PH 107 :Quantum Physics and Applications

Simple Harmonic Oscillator (1D and 3D cases)

Lecture 19: 17-02-2022

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Announcements

Mid-Sem Exam (Repeat)

19-02-2022 : 10am-12noon

Link for adding your questions for Saturday doubt session   Saturday; 19-02-2022: 11am

https://docs.google.com/spreadsheets/d/1OIe0cgIGs4s7UOAHzHZJelbaM_Uco2ZJf6O09d
YljUo/edit?usp=sharing

Derivation of Transmission coefficient for potential barrier available in Ms teams

Doubt-Midsem problem 2c

Wave Equation (Recall Lecture 8; Slide # 29)

The equation governing classical wave dynamics

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \varphi}{\partial t^2}$$
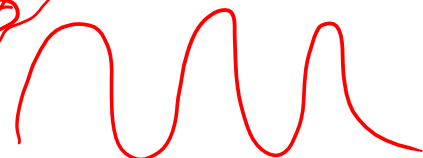
Possible solution are

$$\varphi(x,t) = A\cos(kx - \omega t)$$
$$\varphi(x,t) = A\sin(kx - \omega t)$$
$$\varphi(x,t) = Ae^{i(kx-\omega t)}$$
$$\varphi(x,t) = Ae^{-i(kx-\omega t)}$$

Solutions of this equation must superimpose.

$$\checkmark \quad \phi(x,t) = A \sin(kx - \omega t)$$

$$\vartheta_P = \frac{\omega}{k}$$

$$\omega \rightarrow \omega' + i\omega''$$
$$\quad\quad \uparrow RP \quad\quad \downarrow IP$$

$$\phi(x,t) = \text{Img } A e^{i(kx - \omega t)}$$

$$= \text{Img } A e^{i[kx - (\omega' + i\omega'')t]}$$

$$= \text{Img } A \left[e^{ikx - \omega't} \cdot \underline{e^{+i^2\omega''t}} \right]$$

$$= \text{Img } A \left[e^{i(kx - \omega't)} \right]$$

$$= e^{+\omega''t} \text{ Img } A \left[e^{i(kx - \omega't)} \right]$$

$$\boxed{\phi(x,t) = e^{\omega''t} \sin(kx - \omega't)} \quad \rightarrow \text{normal.}$$
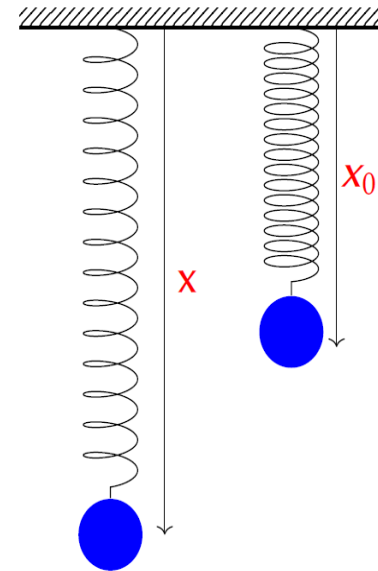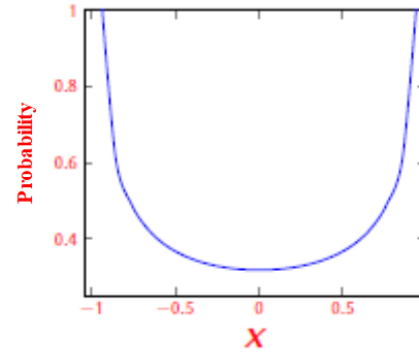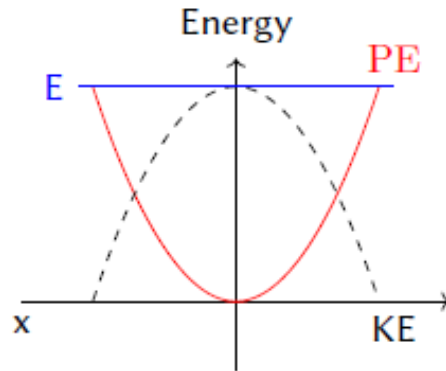
At imaginary(ω)
$\phi(x,t)$ represents a wave propagating with $\vartheta_P = \omega'/k$, with amplitude which is exponentially increasing.

Recap
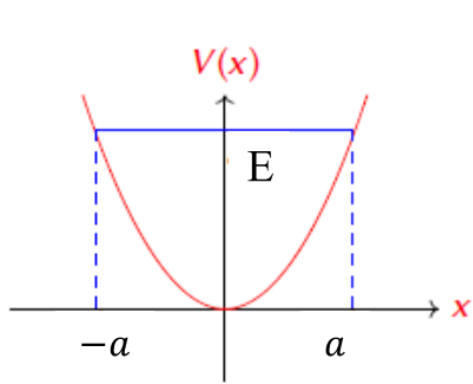
Turning Points $\implies a = \pm\sqrt{\dfrac{2E}{k}}$

k is spring constant
m is mass of the ball
spring is massless

- The frequency of the oscillator is determined by the effective mass M and the effective force constant K of the oscillating system and does not change unless one of these quantities is changed.

