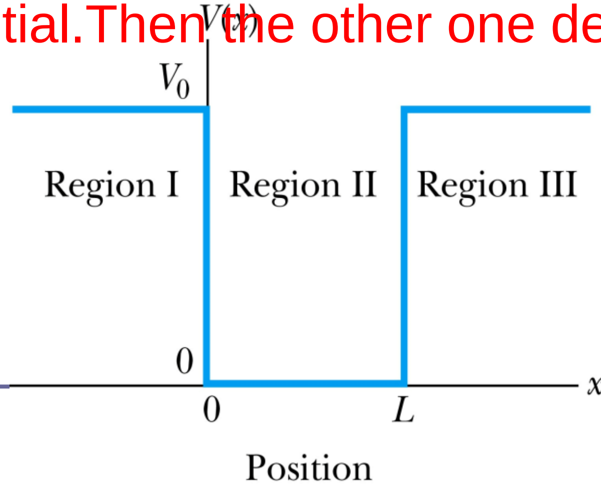
6.4: Finite Square-Well Potential

- The finite square-well potential is $V(x) = \begin{cases} V_0 & x \le 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \ge L & \text{region III} \end{cases}$

- The Schrödinger equation outside the finite well in regions I and III is

$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E - V_0$ regions I, III or using $\alpha^2 = 2m(V_0 - E)/\hbar^2$

yields $\frac{d^2\psi}{dx^2} = \alpha^2\psi$. The solution to this differential has exponentials of the form $e^{\alpha x}$ and $e^{-\alpha x}$. In the region x > L, we reject the positive exponential and in the region x < L, we reject the negative exponential.Then the other one decays into the classically forbidden region



$\psi_{\mathrm{I}}(x) = Ae^{\alpha x}$ region I, $x < 0$

$\psi_{\mathrm{III}}(x) = Be^{-\alpha x}$ region III, $x > L$

Finite Square-Well Solution

- Inside the square well, where the potential V is zero, the wave equation becomes $\frac{d^2\psi}{dx^2} = -k^2\psi$ where $k = \sqrt{(2mE)/\hbar^2}$

Larger wavelength
Smaller momentum and energy

- Instead of a sinusoidal solution we have

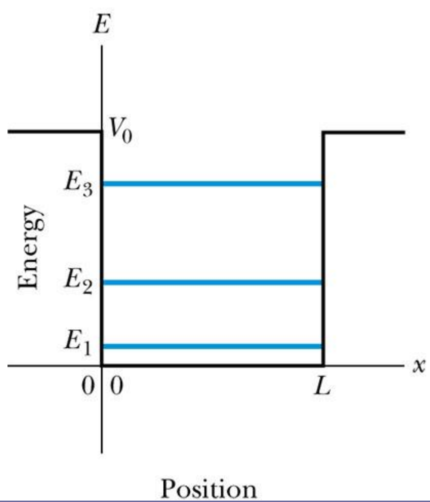
$$\psi_{II} = Ce^{ikx} + De^{-ikx} \qquad \text{region II, } 0 < x < L$$

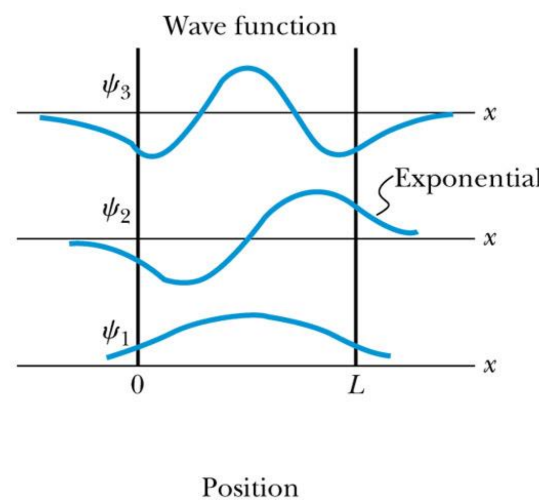
- The boundary conditions require that

$$\psi_I = \psi_{II} \text{ at } x = 0 \text{ and } \psi_{II} = \psi_{III} \text{ at } x = L$$

and the wave function must be smooth where the regions meet.

- Note that the wave function is nonzero outside of the box.





We will skip the tedious procedure of fulfilling the above boundary conditions, but discuss the results

Clicker - Questions

13) Compare the results of the finite and infinite square well potential?

a) The wavelengths are longer for the finite square well.

b) The wavelengths are shorter for the finite square well.

c) The wavelengths are the same.

Clicker - Questions

13) Compare the finite and infinite square well potentials and chose the correct statement.

a) There is a finite number of bound energy states for the finite potential.

b) There is an infinite number of bound energy states for the finite potential.

c) There are bound states which fulfill the condition $E>V_o$.

