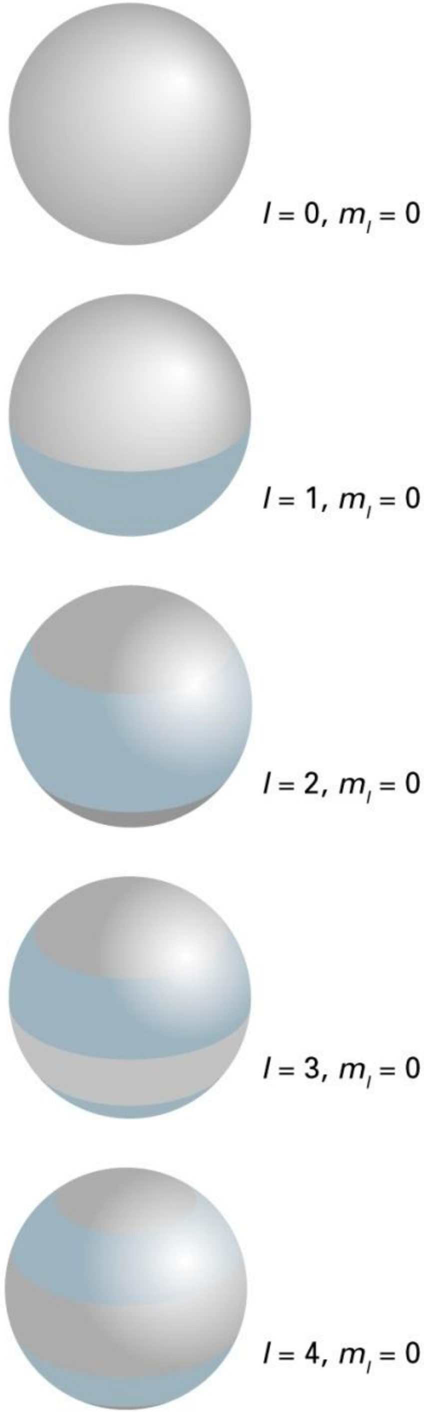
The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^{\pi}\int_0^{2\pi} Y_{l',m_l'}(\theta,\phi)^* Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi = \delta_{l'l}\delta_{m_l'm_l}$$

An important 'triple integral' is

$$\int_0^{\pi}\int_0^{2\pi} Y_{l'',m_l''}(\theta,\phi)^* Y_{l',m_l'}(\theta,\phi) Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi$$

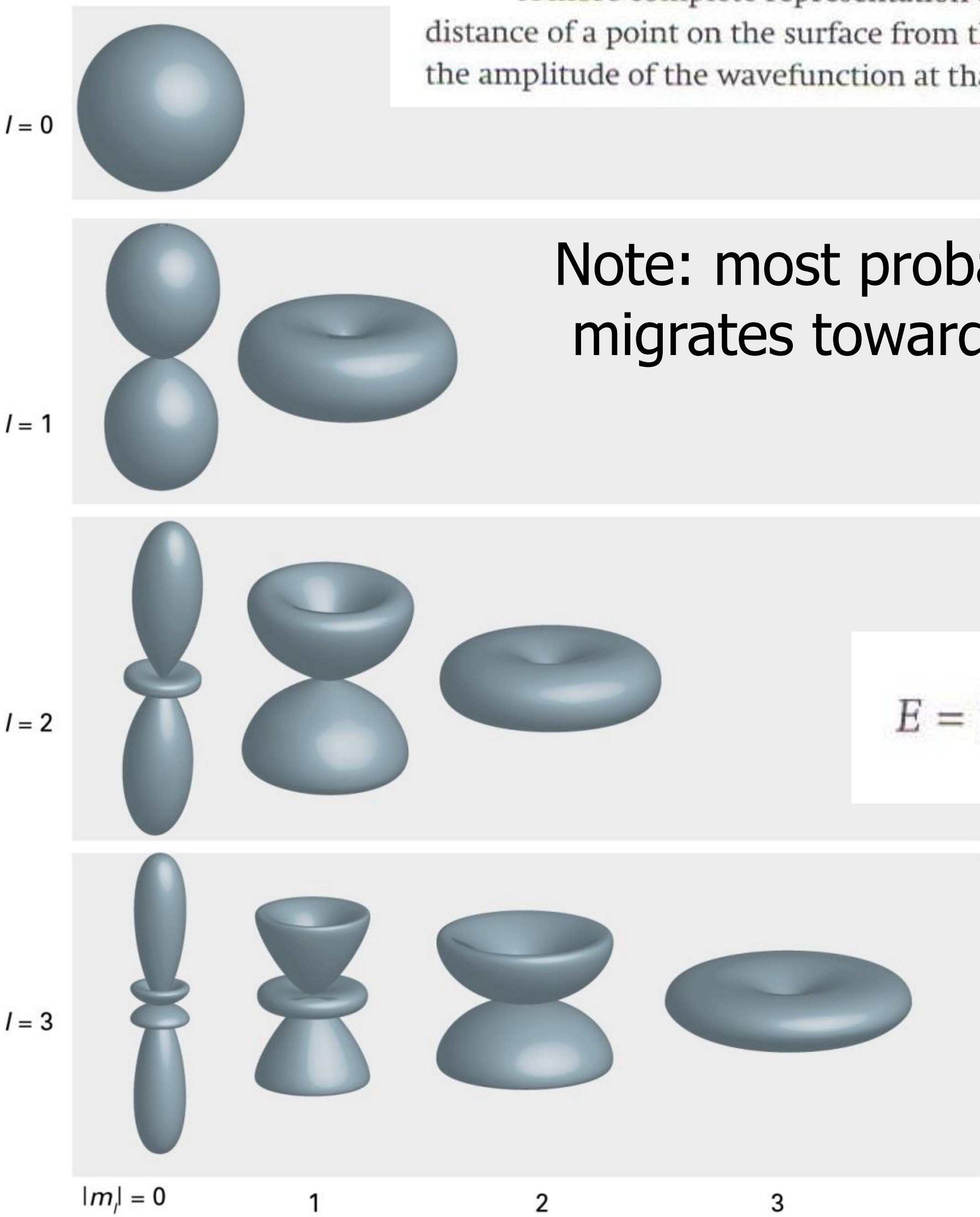
$= 0$ unless $m_l'' = m_l' + m_l$ and l'', l', and l can form a triangle.