- There are no restrictions on the energy of the oscillator.

- Changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

- Probability of finding the particle is maximum at end of the motion.

Recap

Turning Points $\implies a = \pm\sqrt{\dfrac{2E}{k}}$
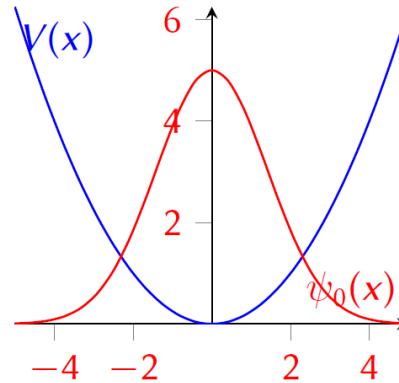
The ground state wave function,

$$\psi_o(x) = C_o\, e^{-m\omega x^2/2\hbar}$$
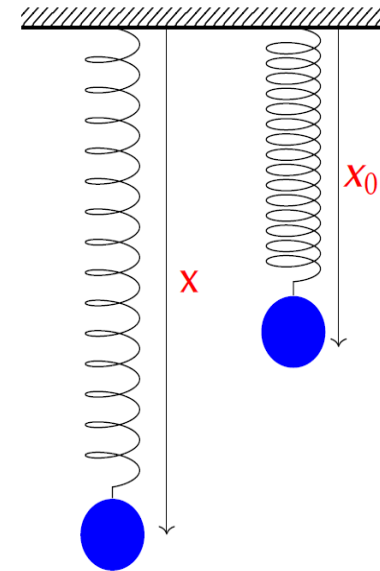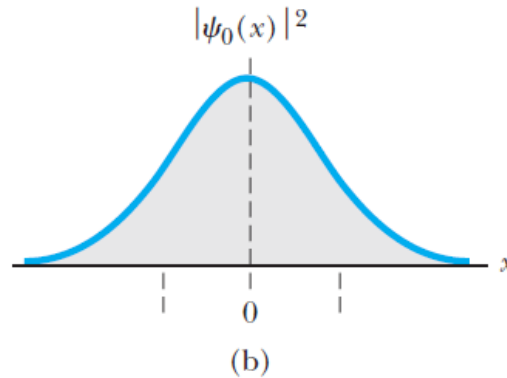
The ground state energy,

$$E = \frac{1\hbar\omega}{2}$$

$V(x)$

$\psi_0(x)$

$|\psi_0(x)|^2$

x_0

x

k is spring constant
m is mass of the ball
spring is massless

(b)

The probability to find particle in classically forbidden region in non-zero. Wavefunction exits in the region beyond classical turning points.

Normalizing ground state of QHO

$$\psi_o(x) = C_o \, e^{-\alpha x^2} \qquad\qquad \alpha = \frac{m\omega}{2\hbar}$$

$$\int_{-\infty}^{\infty} \psi_0^*(x)\psi_0(x)\,dx = 1 \qquad\qquad \boxed{\int_{-\infty}^{\infty} e^{-\beta x^2}\,dx = \left(\frac{\pi}{\beta}\right)^{1/2}}$$

$$|C_o|^2 \int_{-\infty}^{\infty} \exp\left(-2\alpha x^2\right)dx = |C_o|^2 \left(\frac{\pi}{2\alpha}\right)^{1/2} = 1$$

$$C_o = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

First excited eigenstates and eigen values of HO

The general solution of SE has the form ; $\psi_m(x) = e^{-\alpha x^2} \sum_m C_m x^m$

First excited state is antisymmetric around x =0 ; and have one node.

$$\psi_1(x) = C_1 x \psi_o(x) = C_1 x \, e^{-m\omega x^2/2\hbar}$$

Substitute in SE and check that, $E_1 = \dfrac{3\hbar\omega}{2}$

Properties of ground state and first excited state

Eigen functions: $\psi_o(x) = C_o e^{-m\omega x^2/2\hbar}$ $\qquad$ $\psi_1(x) = C_1 x\, e^{-m\omega x^2/2\hbar}$

- $\psi_o(-x) = \psi_o(x)$; Ground state eigen function is symmetric with respect to x and most likely to be found in the center.

