Schrödinger equation

In the previous discussion, we learnt how to calculate various thermodynamic properties using partition function. The partition function in turn was composed of Boltzmann factors summed over all accessible quantum states. Calculation of Boltzmann factor requires the energy of the system. It has not been described yet how to calculate the energy of a particle. This is possible by employing the governing equation of quantum mechanics called Schrödinger equation. The equation is given as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}\right) + \hat{V}\Psi \qquad -(1)$$

$\Psi(x,y,z,t)$ is called the wavefunction. The other terms are

$i\hbar\frac{\partial}{\partial t} \rightarrow$ operator giving the time-variation of Ψ

$-i\hbar\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) \rightarrow$ momentum operator

$\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \rightarrow$ kinetic energy operator

$\hat{V} \rightarrow$ potential energy operator

* Observables of classical mechanis have corresponding operators in quantum mechanics.

If the potential energy operator is considered to be only a function of the spatial coordinates then Eq^n (1) can be solved using separation of variables technique. For a 1-D system,

$$\Psi = \Psi(x,t)$$

Let $\Psi(x,t) = \psi(x)\phi(t)$

$$\Rightarrow i\hbar \frac{\partial}{\partial t}\left\{\psi(x)\phi(t)\right\} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{\psi(x)\phi(t)\right\}$$

$$+ V(x)\psi(x)\phi(t)$$

$$\Rightarrow i\hbar\psi(x)\frac{\partial\phi(t)}{\partial t} = \left(-\frac{\hbar^2\phi(t)}{2m}\right)\frac{\partial^2\psi(x)}{\partial x^2}$$

$$+ V(x)\psi(x)\phi(t) \quad -(2)$$

Division of Eq^n (2) by $\psi(x)\phi(t)$ on both the sides gives

$$i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)$$

— (3)

It can be seen that the LHS of Eq^n (3) is a function of t only while the RHS is a function of x only. This equality is possible only if both the sides are individually equal to a same constant. This constant happens to be the energy of the system.

$$\Rightarrow \quad i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = E \qquad -(4)$$

$$\frac{-\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) = E \quad -(5)$$

Let us first consider the time-dependent part. Solution of Eq^n (4) can be obtained as follows:

$$\frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = \frac{-iE}{\hbar}$$

$$\Rightarrow \quad \phi(t) = c_1 \exp\left(\frac{-iEt}{\hbar}\right) \qquad -(6)$$

The solution to the time-independent part can be obtained only after having a knowledge of the exact form of $V(x)$. Therefore, in general

$$\Psi(x,t) = c\, e^{(-iEt/\hbar)}\, \psi(x) \qquad -(7)$$

$\Psi(x,t)^* \Psi(x,t)\, dx$ gives the probability of finding the particle from x to $x+dx$.

$$\Psi^* \Psi = \psi^*(x)\, e^{(iEt/\hbar)} \cdot \psi(x)\, e^{(-iEt/\hbar)}$$

$$\Rightarrow \hat{\Psi}^* \Psi = \psi^* \psi$$

We have not considered the constant c the reason for which is normalization which will be discussed later.

The expectation value of a variable A is given by the operation

$$\langle A \rangle = \langle \hat{\Psi}^* | A | \hat{\Psi} \rangle \qquad -(8)$$

The above is an inner product operation and is easy to see that

$$\langle A \rangle = \langle \psi^* | A | \psi \rangle \qquad -(9)$$

i.e. the expectation value of stationary-state properties can be obtained from a knowoledge of just the time independent part. The time-independent Schröding equation can be cast as

$$\hat{H} \psi = E \psi$$

where $\hat{H}$ is the Hamiltonian operator.

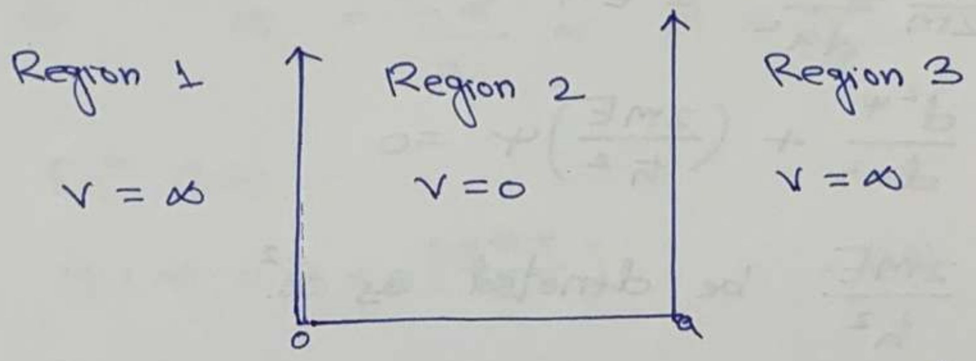
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \qquad -(10)$$

A particle in an infinite 1-D well :

Suppose that a particle is present in a potential such that

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{everywhere else} \end{cases}$$

The situation can be described pictorically as shown below



The particle experiences zero potential inside the well i.e. it is completely free inside the well. Outside the well, the potential is infinite. Therefore, we analyze and solve Schrödinger equation in three different regions

Regions 1 and 3 :

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad ; V = \infty$$

$$\Rightarrow \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (E - \infty)\psi$$

$$\Rightarrow \psi = \left(\frac{1}{\infty}\right) \frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = 0 \qquad -(11)$$

Therefore the probability of finding the particle in regions 1 and 3 is zero. The particle cannot be found in these regions.