A representation of the wavefunctions of a particle on the surface of a sphere which emphasizes the location of angular nodes: dark and light shading correspond to different signs of the wavefunction. Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to $m_l = 0$; a path round the vertical z-axis of the sphere does not cut through any nodes.

Figure 8.34

A more complete representation of the wavefunctions for $l = 0, 1, 2$, and 3. The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wavefunction at that point.



Note: most probable location of particles migrates towards xy plane as $|m_l|$ increases

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots$$

- m_l doesn't affect E
- 2l+1 degeneracy

Angular momentum

$E = J^2/2I$ angular momentum J

Magnitude of angular momentum $= \{l(l+1)\}^{1/2}\hbar$

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

z-component of angular momentum $= m_l\hbar$

$m_l = l, l-1, \ldots, -l$

$\psi_{l,m_l}(\theta, \phi)$ Number of node $\uparrow$ w/ l

Higher momentum, Higher E_k

More nodal lines cut the equator

(note: the curvature is greater in the direction)

Space Quantization [1]

- For a given l,

Angular momentum for z-axis: $2l+1$

- Discrete range of orientations
- The orietation of rotating body is quantized

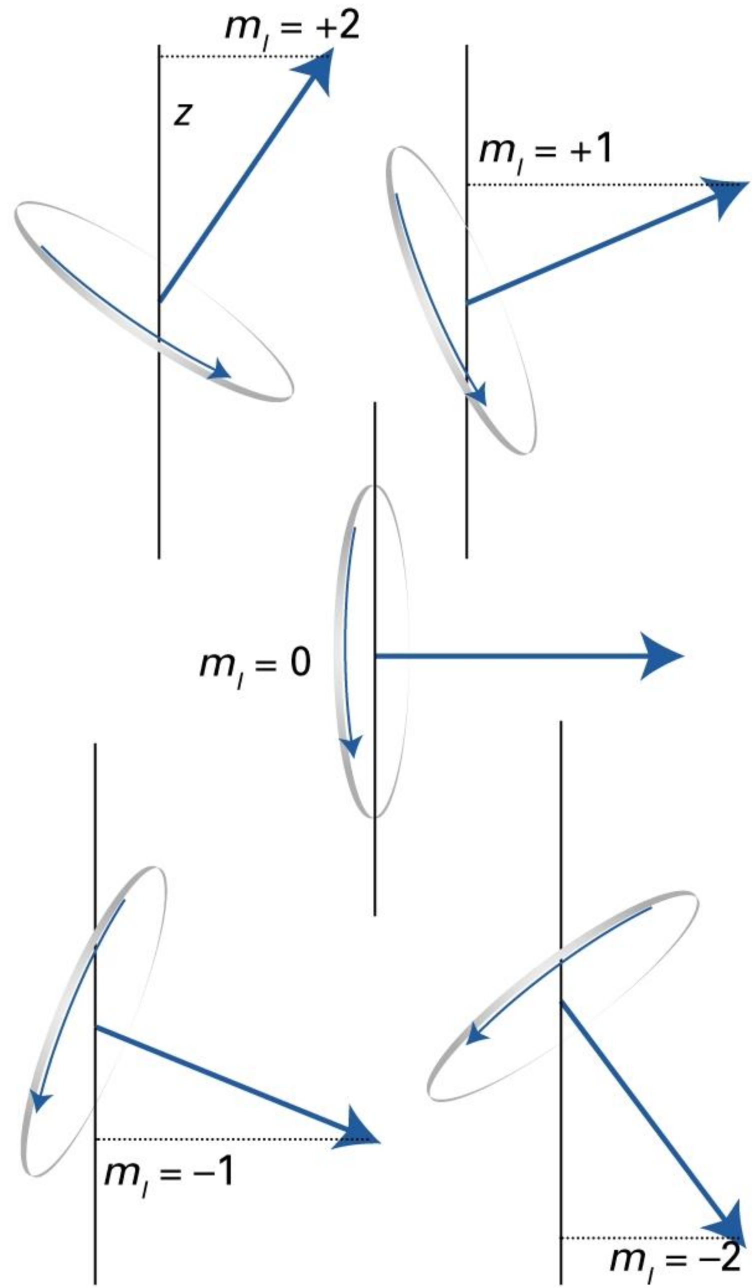
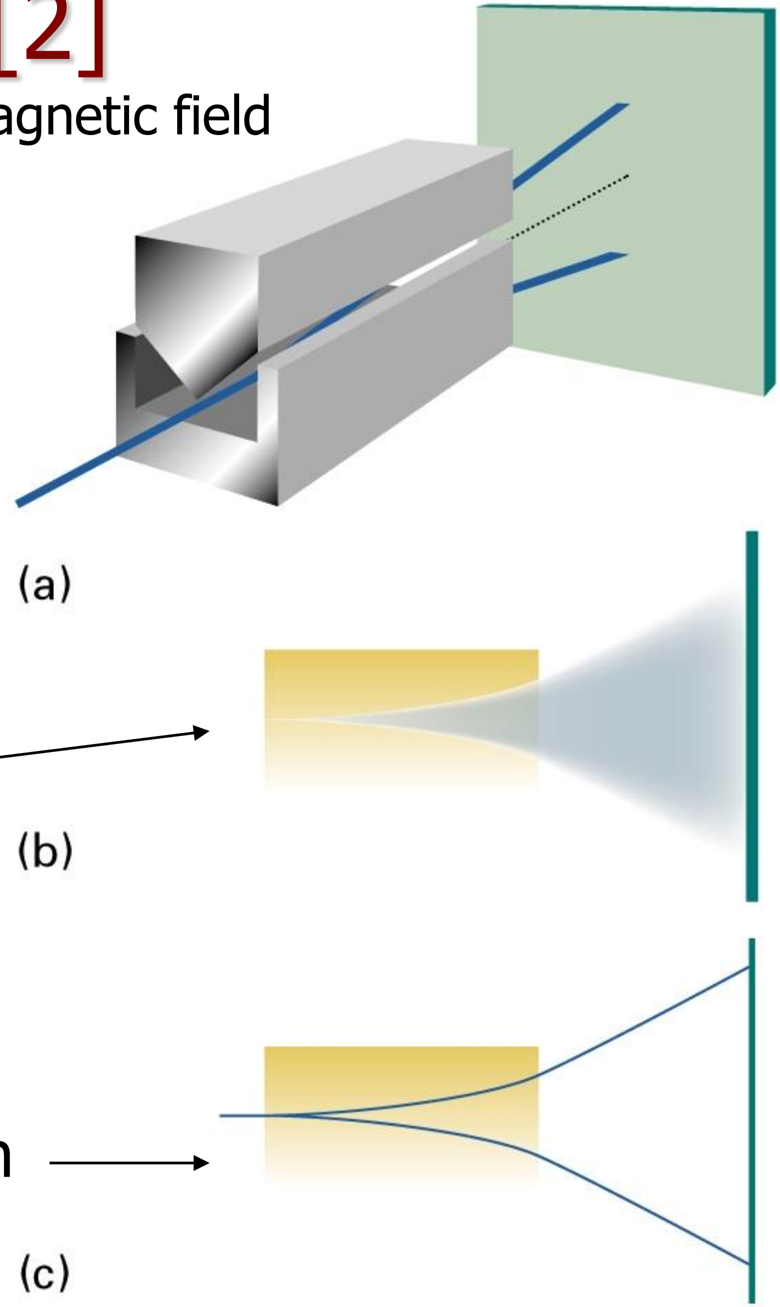


Figure 8.35 The permitted orientations of angular momentum when $l = 2$. We shall see soon that this representation is too specific because the azimuthal orientation of the vector (its angle around z) is indeterminate.