- $\psi_1(-x) = -\psi_1(x)$; First excited eigen function is anti-symmetric with respect to x and most likely to be found away from the center.
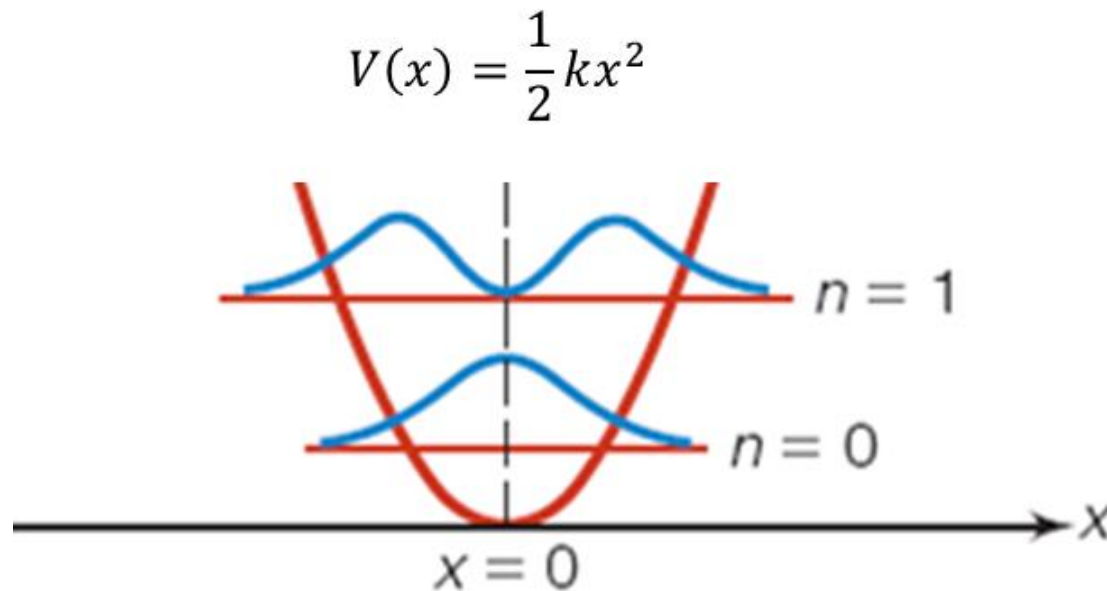
$$V(x) = \frac{1}{2}kx^2$$

Zero point energy: This implies that molecules are not completely at rest, even at absolute zero temperature.

Eigen values of HO

In general,

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

Energy states are equi-spaced.

$U(x)$

$E_5 = \frac{11}{2} \hbar \omega$

$E_4 = \frac{9}{2} \hbar \omega$

$E_3 = \frac{7}{2} \hbar \omega$

$E_2 = \frac{5}{2} \hbar \omega$

$\Delta E = \hbar \omega$

$E_1 = \frac{3}{2} \hbar \omega$
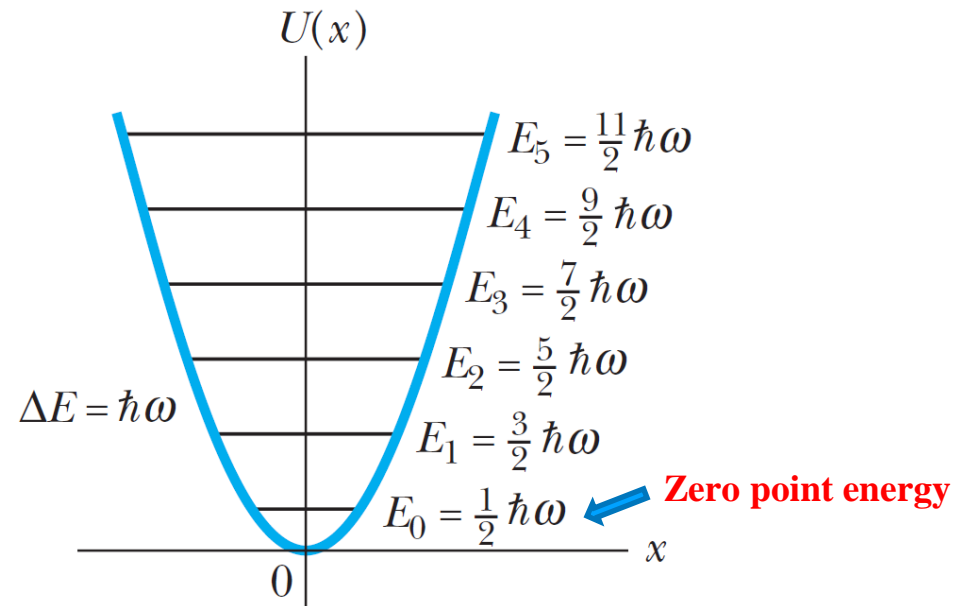
$E_0 = \frac{1}{2} \hbar \omega$ **Zero point energy**
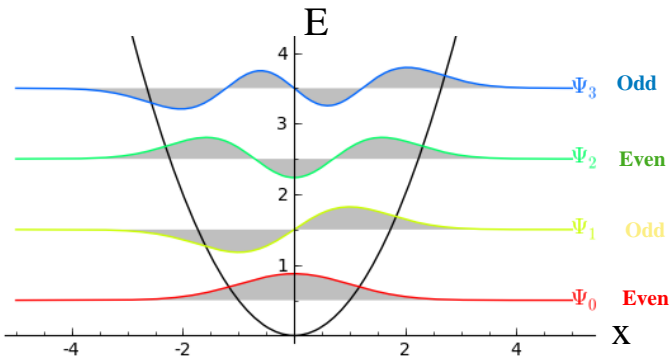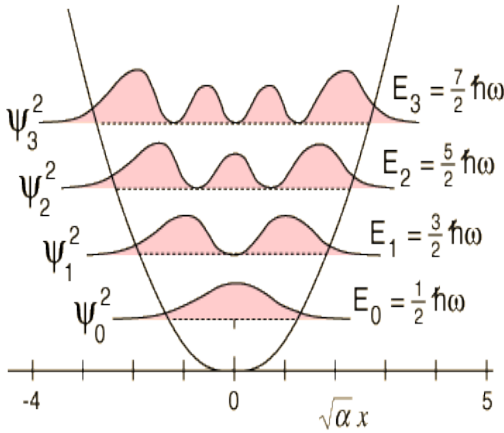
x