6.5: Three-Dimensional Infinite-Potential Well

- The wave function must be a function of all three spatial coordinates. We begin with the conservation of energy $E = K + V = \frac{p^2}{2m} + V$
- Multiply this by the wave function to get

$$\frac{p^2}{2m}\psi + V\psi = E\psi$$

- Now consider momentum as an operator acting on the wave function. In this case, the operator must act twice on each dimension. Given:

$$p^2 = p_x^{\ 2} + p_y^{\ 2} + p_z^{\ 2}, \text{ and} \quad \hat{p}_x\psi = -i\hbar\frac{\partial\psi}{\partial x} \quad \hat{p}_y\psi = -i\hbar\frac{\partial\psi}{\partial y} \quad \hat{p}_z\psi = -i\hbar\frac{\partial\psi}{\partial z}$$

- The three dimensional Schrödinger wave equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi \quad \text{or} \quad -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$\triangle = \nabla^2$ Laplace operator

Time independent Schroedinger equation

Particle in3-D box

Consider a free particle inside a box with lengths L_1, L_2, and L_3 along the x, y, and z axes, respectively, as shown in Figure 6.6. The particle is constrained to be inside the box. Find the wave functions and energies. Then find the ground-state energy and wave function and the energy of the first excited state for a cube of sides L.

Strategy We employ some of the same strategies to solve this problem as we used for the one-dimensional case. First, because we are considering the walls of the box to be absolutely closed, they are infinite potential barriers, and the wave function ψ must be zero at the walls and beyond. We expect to see standing waves similar to Equation (6.31).

But how should we write the wave function so as to properly include the x, y, and z dependence of the wave function? In this case the mathematics will follow from the physics. The particle is free within the box. Therefore, the x-, y-, and z-dependent parts of the wave function must be independent of each other. Inside the box $V = 0$, so the wave equation we must solve is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \tag{6.46}$$

It is therefore reasonable to try a wave function of the form

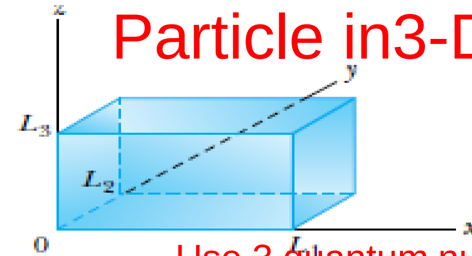
$$\boxed{\psi(x, y, z) = A\sin(k_1x)\sin(k_2y)\sin(k_3z)} \tag{6.47}$$

where A is a normalization constant. The quantities k_i (i = 1, 2, 3) are determined by applying the appropriate boundary conditions. To find the energies, we substitute the wave function into the Schrödinger equation and solve for E.

Solution The condition that $\psi = 0$ at $x = L_1$ requires that $k_1L_1 = n_1\pi$ or $k_1 = n_1\pi/L_1$. The values for the k_i are

$$\boxed{k_1 = \frac{n_1\pi}{L_1} \qquad k_2 = \frac{n_2\pi}{L_2} \qquad k_3 = \frac{n_3\pi}{L_3}} \tag{6.48}$$

where n_1, n_2, and n_3 are integers. Not surprisingly, we have found that in three dimensions, it is necessary to use *three* quantum numbers to describe the physical state.



Use 3 quantum numbers n

Figure 6.6 A three-dimensional box that contains a free particle. The potential is infinite outside the box, so the particle is constrained to be inside the box.

In order to find the energies using Equation (6.43), we first need to take the appropriate derivatives of the wave function. We do this first for the variable x.

$$\frac{\partial\psi}{\partial x} = \frac{\partial}{\partial x}[A\sin(k_1x)\sin(k_2y)\sin(k_3z)]$$

$$= k_1A\cos(k_1x)\sin(k_2y)\sin(k_3z)$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}[k_1A\cos(k_1x)\sin(k_2y)\sin(k_3z)]$$

$$= -(k_1)^2A\sin(k_1x)\sin(k_2y)\sin(k_3z)$$

$$= -k_1^2\psi$$

The derivatives for y and z are similar, and Equation (6.43) becomes

$$\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\psi = E\psi$$

This gives

$$E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)$$

We substitute the values of k_i from Equation (6.48) in this equation to obtain

$$\boxed{E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)} \tag{6.49}$$

Degeneracy

- Analysis of the Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy.
- A quantum state is degenerate when there is more than one wave function for a given energy.
- Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy (to be shown later).

Problem6.26

For a cubical box L1=L2=L3=L

Find the energies of the second, third, fourth, and fifth levels for the three dimensional cubical box. Which energy levels are degenerate?