Space Quantization [2]

- Magnetic field
- Beam of silver atom
- Classically expected
- Observation



The vector model [1]

- No reference to x,y axis
- Once I_z is known, I_x and I_y can't be known

(due to uncertainty principle)

- I_z is known, I_x and I_y are complementary

(they are not commute)

The vector model [2]

Schematic diagram

Better schematic diagram

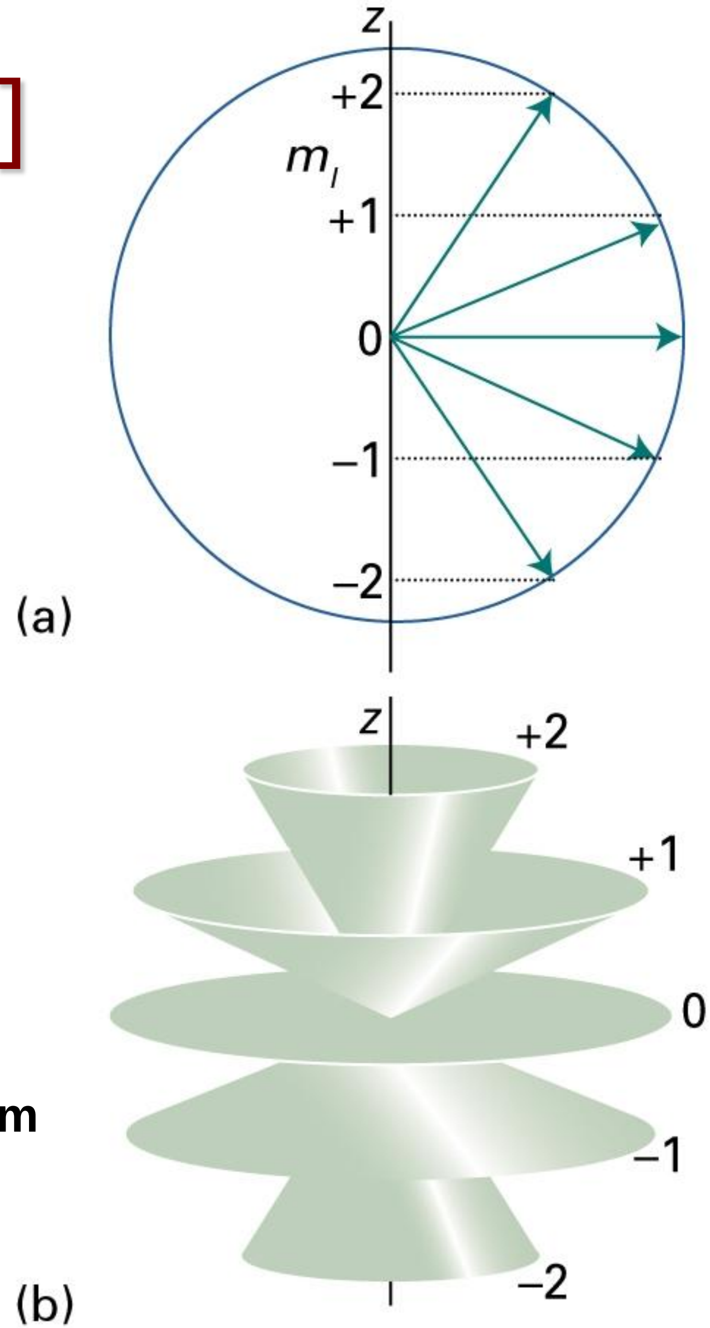


Figure 8.37

8.8 Spin

: not the actual spin motion
interact w/ magnetic field

Stern and Gelach observed two band
(2/+1=2…/=1/2 ? … s instead /)

n quantum number: s

n magnetic quantum number: m_s

for electron:

s=1/2

m_s=1/2 (↑), -1/2 (↓)