0

Zero point energy: This implies that molecules are not completely at rest, even at absolute zero temperature.

General Eigenstates , Eigen energies and Probability density

$$E_n = (n + \frac{1}{2})\hbar\omega \; ; \; n = 0,1,2,3 \ldots$$

First four harmonic oscillator normalized wavefunctions

$$\Psi_0 = \left(\frac{\alpha_1}{\pi}\right)^{1/4} e^{-y^2/2} \qquad\qquad E_o = \frac{1}{2}\hbar\omega$$

$$\Psi_1 = \left(\frac{\alpha_1}{\pi}\right)^{1/4} \sqrt{2}y\, e^{-y^2/2} \qquad\qquad E_1 = \frac{3}{2}\hbar\omega$$

$$\Psi_2 = \left(\frac{\alpha_1}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}}(2y^2 - 1)e^{-y^2/2} \qquad E_2 = \frac{5}{2}\hbar\omega$$

$$\Psi_3 = \left(\frac{\alpha_1}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}}(2y^3 - 3y)e^{-y^2/2} \qquad E_3 = \frac{7}{2}\hbar\omega$$

$$\alpha_1 = \frac{m\omega}{\hbar} \qquad y = \sqrt{\alpha_1}x$$

$$\Psi_n(y) = \left(\frac{\alpha_1}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y)e^{-y^2/2}$$

n	$H_n(y)$	E_n
0	1	$\frac{1}{2}\hbar\omega$
1	$2y$	$\frac{3}{2}\hbar\omega$
2	$4y^2 - 2$	$\frac{5}{2}\hbar\omega$
3	$8y^3 - 12y$	$\frac{7}{2}\hbar\omega$
4	$16y^4 - 48y^2 + 12$	$\frac{9}{2}\hbar\omega$
5	$32y^5 - 160y^3 + 120y$	$\frac{11}{2}\hbar\omega$

Comparison with CHO

- The most probable value of position for the lower states is very different from the classical harmonic oscillator where it spends more time near the end of its motion.

- As the quantum number increases, the probability distribution becomes more like that of the classical oscillator - this tendency to approach the classical behavior for high quantum numbers is called the correspondence principle.

- The energy of the quantum oscillator is quantized and the allowed quantized energy levels are equally spaced and are related to the oscillator frequencies. There are no restrictions on the energy of the classical oscillator.

- QHO posses zero-point energy which implies the atoms in a molecule must be moving even in the lowest vibrational energy state and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

- At large "n" ; higher energy states the tunneling of the wave function in the classically forbidden region decreases.