Region 2:

Here we have $V(x) = 0$. Therefore the time-independent Schrödinger equation for this case becomes

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

$$\Rightarrow \frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2}\right)\psi = 0$$

Let $\frac{2mE}{\hbar^2}$ be denoted as α^2.

$$\Rightarrow \frac{d^2\psi}{dx^2} + \alpha^2\psi = 0$$

$$\Rightarrow \psi(x) = A\sin\alpha x + B\cos\alpha x \quad -(12)$$

A requirement for a function to be a wavefunction is that it should be continuous everywhere. Eqn (11) provides the conditions needed to be imposed on Eqn (12)

$$\psi(0) = 0$$

$$\psi(a) = 0$$

$$\Rightarrow A\sin(0) + B\cos(0) = 0$$

$$\Rightarrow B = 0$$

$$\Rightarrow \psi(x) = A\sin\alpha x \quad -(13)$$

$$\Rightarrow \quad A\sin(\alpha a) = 0$$

$$\Rightarrow \quad A = 0 \quad \text{or} \quad \sin(\alpha a) = 0$$

A cannot be zero as $A = 0$ makes $\psi = 0$ everywhere which means that the particle cannot be found anywhere.

$$\Rightarrow \quad \sin(\alpha a) = 0$$

$$\Rightarrow \quad \alpha a = n\pi \quad ; \quad n \in \mathbb{I} - \{0\}$$

$$\Rightarrow \quad a = \frac{n\pi}{\alpha} \quad \text{or} \quad \alpha = \frac{n\pi}{a}$$

From Eq^n (13)

$$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right) \qquad - (14)$$

Now after getting the expression for the wavefunction, the expression for energy is desired.

$$\alpha = \frac{n\pi}{a}$$

$$\Rightarrow \alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$\Rightarrow E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad ; \quad n \in \mathbb{I} - \{0\} \qquad - (15)$$

We have replaced E by E_n to highlight the 'n' appearing on RHS of Eq^n (15). It can be seen that the energies of the particles are not continuous. The marked appearence of n^2 on the RHS suggests that the energies are quantized.

The constant A in Eq^n (14) remains to be determined. We make use of the fact that the probability of finding the particle in the entire region must be normalized.

$$\Rightarrow \int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

$$\Rightarrow \int_{-\infty}^{0} \psi^* \psi \, dx + \int_{0}^{a} \psi^* \psi \, dx + \int_{a}^{\infty} \psi^* \psi \, dx = 1$$

$$\Rightarrow \int_{0}^{a} \psi^* \psi \, dx = 1$$

$$\Rightarrow \int_{0}^{a} A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

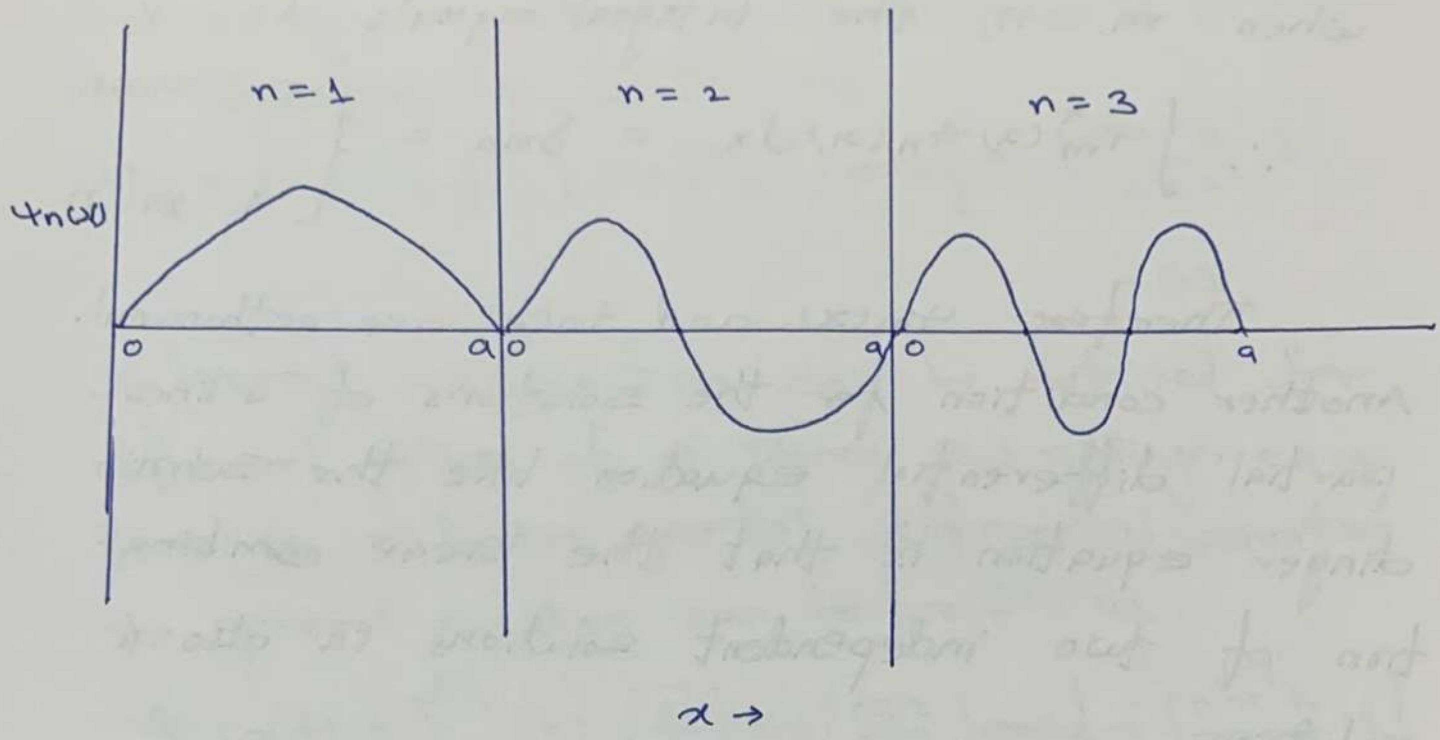
$$\Rightarrow A^2 \left(\frac{a}{2}\right) = 1$$

$$\Rightarrow A = \sqrt{2/a} \qquad -(16)$$

$$\Rightarrow \psi_n(x) = \left(\sqrt{\frac{2}{a}}\right) \sin\left(\frac{n\pi x}{a}\right) \qquad -(17)$$

The energy corresponding to the lowest possible value of n (i.e. n = 1) is called the ground state energy. The higher values of n will give excited state wavefunctions and correspondiy energies.