A given state is degenerate when there is more than one wave function for a given energy

$E = \frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right) = E_0\left(n_1^2 + n_2^2 + n_3^2\right)$ where $E_0 = \frac{\pi^2\hbar^2}{2mL^2}$. Then the second, third, fourth, and fifth levels are

ground state wavefunction E1 is not degenerate

1. :

$E_2 = \left(2^2 + 1^2 + 1^2\right)E_0 = 6E_0$ (degenerate)

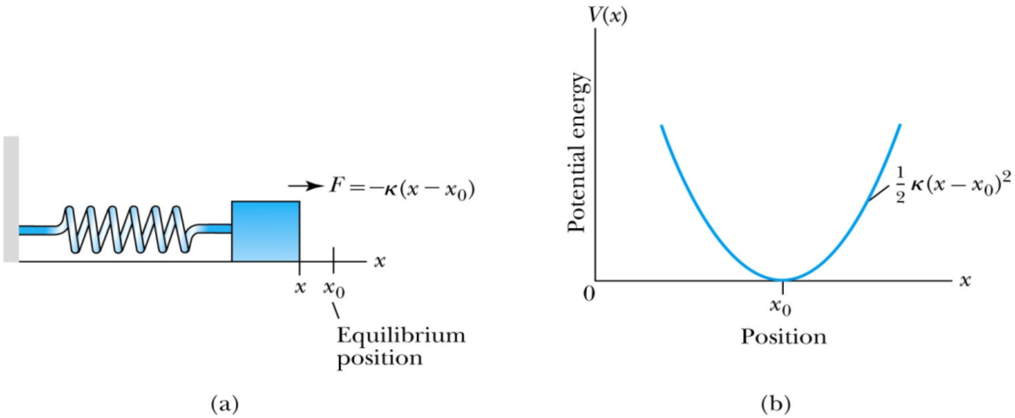
$E_3 = \left(2^2 + 2^2 + 1^2\right)E_0 = 9E_0$ (degenerate)

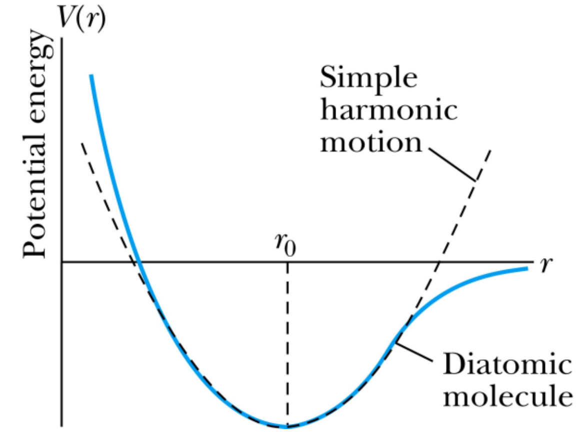
$E_4 = \left(3^2 + 1^2 + 1^2\right)E_0 = 11E_0$ (degenerate)

$E_5 = \left(2^2 + 2^2 + 2^2\right)E_0 = 12E_0$ (not degenerate)

6.6: Simple Harmonic Oscillator

- Simple harmonic oscillators describe many physical situations: springs, diatomic molecules and atomic lattices.





- Consider the Taylor expansion of a potential function:

$$V(x) = V_0 + V_1(x - x_0) + \tfrac{1}{2}V_2(x - x_0)^2 + \ldots$$

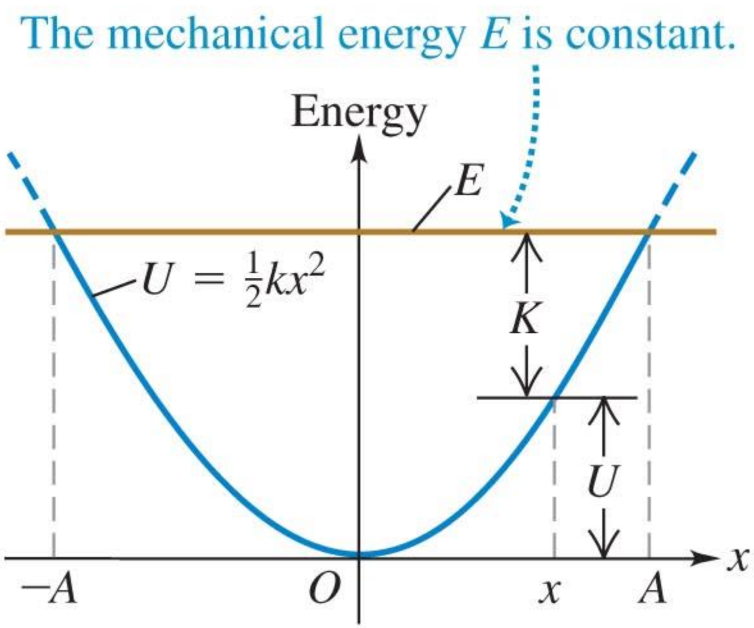
Redefining the minimum potential and the zero potential, we have