n=0

n=1

n=2

n=3

n=10
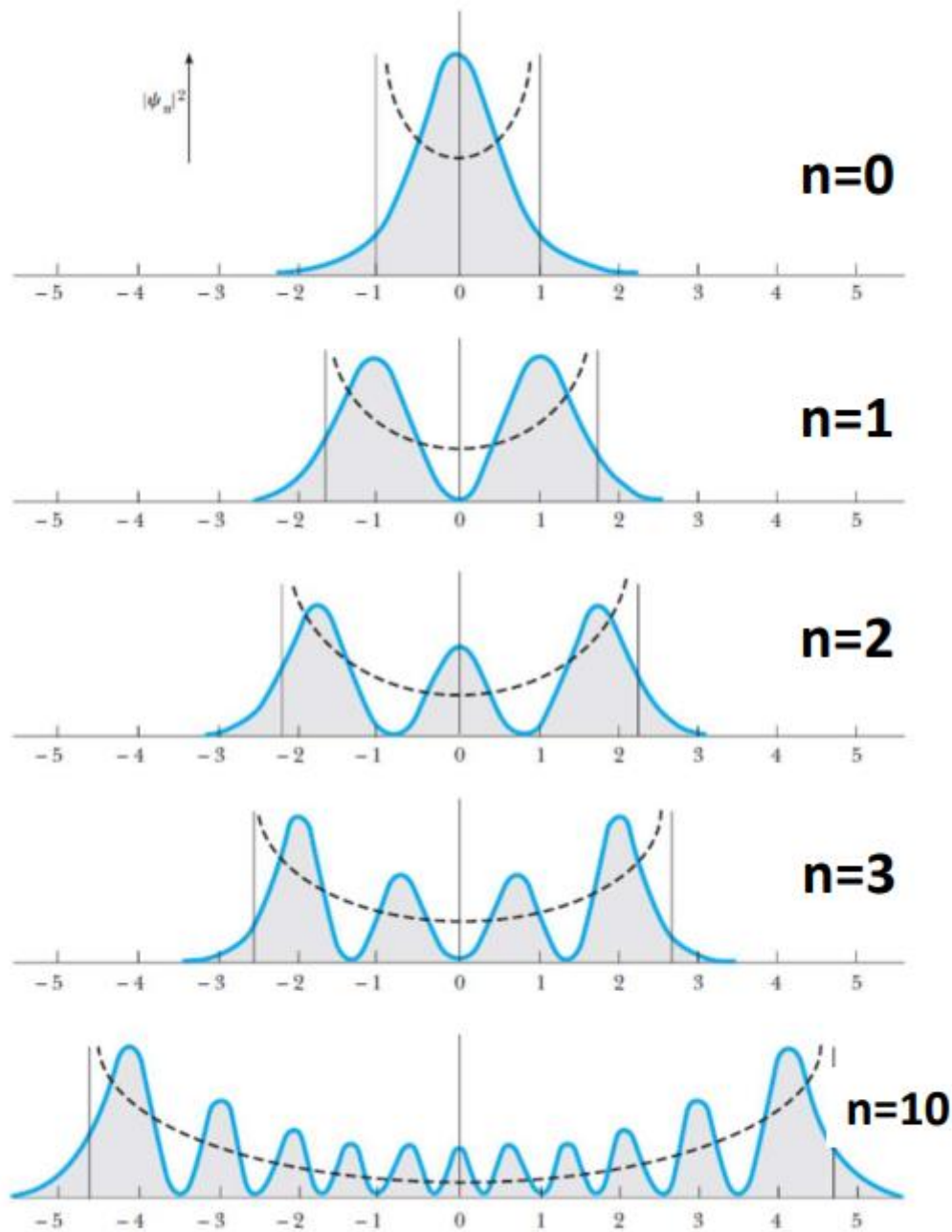
Figure 6.20 Probability densities for a few states of the quantum oscillator. The dashed curves represent the classical probabilities corresponding to the same energies.

Tunneling in Quantum Physics

- Due to the continuity requirement of the wave function at the boundaries when solving time-independent Schroedinger equation.

- The wave function cannot die off suddenly at the boundaries of a finite potential well or HO

  The wave function can only diminish in an exponential manner which then allow the wave function to extends slightly beyond the boundaries.

- The quantum tunneling effect is a manifestation of the wave nature of particle, which is governed by the Schroedinger equation.

- In classical physics, particles are just particles, hence never display tunneling effect.

Uncertainty relation for ground state of QHO

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

$$\langle x \rangle = \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-2\alpha x^2} \, dx = 0$$

$$\langle x^2 \rangle = \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} \, dx = \left(\frac{2\alpha}{\pi}\right)^{1/2} \frac{\pi^{1/2}}{2(2\alpha)^{3/2}} = \frac{\hbar}{2m\omega}$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{2m\omega}}$$

$$\langle p \rangle = -i\hbar \left(\frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \frac{\partial}{\partial x} e^{-\alpha x^2} dx = (-i\hbar) \left(\frac{2\alpha}{\pi} \right)^{1/2} (-2\alpha) \int_{-\infty}^{\infty} x e^{-2\alpha x^2} dx = 0$$

$$\langle p^2 \rangle = (-i\hbar)^2 \left(\frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \frac{\partial^2}{\partial x^2} e^{-\alpha x^2} dx$$

$$= (-i\hbar)^2 \left(\frac{2\alpha}{\pi} \right)^{1/2} \left[(-2\alpha) \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx + (4\alpha^2) \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx \right]$$

$$= (-i\hbar)^2 \left(\frac{2\alpha}{\pi} \right)^{1/2} \left[(-2\alpha) \left(\frac{\pi}{2\alpha} \right)^{1/2} + (4\alpha^2) \left(\frac{\pi^{1/2}}{2(2\alpha)^{3/2}} \right) \right] = \hbar^2 \alpha$$