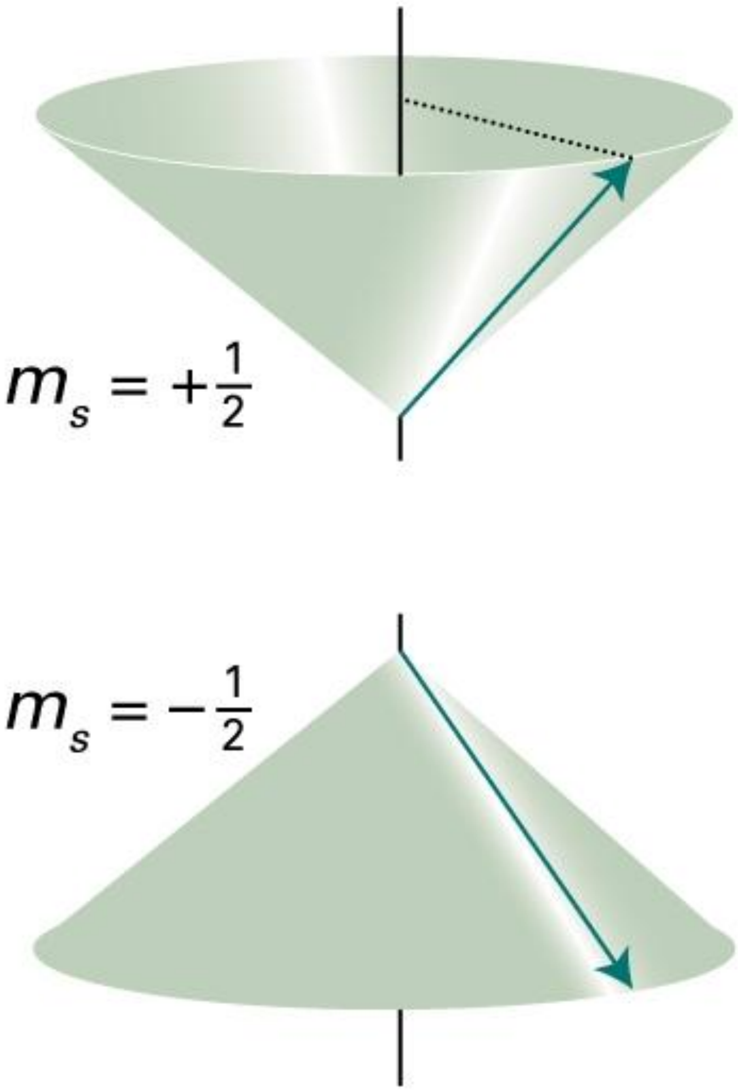


Figure 8.38

An electron spin ($s = \frac{1}{2}$) can take only two orientations with respect to a specified axis. An α electron (top) is an electron with $m_s = +\frac{1}{2}$; a β electron (bottom) is an electron with $m_s = -\frac{1}{2}$. The vector representing the spin angular momentum lies at an angle of 55° to the z-axis (more precisely, the half-angle of the cones is $\arccos(\frac{1}{3})^{1/2}$).

- Electron, proton and neutron: spin ½ particles (s=1/2)

with the angular momentum of $(3/4)^{1/2}\hbar$

Despite the mass difference, they have the same spin angular momentum

(In CM, proton and neutrons should spin slower.)

- Photon:

Spin 1 particles (s=1)

with the angular momentum of $(2)^{1/2}\hbar$

zero rest mass

zero charge

an energy *hv*

linear momentum *hv/c*

speed: c

- Fermion:

particles with half-integral spins
All the elementary particles that constitutes matter

ex) electron and protons

- Boson:

particles with integral spins
fundamental particles that are responsible for the forces that binds fermions together

ex) photons (transmit EM forces that binds together electrically charged particles)

- Matter: is an assembly of fermions held together by bosons

Table 8.3

Table 8.3 Properties of the angular momentum of an electron

Quantum number	Symbol†	Values	Specifies
Orbital angular momentum	l	$0, 1, 2, \ldots$ ‡	Magnitude, $\{l(l+1)\}^{1/2}\hbar$
Magnetic	m_l	$l, l-1, \ldots, -l$	Component on z-axis, $m_l\hbar$
Spin	s	$\frac{1}{2}$	Magnitude, $\{s(s+1)\}^{1/2}\hbar$
Spin magnetic	m_s	$\pm\frac{1}{2}$	Component on z-axis, $m_s\hbar$
Total*	j	$l+s, l+s-1, \ldots, \lvert l-s \rvert$	Magnitude, $\{j(j+1)\}^{1/2}\hbar$
Total magnetic	m_j	$j, j-1, \ldots, -j$	Component on z-axis, $m_j\hbar$

* To combine two angular momenta, use the Clebsch–Gordan series (see Section 9.10a):

$$j = j_1 + j_2, j_1 + j_2 - 2, \ldots, |j_1 - j_2|$$

† For many-electron systems, the quantum numbers are designated by upper-case letters (L, M_L, S, M_S, etc.).

‡ Note that the quantum numbers for magnitude (l, s, j, etc.) are never negative.