- $$V(x) = \tfrac{1}{2}V_2(x - x_0)^2 = \frac{\kappa x^2}{2}$$

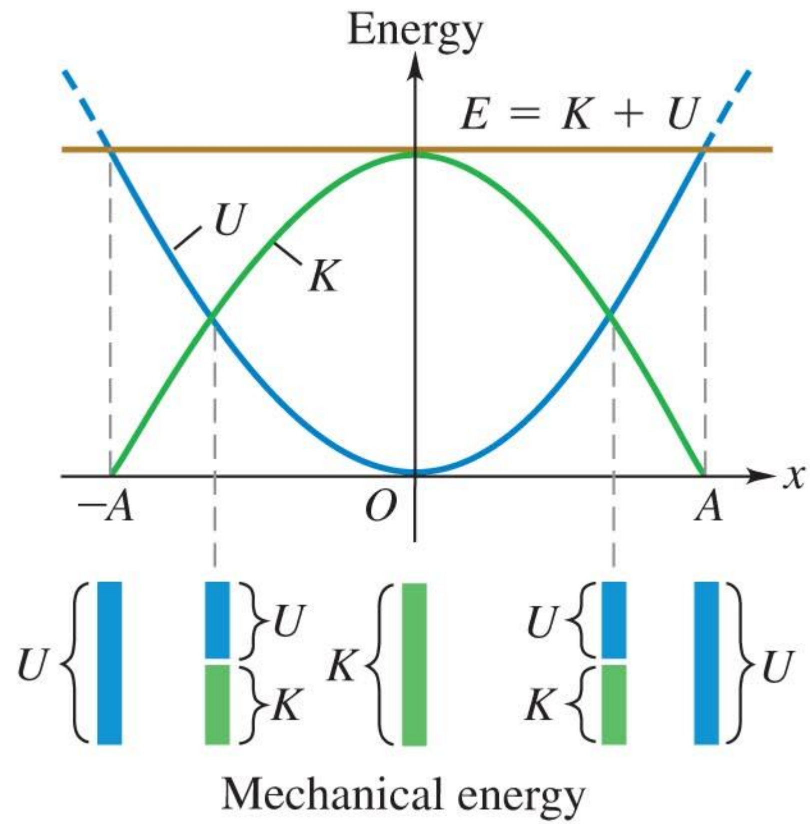
Substituting this into the wave equation:

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{\kappa x^2}{2}\right)\psi = \left(-\frac{2mE}{\hbar^2} + \frac{m\kappa x^2}{\hbar^2}\right)\psi$$

Let $\alpha^2 = \dfrac{m\kappa}{\hbar^2}$ and $\beta = \dfrac{2mE}{\hbar^2}$ which yields $\dfrac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$

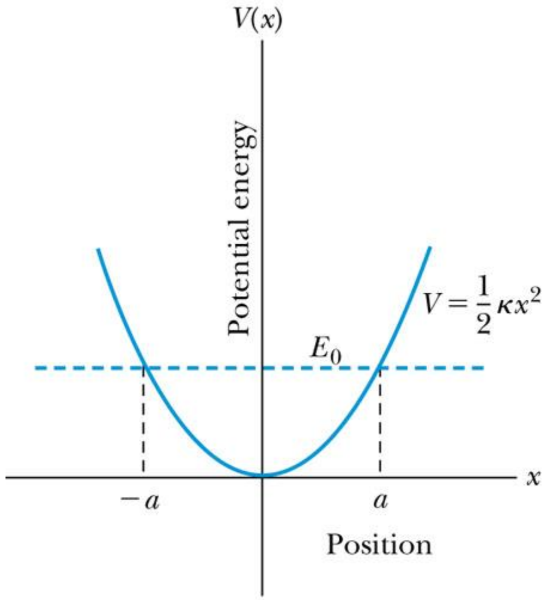


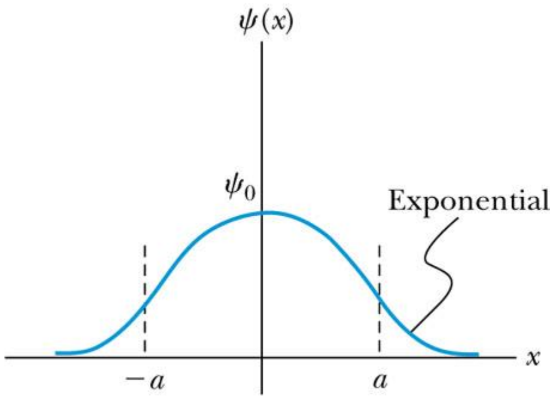
(a) The potential energy U and total energy E of an object in SHM as a function of x position