$\psi_n(x)$ for different values of n are shown below.



The subscript 'n' in $\psi_n(x)$ signifies that there can be more than one wavefunctions associated with a particle. This is precisely what was referred to as the "quantum states" of the system. Another requirement of the wavefunctions is that they all should be orthogonal. Consider two wavefunctions given by $\psi_n(x)$ and $\psi_m(x)$.

$$\int_0^a \psi_m^*(x)\,\psi_n(x)\,dx = \int_0^a \left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{m\pi x}{a}\right)\left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{2}{a}\int_0^a \left[\frac{1}{2}\left\{\cos\left(\frac{m-n}{a}\right)\pi x - \cos\left(\frac{m+n}{a}\right)\pi x\right\}\right]dx$$

$$= \left(\frac{1}{m-n}\right)\frac{1}{\pi}\sin\left(\frac{m-n}{a}\right)\pi x - \left(\frac{1}{m+n}\right)\frac{1}{\pi}\sin\left(\frac{m+n}{a}\right)\pi x\,\Bigg|_0^a$$

When $m \neq n$, the integral equals zero and when $m = n$, the integral equals 1.

$$\therefore \int \psi_m^*(x)\psi_n(x)\,dx = \delta_{mn} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

Therefore, $\psi_m(x)$ and $\psi_n(x)$ are orthonormal. Another condition for the solutions of a linear partial differential equation like the Schrödinger equation is that the linear combination of two independent solutions is also a solution.

$$\psi(x) = \sum_{m=1}^{\infty} c_m \psi_m(x)$$

$$\Rightarrow \psi(x) = \left(\sqrt{\frac{2}{a}}\right)\sum_{m=1}^{\infty} c_m \sin\left(\frac{m\pi x}{a}\right) \quad -(18)$$

A knowledge of the coefficients c_m's is required to obtain a complete set of solutions. One can use the orthogonality condition to obtain the coefficients.

$$\int \psi_m^*(x)\psi_p(x)\,dx = \sum_{p=1}^{\infty} c_p \int \psi_m^*(x)\psi_p(x)\,dx$$

$$= \sum_{p=1}^{\infty} c_p \delta_{mp}$$

$$= c_m$$

The wavefunction following the time-dependent Schrödinger equation in 1-D infinite potential can, therefore, be written as

$$\Psi_n(x,t) = \left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{n\pi x}{a}\right)\exp\left\{-i\left(\frac{n^2\pi^2\hbar}{2ma^2}\right)t\right\}$$

– (19)

Different wavefunctions can be obtained for different values of n. Since Schrödinger equation is a linear partial differential equation, the general solution can be written as:

$$\Psi_n(x,t) = \sum_{n=1}^{\infty} C_n\left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{n\pi x}{a}\right)\exp\left\{-i\left(\frac{n^2\pi^2\hbar}{2ma^2}\right)t\right\}$$

– (20)

While solving the spatial part, we have two possible solutions:

$$\psi(x) = A\sin\alpha x + B\cos\alpha x$$

and

$$\psi(x) = Ae^{-\alpha x} + Be^{\alpha x}$$

depending upon whether α^2 is positive or negative. If $\alpha^2 < 0$, $2mE/\hbar^2 < 0$. Since m and $\hbar$ are positive constants, $E < 0$ in such a case. However, the energy cannot be lesser than the applied potential. Since $V = 0$, E cannot be lesser than zero. Hence $\alpha^2 > 0$ and we choose the solutions in terms of cos and sin.

Particle in a three-dimensional box:

Consider a particle in a 3-D box subject to a potential given by

$$V(x,y,z) = \begin{cases} 0 & \begin{cases} 0 \leq x \leq a \\ 0 \leq y \leq b \\ 0 \leq \cancel{y}z \leq c \end{cases} \\ \infty & \text{everywhere else} \end{cases}$$

The time-independent Schrödinger equation for this system is

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

$$= E\psi(x,y,z) \qquad -(21)$$

The equation is still a partial differential equation and we carry out separation of variables as follows:

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

Learning from the previous case of 1-D well, we solve for only the particle inside the box with $V(x,y,z)=0$ inside the box.

$$\Rightarrow -\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}\right) = EXYZ$$

$$\Rightarrow \frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

$$-(22)$$

We define the single-variable ordinary differential equations as

$$\frac{1}{X}\frac{d^2X}{dx^2} = E_x\left(\frac{-2m}{\hbar^2}\right)$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = E_y\left(\frac{-2m}{\hbar^2}\right)$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = E_z\left(\frac{-2m}{\hbar^2}\right)$$

with $E_x + E_y + E_z = E$. Now consider the first of these equations.