$$= \hbar^2 \frac{m\omega}{2\hbar} = \frac{\hbar m\omega}{2}$$

$$\boxed{\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{\hbar m\omega}{2}}}$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{2m\omega}}$$
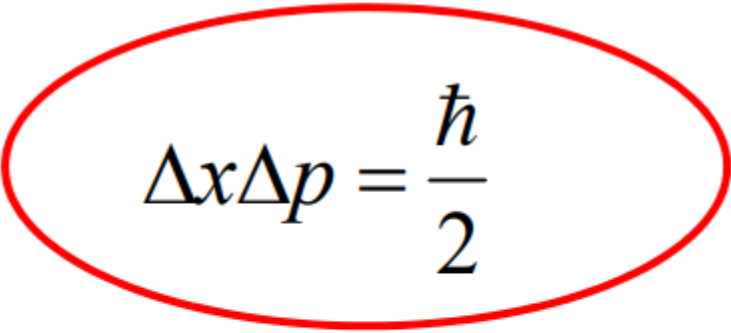
$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{\hbar m \omega}{2}}$$

$$\Delta x \Delta p = \frac{\hbar}{2}$$

Harmonic oscillator ground state is a minimum uncertainty state

Quantum Mechanical Problems in Three Dimensions

From 1D to 2D

So far we have been discussing only one-dimensional problems. What happens when we venture out in higher dimensions (2D/3D)?

Life immediately becomes complicated! In 1D, we could move in only two directions: forward or backward.

In a 2D/3D, there are an infinite number of directions to choose from!

In 1D, bound motion is necessarily oscillatory. In 2D/3D, another type of bound motion becomes possible. Rotational motion!

Potentials from 1D to 2D/3D

Consider the potential can be written as the sum of two/three terms, i.e.

$$V(x, y) = V(x) + V(y) \quad \text{(In 2D)}$$

and

$$V(x, y, z) = V(x) + V(y) + V(z) \quad \text{(In 3D)}$$

As an example, we consider the potential

$$V(x, y, z) = \frac{1}{2} m\omega^2 (x^2 + y^2 + z^2)$$

$$= V(x) + V(y) + V(z)$$

In this case (as will be shown now), the problem neatly separates into 3 sub-problems.

Operators in 3D

Position operator:
$$\vec{r} = \hat{e}_x x + \hat{e}_y y + \hat{e}_z z$$

Momentum operator:
$$\vec{p} = -i\hbar \left(\hat{e}_x \frac{\partial}{\partial x} + \hat{e}_y \frac{\partial}{\partial y} + \hat{e}_z \frac{\partial}{\partial z} \right) = -i\hbar \vec{\nabla}$$

Kinetic energy operator:
$$T = \frac{\vec{p} \cdot \vec{p}}{2m} = -\frac{\hbar^2}{2m} \nabla \cdot \nabla = -\frac{\hbar^2}{2m} \nabla^2$$

$$\text{Laplacian } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Hamiltonian:
$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$$

Wave function:
$$\psi(\vec{r}) = \psi(x, y, z)$$

How do we solve the TISE?

In the case $V(x, y, z) = V(x) + V(y) + V(z)$

we first start by writing the TISE in 3D

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(x, y, z) + V(x, y, z)\Psi(x, y, z) = E\Psi(x, y, z)$$

where

$$\nabla^2 \Psi(x, y, z) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z)$$

We try the same old trick of separation of variables, i.e. start with a trial solution

$$\Psi(x, y, z) = \phi(x)\eta(y)\zeta(z)$$

How do we solve the TISE?

So we have,

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x) + V(y) + V(z)\right]\phi(x)\eta(y)\zeta(z) = E\phi(x)\eta(y)\zeta(z)$$

or

$$\left[\frac{\partial^2}{\partial x^2} + \frac{2m}{\hbar^2}V(x)\right]\phi\eta\zeta + \left[\frac{\partial^2}{\partial y^2} + \frac{2m}{\hbar^2}V(y)\right]\phi\eta\zeta + \left[\frac{\partial^2}{\partial z^2} + \frac{2m}{\hbar^2}V(z)\right]\phi\eta\zeta + \frac{2m}{\hbar^2}E\phi\eta\zeta = 0$$

or

$$\left[\eta\zeta\frac{\partial^2\phi}{\partial x^2} + \frac{2m}{\hbar^2}V(x)\phi\right] + \left[\phi\zeta\frac{\partial^2\eta}{\partial y^2} + \frac{2m}{\hbar^2}V(y)\eta\right] + \left[\phi\eta\frac{\partial^2\zeta}{\partial z^2} + \frac{2m}{\hbar^2}V(z)\zeta\right] + \frac{2m}{\hbar^2}E\phi\eta\zeta = 0$$

Dividing by $\phi\eta\zeta$, we get

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

How do we solve the TISE?