(b) The same graph as in **(a)**, showing kinetic energy K as well

Parabolic Potential Well

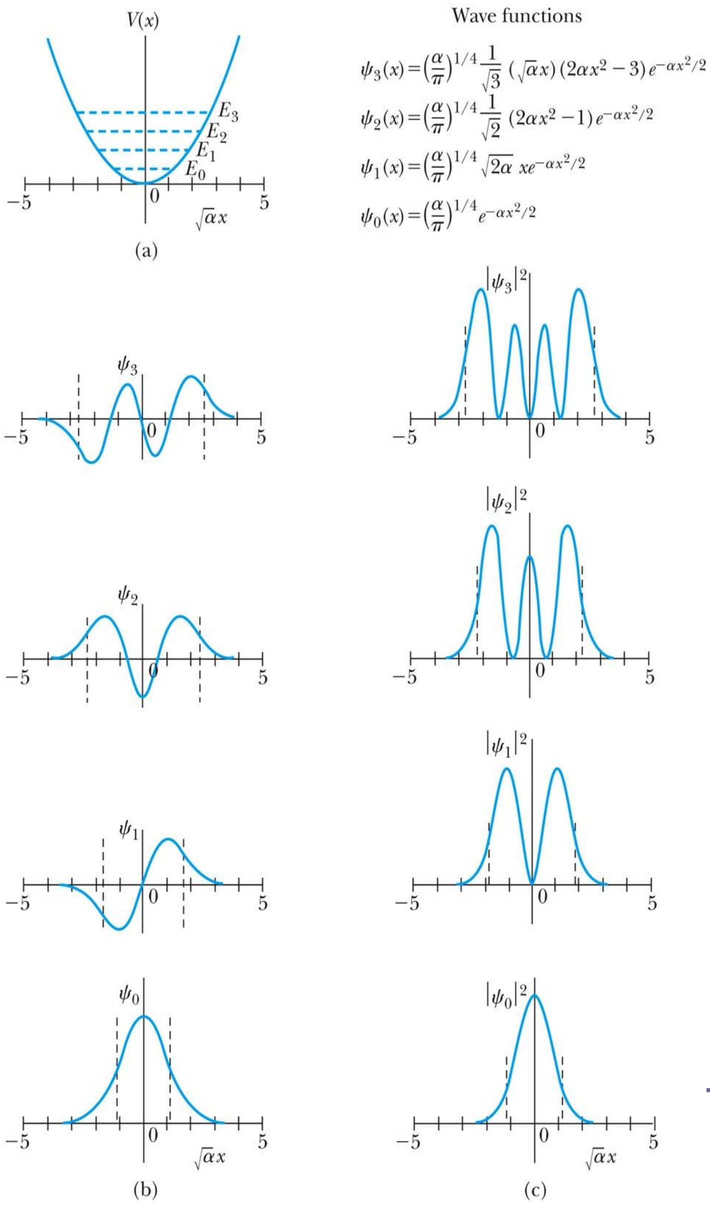


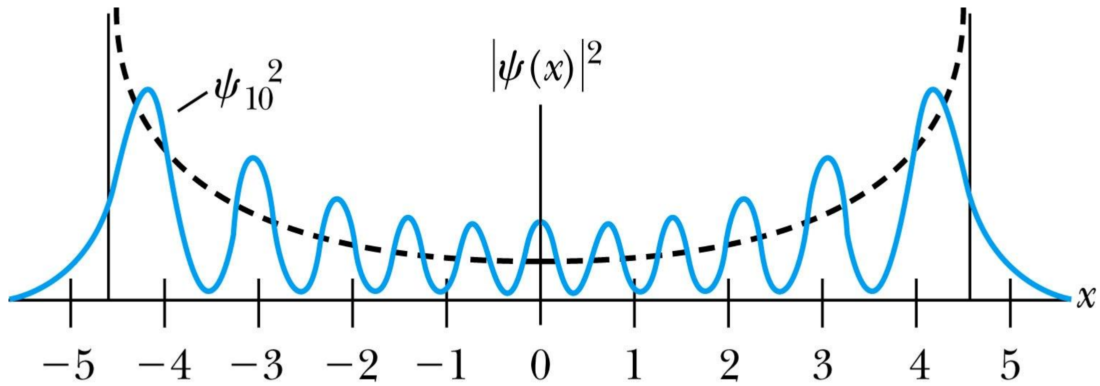


- If the lowest energy level is zero, this violates the uncertainty principle.
- The wave function solutions are $\psi_n = H_n(x)e^{-\alpha x^2/2}$ where $H_n(x)$ are Hermite polynomials of order n.

- In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small x. The exponential tail is provided by the Gaussian function, which dominates at large x.

Analysis of the Parabolic Potential Well





Wave functions

$$\psi_3(x)=\left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{3}}\left(\sqrt{\alpha}x\right)(2\alpha x^2-3)e^{-\alpha x^2/2}$$

$$\psi_2(x)=\left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{2}}(2\alpha x^2-1)e^{-\alpha x^2/2}$$

$$\psi_1(x)=\left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{2\alpha}\,xe^{-\alpha x^2/2}$$

$$\psi_0(x)=\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha x^2/2}$$

ty

at the center.

Hermite polynomial functions are shown above

A hydrogen molecule can be approximated as a simple harmonic oscillator with force constant k=1.1x10^3 N/m. Find (a) the energy levels and (b) the possible wavelengths of photons emitted when the H2 molecule decays from the second excited state eventually to the ground state.