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2}$$

$$\Rightarrow \frac{d^2X}{dx^2} + \left(\frac{2mE_x}{\hbar^2}\right)X = 0$$

Assuming $\frac{2mE_x}{\hbar^2} = \alpha^2$

$$\frac{d^2X}{dx^2} + \alpha^2 X = 0$$

$$\Rightarrow X = A\sin\alpha x$$

with $\alpha = \frac{n_x\pi}{a}$; $n_x \in \mathbb{I} - \{0\}$

$$E_x = \frac{n_x^2\pi^2\hbar^2}{2ma^2} \quad - (23)$$

and

$$X(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right) \quad - (24)$$

Similar expressions can be obtained for the y- and z- directions.

$$E_x = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2} \quad ; \quad X(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a}\right)x$$

$$E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mb^2} \quad ; \quad Y(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b}\right)y$$

$$E_z = \frac{n_z^2 \pi^2 \hbar^2}{2mc^2} \quad ; \quad Z(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi}{c}\right)z$$

The overall wavefunction can be written as

$$\psi(x,y,z) = \left(\sqrt{\frac{8}{abc}}\right) \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \quad -(25)$$

Degeneracy:

The total energy of the particle in the 3-D box is given by

$$E = E_x + E_y + E_z$$

$$\Rightarrow E = \frac{\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad -(26)$$

The lowest energy state is unique which is given by $n_x = n_y = n_z = 1$

$$E(1\,1\,1) = \frac{\hbar^2}{2m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right) \quad -(27)$$

Now consider a box for which $a = b = c$

$$E = \frac{\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\Rightarrow \quad E(111) = \frac{3\hbar^2}{2ma^2}$$

However, for $n_x = 2;\ n_y = 1;\ n_z = 1$

or $n_x = 1;\ n_y = 2;\ n_z = 1$

or $n_x = 1;\ n_y = 1;\ n_z = 2$

$$E(211) = E(121) = E(112) = \frac{3\hbar^2}{ma^2}$$

Therefore, there are three states with the same energy. Hence the three states are degenerate.

Average quantities from wavefunction:

Consider the case of a particle in a 1-D infinite potential well. The wavefunction of the particle inside the well was determined to be

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

The expectation value for the position of the particle is given as

$$\langle x \rangle = \int_0^a \psi^* \hat{x}\, \psi \, dx$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{n\pi x}{a}\right) \cdot x \cdot \left(\sqrt{\frac{2}{a}}\right)\sin\left(\frac{n\pi x}{a}\right) dx$$

$$\Rightarrow \langle x \rangle = \frac{2}{a}\int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$\Rightarrow \langle x \rangle = \frac{a}{2} \qquad -(28)$$

The average position of the particle is at the centre of the box. The average momentum can be determined in an analogous manner.

$$\langle p \rangle = \int_0^a \psi^* \hat{p} \psi \, dx$$

$$\Rightarrow \langle p \rangle = \int_0^a \left(\sqrt{\frac{2}{a}}\right) \sin\left(\frac{n\pi x}{a}\right) - i\hbar \frac{d}{dx}\left\{\left(\sqrt{\frac{2}{a}}\right) \sin\left(\frac{n\pi x}{a}\right)\right\} dx$$

$$= \left(\frac{2}{a}\right)\left(\frac{-i\hbar n\pi}{a}\right) \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx$$

$$\Rightarrow \langle p \rangle = 0 \qquad -(29)$$

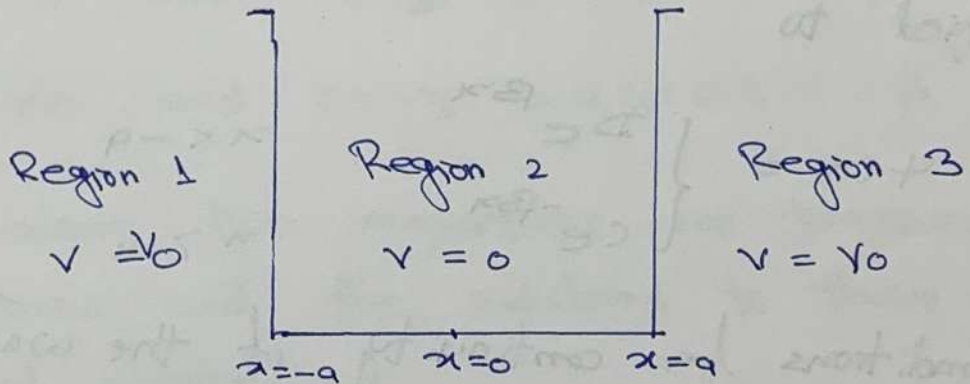
The average momentum of the particle in a 1-D infinite well is zero.

Particle in a finite potential well:

Consider a particle in a finite potential defined as

$$V(x) = \begin{cases} 0 & -a \leqslant x \leqslant a \\ V_0 & x < -a \,;\ x > a \end{cases}$$

Pictorically, the situation can be described as shown below.



The Schrödinger equation for the system is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \qquad -(1)$$

From the symmetry of the system, we consider solving regions 1 and 3 together. In these regions $V = V_0$. In region 2, $V = 0$. Hence,

$$\psi(x) = A\sin\alpha x + B\cos\alpha x \qquad -(2)$$

with $\alpha^2 = \dfrac{2mE}{\hbar^2}$

In regions 1 and 3,

$$\frac{d^2\psi}{dx^2} = \frac{2m(V_0-E)}{\hbar^2}\psi \qquad -(3)$$

$$\Rightarrow \psi(x) = Ce^{-\beta x} + De^{\beta x} \qquad -(4)$$

$$\text{where } \beta^2 = \frac{2m(V_0-E)}{\hbar^2}$$

The exponentially increasing terms of the solution given by Eq^n (4) will make the wavefunction non-normalizable. Therefore, Eq^n (4) must be modified to

$$\psi(x) = \begin{cases} De^{\beta x} & x < -a \\ Ce^{-\beta x} & x > a \end{cases} \qquad -(5)$$