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

Since the RHS is a constant, each term in LHS should be equated to a constant. We can write,

$$\frac{1}{\phi}\frac{d^2\phi}{dx^2} + \frac{2m}{\hbar^2}V(x) = -\frac{2m}{\hbar^2}E_x$$

$$\frac{1}{\eta}\frac{d^2\eta}{dy^2} + \frac{2m}{\hbar^2}V(y) = -\frac{2m}{\hbar^2}E_y$$

$$\frac{1}{\zeta}\frac{d^2\zeta}{dz^2} + \frac{2m}{\hbar^2}V(z) = -\frac{2m}{\hbar^2}E_z$$

This way we are equating ; $E = E_x + E_y + E_z$

How do we solve the TISE?

So, the 3D TISE simplifies to three 1D sub-TISEs:

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V(x)\phi = E_x\phi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\eta}{dy^2} + V(y)\eta = E_y\eta$$

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

We can solve each of them the way we did previously.

The solutions we get will be the corresponding eigenstates $\phi_n(x), \eta_m(y),$ and $\zeta_p(z)$, so that

$$\Psi_{n,m,p}(x,y,z) = \phi_n(x)\eta_m(y)\zeta_p(z)$$

and the corresponding eigenvalues E_n, E_m, and E_p add up to give the total energy of the particle, i.e.
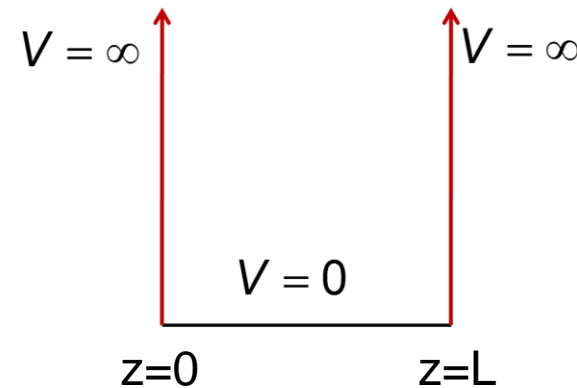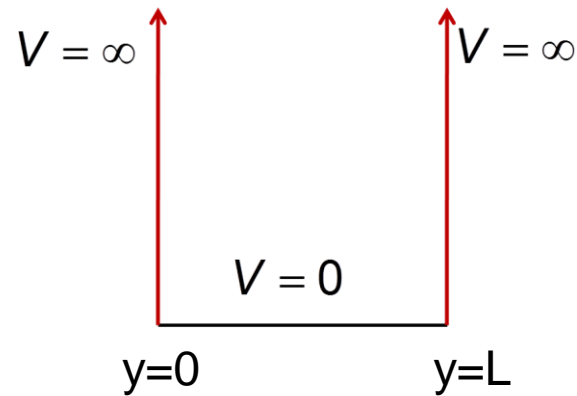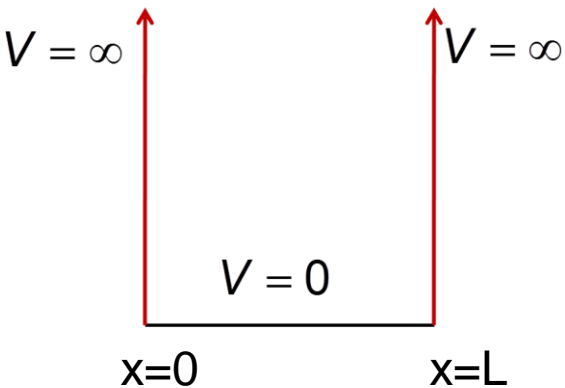
$$E = E_n + E_m + E_p$$

Example 1: Particle in an infinite 3D box (Cubic)

$$V(x, y, z) = V(x) + V(y) + V(z)$$

such that,

$$V(x) = V(y) = V(z) = 0 \qquad \forall \ 0 \leq x, y, z \leq L$$

$$V(x) = V(y) = V(z) = \infty \quad otherwise$$

$V = \infty$ $V = \infty$ $V = \infty$ $V = \infty$ $V = \infty$ $V = \infty$

$V = 0$ $V = 0$ $V = 0$

x=0   x=L   y=0   y=L   z=0   z=L

Example 1: Particle in an infinite 3D box

The solution $\Psi_{n,m,p}(x,y,z) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)\sqrt{\frac{2}{L}}\sin\left(\frac{m\pi}{L}y\right)\sqrt{\frac{2}{L}}\sin\left(\frac{p\pi}{L}y\right)$

$$= \left(\frac{2}{L}\right)^{\frac{3}{2}}\sin\left(\frac{n\pi}{L}x\right)\sin\left(\frac{m\pi}{L}y\right)\sin\left(\frac{p\pi}{L}y\right)$$

$$E = E_n + E_m + E_p$$

i.e. $\qquad E = \frac{\pi^2\hbar^2}{2mL^2}(n^2 + m^2 + p^2) \; ; \; n,m,p = 1,2,3\ldots$

$$N = n^2 + m^2 + p^2$$

So we can label the states as (n, m, p), i.e. $(1,1,1), (2,1,1), (1,2,1), (1,1,2)$ etc.