39. The classical frequency for a two-particle oscillator is [see Chapter 10, Equation (10.4)] $\omega = \sqrt{k/\mu} = \sqrt{k(m_1+m_2)/m_1 m_2} = \sqrt{2k/m}$ since the masses are equal in this case. The energies of the ground state (E_0) and the first three excited states are given by $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$ so the possible transitions (from E_3 to E_2, E_3 to E_1, etc. are $\Delta E = \hbar\omega$, $2\hbar\omega$, and $3\hbar\omega$. Specifically these calculations give:

$\hbar\omega = \hbar\sqrt{\frac{2k}{m}} = \left(6.582\times10^{-16}\ \text{eV}\cdot\text{s}\right)\sqrt{\frac{2\left(1.1\times10^{3}\ \text{N/m}\right)}{1.673\times10^{-27}\ \text{kg}}} = 0.755\ \text{eV}$ with a wavelength

$$\lambda = \frac{hc}{E} = \frac{1240\ \text{eV}\cdot\text{nm}}{0.755\ \text{eV}} = 1640\ \text{nm}\ .$$

$$2\hbar\omega = 2\left(6.582\times10^{-16}\ \text{eV}\cdot\text{s}\right)\sqrt{\frac{2\left(1.1\times10^{3}\ \text{N/m}\right)}{1.673\times10^{-27}\ \text{kg}}} = 1.51\ \text{eV}$$

$$\lambda = \frac{hc}{E} = \frac{1240\ \text{eV}\cdot\text{nm}}{1.51\ \text{eV}} = 821\ \text{nm}$$

Deuteron in a nucleus

22. Consider a finite square-well potential well of width 3.00×10^{-15} m that contains a particle of mass $1.88\ \mathrm{GeV}/c^2$. How deep does this potential well need to be to contain three energy levels? (This situation approximates a deuteron inside a nucleus.)

We approximate with the infinite square well energy

$$E = \frac{n^2 h^2}{8 m L^2} = \frac{9\, h^2 c^2}{8\, mc^2\, L^2} = \frac{9\,(1240\ \mathrm{eV\,nm})^2}{8\,(1.88\times 10^{9}\ \mathrm{eV})\times(3\times10^{-6}\ \mathrm{nm})^2}$$

$$\boxed{E = 102\ \mathrm{MeV}}$$

See Appendix 3A Mathematical Relations

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

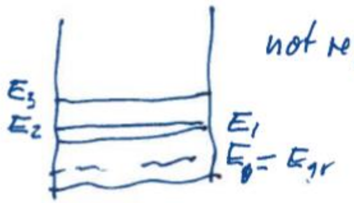
11. A wave function has the value $A \sin x$ between $x = 0$ and π but zero elsewhere. Normalize the wave function and find the probability that the particle is (a) between $x = 0$ and $x = \pi/4$ and (b) between $x = 0$ and $\pi/2$.

normalize:
$$\int_0^{\pi} \psi^*\psi\,dx = A^2\int_0^{\pi} \sin^2(x)\,dx \left\{ \left(\frac{1}{2}x - \frac{1}{4}\sin 2x\right)\Big|_0^{\pi} = \frac{\pi}{2} \right\} = A^2\frac{\pi}{2} = 1 \rightarrow A = \sqrt{\frac{2}{\pi}}$$

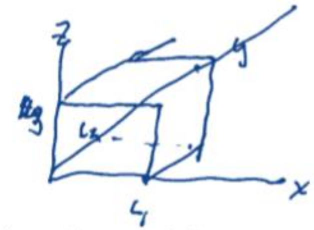
(a) $$P = \int_0^{\pi/4} \psi^*\psi\,dx = \frac{2}{\pi}\left(\frac{x}{2} - \frac{1}{4}\sin(2x)\right)\Big|_0^{\pi/4} = \frac{2}{\pi}\left(\frac{\pi}{8} - \frac{1}{4}\right) = \frac{1}{4} - \frac{1}{2\pi} = 0.091$$

(b) $$P = \frac{2}{4}\left(\frac{x}{2} - \frac{1}{4}\sin 2x\right)\Big|_0^{\pi/2} = \frac{2}{\pi}\left(\frac{\pi}{4} - 0\right) = \frac{1}{2} = 0.5$$

Rectangular box



not regular spaced!



31. A particle is trapped in a rectangular box having sides L, $2L$, and $4L$. Find the energy of the ground state and first three excited states. Are any of these states degenerate?

$$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2}{L^2} + \frac{n_2^2}{4L^2} + \frac{n_3^2}{16L^2}\right)$$

for groundstate $n_1 = n_2 = n_3 = 1$ $\quad E_{gr} = \frac{\pi^2\hbar^2}{2mL^2}\left(1 + \frac{1}{4} + \frac{1}{16}\right) = \frac{21}{32}\frac{\pi^2\hbar^2}{mL^2}$

for smallest additional energy = first excited state, make $n_3 = 2$

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2}\left(1 + \frac{1}{4} + \frac{1}{4}\right) = \frac{3}{4}\frac{\pi^2\hbar^2}{mL^2} \quad \text{(not degenerate)}$$

second excited state $\quad n_1=1, n_2=1, n_3=3 \qquad n_1=1, n_2=2, n_3=1$

$$E_2 = \frac{\pi^2\hbar^2}{2mL^2}\left(1 + \frac{1}{4} + \frac{9}{16}\right) = \frac{29}{32}\frac{\pi^2\hbar^2}{mL^2} \quad \text{(not degenerate)}, \quad E_3 = \frac{33}{32}\frac{\pi^2\hbar^2}{mL^2}$$

$$\boxed{\text{wave function } \psi(x,y,z) = A \sin\frac{n_1\pi}{L_1} \sin\frac{n_2\pi}{L_2} \sin\frac{n_3\pi}{L_3}}$$

Ch6.