The conditions for continuity of the wavefunction at the boundaries give

$$(\psi)_{-a} = -A\sin\alpha a + B\cos\alpha a = De^{-\beta a}$$

$$(\psi)_{a} = A\sin\alpha a + B\cos\alpha a = Ce^{-\beta a}$$

$$\left(\frac{d\psi}{dx}\right)_{-a} = \alpha A\cos\alpha A + \alpha B\sin\alpha A = \beta De^{-\beta a}$$

$$\left(\frac{d\psi}{dx}\right)_{a} = \alpha A\cos\alpha \overset{a}{\cancel{A}} - \alpha B\sin\alpha a = \beta Ce^{-\beta a}$$

$$\Rightarrow \quad 2A\sin\alpha a = (C-D)e^{-\beta a} \qquad -(6)$$

$$2\alpha A\cos\alpha a = -\beta(C-D)e^{-\beta a} \qquad -(7)$$

$$2B\cos\alpha a = (C+D)e^{-\beta a} \qquad -(8)$$

$$2\alpha B\sin\alpha a = \beta(C+D)e^{-\beta a} \qquad -(9)$$

From the first two equations,

$$\alpha \cot \alpha a = -\beta$$

and from the last two equations,

$$\alpha \tan \alpha a = \beta$$

$$\Rightarrow \tan^2 \alpha a = -1$$

$$\Rightarrow \alpha = \text{imaginary}$$

This cannot be the case. Therefore, Eq^n's 6 - 9 can have an acceptable solution only if

$A = 0$ and $C = D \Rightarrow \alpha \tan \alpha a = \beta$

or $B = 0$ and $C = -D \Rightarrow \alpha \cot \alpha a = -\beta$

The above two equations are transcendental equations and the solutions to these can be obtained graphically.

Let $\alpha a = p$ and $\beta a = q$

$\Rightarrow \alpha \tan \alpha a = \beta$ can be rewritten in terms of p and q.

$$p \tan p = q$$

$$\alpha^2 + \beta^2 = \frac{2mV_0}{\hbar^2}$$

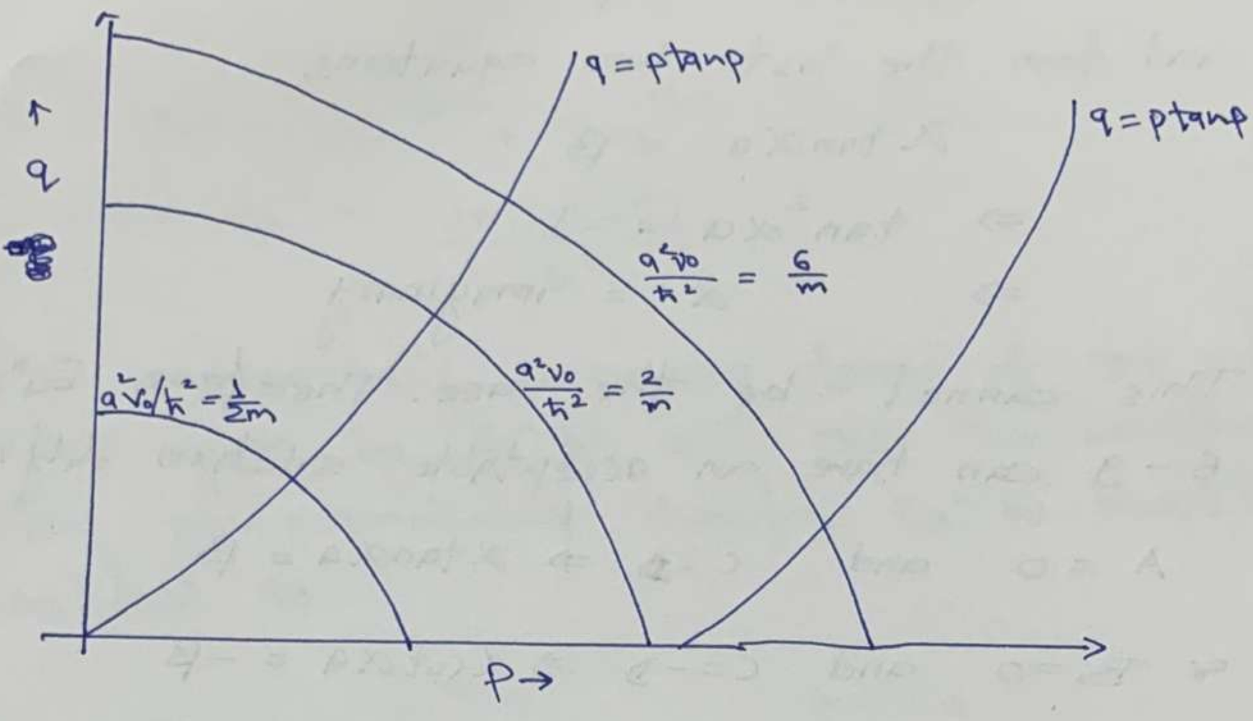
$$\Rightarrow p^2 + q^2 = \frac{2mV_0 a^2}{\hbar^2}$$

Now we have two equations:

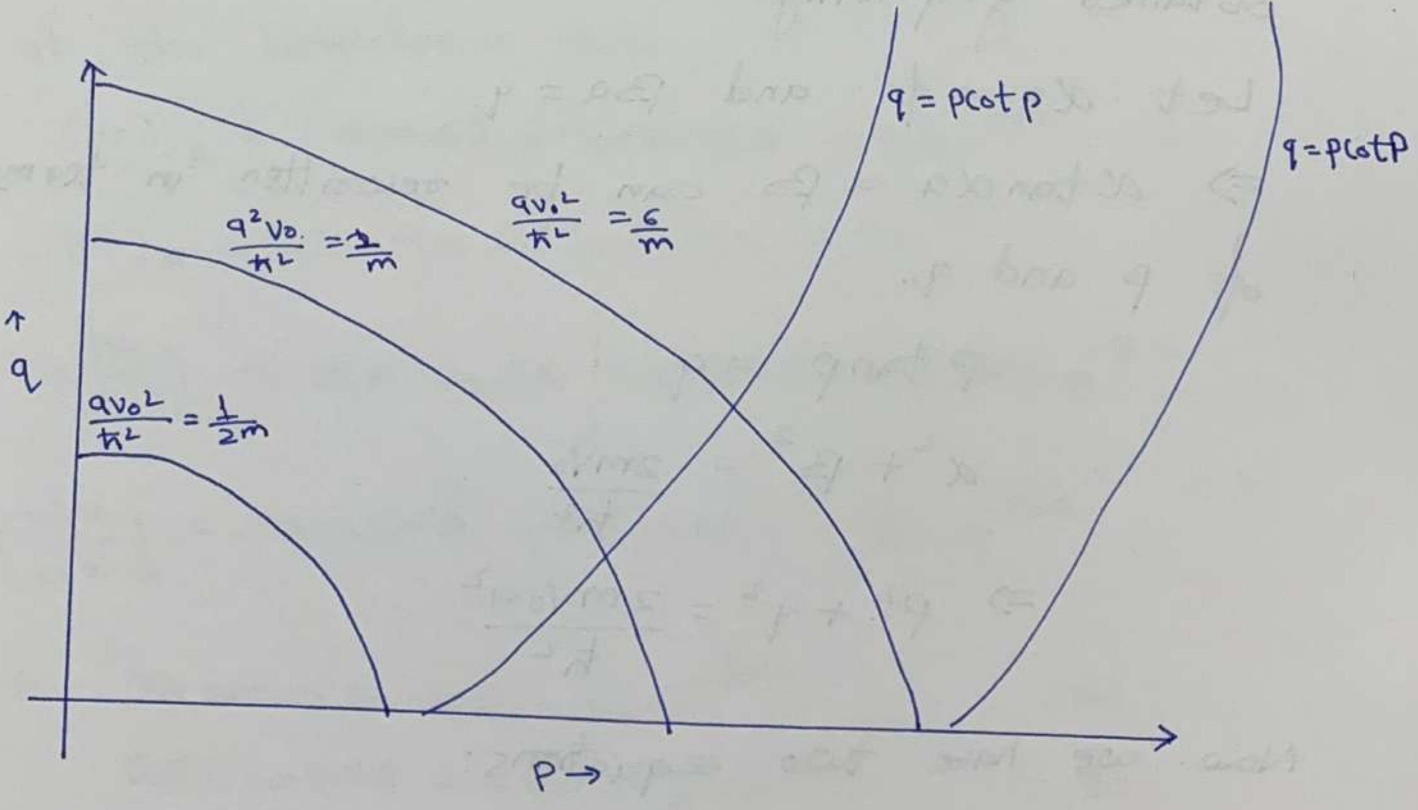
$$p \tan p = q \qquad -(10)$$

$$p^2 + q^2 = 2mV_0 a^2/\hbar^2 \qquad -(11)$$

Graphical solutions of $\alpha \tan \alpha a = \beta$



Graphical solution of $\alpha \cot \alpha a = -\beta$



It can be observed that Eq^n 11 is an equation of circles with p and q as the coordinates and $(2mV_0a^2/\hbar^2)^{1/2}$ as the radius. The intersections of the circles with the curve $p\tan p$ will give the solutions. Similarly, the other set of solutions can be obtained.

It is clear from the figures that the energy levels depend upon the potential V_0 and the size of the box a. When V_0a^2 is between zero and $6\hbar^2/m$ then ~~there~~ is only one energy level and more energy levels appear on changing V_0 or a.

The two classes of wavefunctions corresponding to $\alpha\tan\alpha a = \beta$ and $\alpha\cot\alpha a = -\beta$ are even and odd with respect to x. Consider the equation

$$\frac{-\hbar^2}{2m}\frac{d^2u(x)}{dx^2} + V(x)u(x) = Eu(x) \qquad -(12)$$

If the potential under consideration is an even function i.e. $V(x) = V(-x)$ then

$$\frac{-\hbar^2}{2m}\frac{d^2u(-x)}{dx^2} + V(x)u(-x) = Eu(-x) \qquad -(13)$$

From Eqⁿ (12) and (13), it can be seen that both $u(x)$ and $u(-x)$ are the solutions of the same equation. Further, the resulting eigenvalues are also the same. If only one of the two functions ~~are~~ is linearly independent then the other can be written as a constant times the first one.

$$u(-x) = \epsilon u(x)$$

However, the negative of the negative of x must restore the original function.

$$\Rightarrow \quad \epsilon = \pm 1$$

Hence, the wavefunctions of a symmetrical potential are either odd or even with respect to changes in sign of x. Such wavefunctions are said to have an odd or even parity. If a wavefunction does not have a parity then it may have more than one linearly dependent set of wavefunctions, all with the same eigenvalue.

Using the abovementioned concept of parity, we can now develop the expressions for the solution of Schrödinger equation.