We note that the ground state $(1,1,1)$ is unique with energy

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2} \; ; \text{ non-degenerate}$$

The first excited states $(2,1,1), (1,2,1), (1,1,2)$ have the same energy

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}; \; \text{3 fold degenerate}$$

Example 1: Degeneracies

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$$

Thus we talk of **3-fold degeneracy** of the state with energy $\frac{6\pi^2\hbar^2}{2mL^2}$

Degeneracies: Two or more eigen states of a system may have same energy even though their eigen functions are different.

This 3-fold degeneracy is characteristic of potentials with discrete symmetry $x \leftrightarrow y, y \leftrightarrow z, z \leftrightarrow x$, i.e. if we interchange the co-ordinates, we still have the same potential.

When this symmetry is lost, the degeneracy is also lost.

For example, when the potential box is not cubic.

Example 1: Degeneracies (non-cubic)

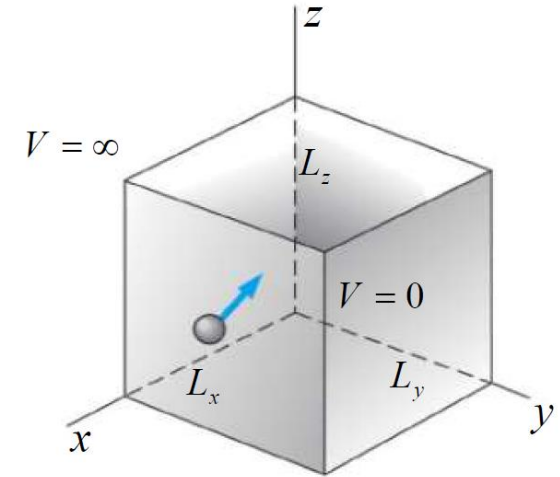i.e., if, $\qquad V(x, y, z) = V(x) + V(y) + V(z)$

such that,

$$V(x) = 0 \qquad\qquad \forall\, 0 \leq x$$

$$V(y) = 0 \qquad\qquad \forall\, 0 \leq y$$

$$V(z) = 0 \qquad\qquad \forall\, 0 \leq z \leq L_z$$

$$V(x) = V(y) = V(z) = \infty \quad otherwise$$

the energy becomes ; $\quad E = \dfrac{\pi^2 \hbar^2}{2m} \left(\dfrac{n^2}{L_x^2} + \dfrac{m^2}{L_y^2} + \dfrac{p^2}{L_z^2} \right)$

SE in 3D, Degeneracy and Symmetry

| **3D box of same length (Cubic box)** | **3D box of varying length (Cubic box)** |

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n^2 + m^2 + p^2)$$

$$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{p^2}{L_z^2}\right)$$

$$E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2}$$

$$E_{211} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{4}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right)$$

$$E_{121} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{1}{L_x^2} + \frac{4}{L_y^2} + \frac{1}{L_z^2}\right)$$

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2}$$

$$E_{112} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{4}{L_z^2}\right)$$

ie. $E_{211} \neq E_{121} \neq E_{112}$

3-fold degeneracy

Non-degenerate

Example 2: 3D Isotropic Simple Harmonic Oscillator

$$V(x, y, z) = \frac{1}{2} m\omega^2 (x^2 + y^2 + z^2)$$

It is easy to see that

$$V(x, y, z) = \frac{1}{2} m\omega^2 x^2 + \frac{1}{2} m\omega^2 y^2 + \frac{1}{2} m\omega^2 z^2$$
$$= V(x) + V(y) + V(z)$$

We can also write

$$\Psi_{000}(x, y, z) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} e^{-(m\omega/2\hbar)(x^2+y^2+z^2)}$$

and
$$E_{nmp} = \left(n + m + p + \frac{3}{2}\right)\hbar\omega$$

Example 2: 3D Simple Harmonic Oscillator

$$E_{000} = \frac{3}{2}\hbar\omega \text{ is unique.}$$

First excited state,

$$E_{100} = E_{010} = E_{001} ; 3\ fold\ degenerate$$

Second excited state,

$$E_{110} = E_{011} = E_{101} = E_{200} = E_{020} = E_{002};\ 6\ fold\ degenerate$$

and so on.

The degeneracy is lost if

$$V(x, y, z) = \frac{1}{2}m\big(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\big)$$

i.e. if the symmetry $x \leftrightarrow y, y \leftrightarrow z, z \leftrightarrow x$ is broken

Ground state is non-degenerate and all other states are degenerate for HO