35. A nitrogen atom of mass 2.32×10^{-26} kg oscillates in one dimension at a frequency of 10^{13} Hz. What are its effective force constant and quantized energy levels?

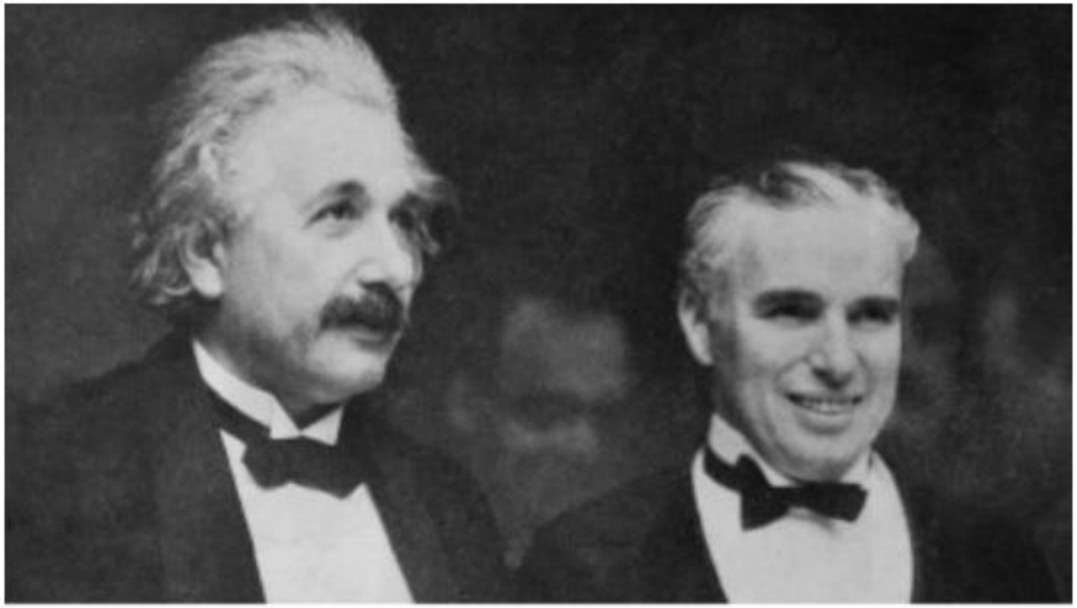
We use relation: $f = \frac{\omega}{2\pi} = \left(\frac{1}{2\pi}\right)\left(\frac{k}{m}\right)^{\frac{1}{2}}$

Force constant:

$$k = m \times (2\pi\, f)^2 = 2.32 \times 10^{-26} \times (2\pi \times 10^{13})^2 = 91.6\frac{N}{m}$$

Energy in eV:

$$E = \frac{h}{2\pi} \times 2\pi f\left(n + \frac{1}{2}\right) = 6.626 \times 10^{-34} \times \frac{10^{13}}{1.602 \times 10^{-19}}$$
$$= 4.136 \times 10^{-2} eV\left(n + \frac{1}{2}\right)$$



Albert Einstein and Charlie Chaplin

Einstein: What I most admire about your art, is your universality. You don’t say a word, yet the world understands you!

Chaplin: True. But your glory is even greater! The whole world admires you, even though they don’t understand a word of what you say.

CHAPTER 7
The Hydrogen Atom

- 7.1 Application of the Schrödinger Equation to the Hydrogen Atom
- 7.2 Solution of the Schrödinger Equation for Hydrogen
- 7.3 Quantum Numbers
- 7.4 Magnetic Effects on Atomic Spectra – The Normal Zeeman Effect

This spherical system has very high symmetry causing very high degeneracy of the wavefunctions

Lecture a

Labelling of corresponding video

Table 6.2 Common Observables and Associated Operators

Observable	Symbol	Associated Operator
Position	x	x
Momentum	p	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Potential energy	U	$U(x)$
Kinetic energy	K	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Hamiltonian	H	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$
Total energy	E	$i\hbar\frac{\partial}{\partial t}$

7.1: Application of the Schrödinger Equation to the Hydrogen Atom

- The approximation of the potential energy of the electron-proton system is electrostatic:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- Rewrite the three-dimensional time-independent Schrödinger Equation.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right] = E - V(r)$$