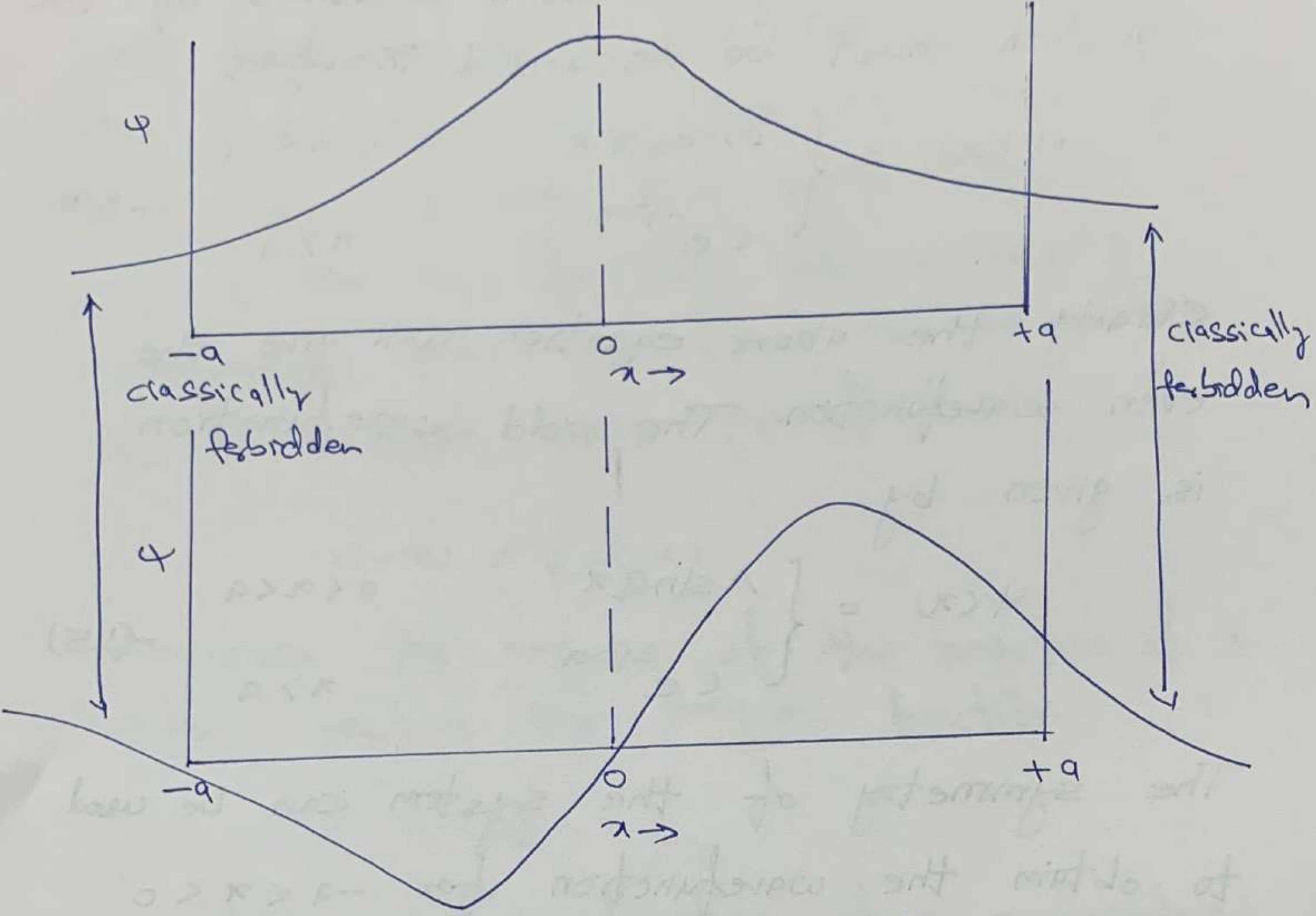
The exponentially increasing solutions of the equation must be discarded. Therefore,

$$\psi(x) = \begin{cases} B\cos\alpha x & 0 < x < a \\ Ce^{-\beta x} & x > a \end{cases} \quad -(14)$$

Clearly, the above equation will give the even wavefunction. The odd wavefunction is given by

$$\psi(x) = \begin{cases} A\sin\alpha x & 0 < x < a \\ Ce^{-\beta x} & x > a \end{cases} \quad -(15)$$

The symmetry of the system can be used to obtain the wavefunction for $-a < x < 0$ and $x \leq a$. It can be seen from the above solutions that the wavefunctions are non-zero at $x = -a$ and at $x = a$. Further the wavefunctions exponentially decay in the regions $x < -a$ and $x > a$. Unlike that observed for the case of a particle in an infinite potential well where the wavefunction become zero at the boundaries the non-zero value of the wavefunction indicate an interesting feature of quantum particles.



In case of a classical particle in a potential well of magnitude V_0, the particle needs to attain at least an amount of energy equal to V_0 to come out of the well. In contrast to the classical situation, we observe from the above plots that there is a non-zero probability of finding the particle outside the box even for the bound states of the particle where the particle has energy which is lesser than the imposed potential. This phenomenon is called quantum tunneling.

Harmonic oscillator :

The potential energy of a classical harmonic oscillator is given by

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \qquad - (1)$$

Therefore the Schrödinger equation for a quantum particle in the above potential can be written as

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi \qquad - (2)$$

The solution of the above problem is different and difficult compared to the cases seen till now due to the appearance of x^2 in the coefficient of ψ. The problem can be solved using two techniques, each of which has been described in detail below.