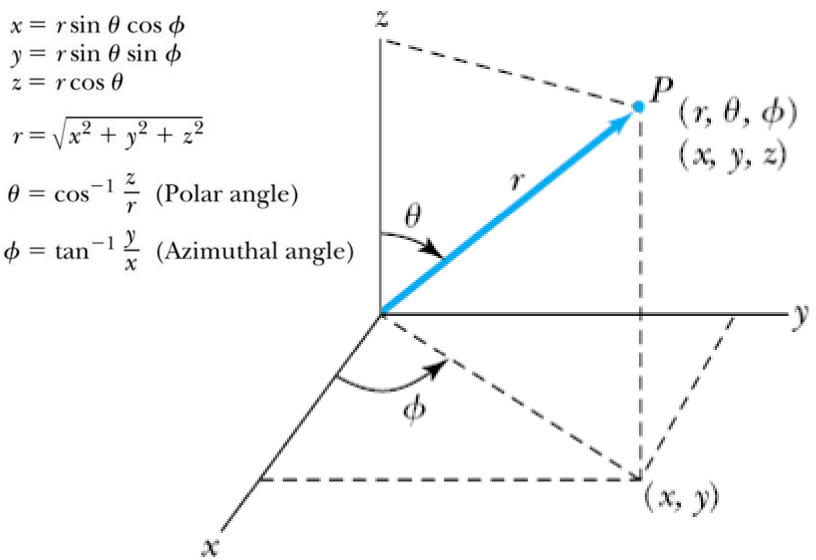
For Hydrogen-like atoms (He^+ or Li^{++})

- Replace e^2 with Ze^2 (Z is the atomic number)
- Use appropriate reduced mass μ

Uranium is a chemical element with the symbol U and atomic number Z=92

Application of the Schrödinger Equation

- The potential (central force) $V(r)$ depends on the distance r between the proton and electron.



Transform to spherical polar coordinates because of the radial symmetry.

Insert the Coulomb potential into the transformed Schrödinger equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0$$

Application of the Schrödinger Equation

- The wave function ψ is a function of r, θ, ϕ

$\longrightarrow$ Equation is separable.

$\longrightarrow$ Solution may be a product of three functions.

$\longrightarrow$ $$\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)$$ Equation 7.3

- We can separate Equation 7.3 into three separate differential equations, each depending on one coordinate: r, θ, or ϕ.

Divide and conquer !!

7.2: Solution of the Schrödinger Equation for Hydrogen

- Substitute Eq (7.4) into Eq (7.3) and separate the resulting equation into three equations: $R(r)$, $f(\theta)$, and $g(\phi)$.

Separation of Variables

- The derivatives from Eq (7.4)

$$\frac{\partial \psi}{\partial r} = fg\frac{\partial R}{\partial r} \qquad \frac{\partial \psi}{\partial \theta} = Rg\frac{\partial f}{\partial \theta} \qquad \frac{\partial^2 \psi}{\partial \phi^2} = Rf\frac{\partial^2 g}{\partial \phi^2}$$

- Substitute them into Eq (7.3)

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rfg = 0$$

- Multiply both sides of Eq (7.6) by $r^2 \sin^2 \theta \,/\, Rfg$

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V) - \frac{\sin\theta}{f}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial \phi^2}$$

Solution of the Schrödinger Equation

- Only r and θ appear on the left side and only ϕ appears on the right side of Eq (7.7)
- The left side of the equation cannot change as ϕ changes.
- The right side cannot change with either r or θ.

- Each side needs to be equal to a constant for the equation to be true. Set the constant $-m_\ell^2$ equal to the right side of Eq (7.7)

$$\frac{d^2 g}{d\phi^2} = -m_\ell^{\ 2} g$$ -------- **azimuthal equation** Eq (7.8)

- It is convenient to choose a solution to be $e^{im_\ell \phi}$

Properties of Valid Wave Functions

Boundary conditions

1) In order to avoid infinite probabilities, the wave function must be finite everywhere.
2) In order to avoid multiple values of the probability, the wave function must be single valued.
3) For finite potentials, the wave function and its derivative must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when *V* is infinite.)
4) In order to normalize the wave functions, they must approach zero as *x* approaches infinity.

Solutions that do not satisfy these properties do not generally correspond to physically realizable circumstances.

$$\Psi(x,t) = Ae^{i(kx-\omega t)} = A[\cos(kx-\omega t) + i\sin(kx-\omega t)]$$ Not normalizable

Solution of the Schrödinger Equation

- $e^{im_\ell \phi}$ satisfies Eq (7.8) for any value of m_ℓ.
- The solution be single valued in order to have a valid solution for any ϕ, which is $g(\phi) = g(\phi + 2\pi)$

  $g(\phi = 0) = g(\phi = 2\pi) \longrightarrow e^0 = e^{2\pi i m_\ell}$
- m_ℓ to be zero or an integer (positive or negative) for this to be true.
- If Eq (7.8) were positive, the solution would not be realized.

- Set the left side of Eq (7.7) equal to $-m_\ell^2$ and rearrange it.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\frac{m_\ell^{\ 2}}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

- Everything depends on r on the left side and θ on the right side of the equation.