Solution using ladder operator :

We know that the momentum operator is given as

$$\hat{p} = -i\hbar\frac{d}{dx} \qquad - (3)$$

Using the above equation, Eq^n (2) can be written as

$$\frac{1}{2m}\left\{\hat{p}^2 + (m\omega\hat{x})^2\right\}\psi = E\psi \qquad - (4)$$

Since $\hat{p}$ and $m\omega\hat{x}$ are operators, they may not necessarily commute. We define the followings :

$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega\hat{x}) \qquad -(5)$$

$$a_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega\hat{x}) \qquad -(6)$$

$$\Rightarrow a_-a_+ = \frac{1}{2\hbar m\omega}\left\{\hat{p}^2 + (m\omega\hat{x})^2 - im\omega(\hat{x}\hat{p} - \hat{p}\hat{x})\right\} \quad -(7)$$

The quantity $\hat{x}\hat{p} - \hat{p}\hat{x}$ is called commutator and is represented as $[\hat{x}, \hat{p}]$.

$$\therefore a_-a_+ = \frac{1}{2\hbar m\omega}\left\{\hat{p}^2 + (m\omega\hat{x})^2 - im\omega[\hat{x}, \hat{p}]\right\}$$

$$-(8)$$

Now $[\hat{x}, \hat{p}]f = \hat{x}\hat{p}f - \hat{p}\hat{x}f$ for some function f.

$$\Rightarrow [\hat{x}, \hat{p}]f = x\left(-i\hbar\frac{df}{dx}\right) - \left(-i\hbar\frac{d}{dx}fx\right)$$

$$\Rightarrow [\hat{x}, \hat{p}]f = i\hbar f \qquad -(9)$$

$$\Rightarrow [\hat{x}, \hat{p}] = i\hbar \qquad -(10)$$

From Eq^n (7) we get

$$a_-a_+\psi = \frac{1}{2\hbar m\omega}\left\{\hat{p}^2 + (m\omega\hat{x})^2 - im\omega(\hat{x}\hat{p} - \hat{p}\hat{x})\right\}\psi$$

$$\Rightarrow a_-a_+\psi = \frac{1}{\hbar\omega}\left\{\left(\frac{\hat{p}^2 + (m\omega\hat{x})^2}{2m}\right) - \frac{i^2\hbar\omega}{2}\right\}\psi$$

$$\Rightarrow a_- a_+ = \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2} \qquad -(11)$$

Similarly, it can be shown that

$$a_+ a_- = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2} \qquad -(12)$$

$$\Rightarrow [a_-, a_+] = a_- a_+ - a_+ a_- = 1 \qquad -(13)$$

From Eq^n (12),

$$\hat{H} = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right) \qquad -(14)$$

Therefor, the Schrödinger equation for harmonic oscillator can be cast in terms of a_+ and a_- as

$$\hbar\omega\left(a_+ a_- + \frac{1}{2}\right)\psi = E\psi$$

or $\qquad -(15)$

$$\hbar\omega\left(a_- a_+ - \frac{1}{2}\right)\psi = E\psi$$

Now consider the quantity $\hat{H} a_+ \psi$.

$$\hat{H} a_+ \psi = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)(a_+\psi)$$

$$= \hbar\omega\left(a_+ a_- a_+ + \frac{1}{2} a_+\right)\psi$$

$$= a_+\left\{\hbar\omega\left(a_- a_+ + \frac{1}{2}\right)\psi\right\}$$

$$= a_+\left\{\hbar\omega\left(a_+ a_- + 1 + \frac{1}{2}\right)\psi\right\}$$

$$= a_+(\hat{H} + \hbar\omega)\psi$$

$$= a_+(E + \hbar\omega)\psi$$

$$= (E + \hbar\omega) a_+ \psi$$

$$\Rightarrow \hat{H}(a_+\psi) = (E + \hbar\omega)(a_+\psi) \qquad -(16)$$

Similarly, it can be shown that

$$\hat{H}(a_-\psi) = (E-\hbar\omega)(a_-\psi) \qquad -(17)$$

From the above two results, it can be seen that a_+ operator increases the energy of the system by $\hbar\omega$. Similarly, a_- operator decreases the energy of the system by $\hbar\omega$. Therefore a_+ can be regarded as the raising while a_- can be regarded as the lowering operator. Consecutive operation of a_+ and a_- operators will change the energy in opposite magnitudes thus nullifying their effects. a_- operator cannot be applied indefinitely as the energy of the system cannot reduce to a value which is lesser than the applied potential. Therefore, there exists a lowest eigenvalued wavefunction ψ_0 such that $a_-\psi_0 = 0$.

$$a_-\psi_0 = 0$$

$$\Rightarrow \frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega\hat{x}\right)\psi_0 = 0$$

$$\Rightarrow \frac{d\psi_0}{dx} = -\frac{m\overset{\omega}{\cancel{\quad}}x}{\hbar}\psi_0$$

$$\Rightarrow \frac{d\psi_0}{\psi_0} = \left(-\frac{m\omega}{\hbar}\right)x\,dx$$

$$\Rightarrow \psi_0 = Ae^{-\frac{m\omega x^2}{2\hbar}} \qquad -(18)$$

Applying the normalization condition we get

$$\int \psi_0^* \psi_0 \, dx = 1$$

$$\Rightarrow A^2 \int_{-\infty}^{\infty} e^{-\frac{m\omega x^2}{2\hbar}} \, dx = 1$$

$$\Rightarrow A^2 \sqrt{\frac{\pi \hbar}{m\omega}} = 1$$

$$\Rightarrow A = \left(\frac{m\omega}{\pi \hbar}\right)^{1/4} \qquad - (19)$$

$$\Rightarrow \psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} \qquad - (20)$$

The equation shown above gives the lowest energy eigenfunction. The corresponding lowest energy can be found using the Schrödinger equation.

$$\hbar\omega\left(a_+ a_- + \frac{1}{2}\right)\psi_0 = E_0 \psi_0$$

$$\Rightarrow \hbar\omega \, a_+ (a_- \psi_0) + \frac{\hbar\omega}{2} \psi_0 = E_0 \psi_0$$

But $a_- \psi_0 = 0$. Therefore,

$$\frac{\hbar\omega}{2} \psi_0 = E_0 \psi$$

$$\Rightarrow E_0 = \frac{1}{2} \hbar\omega \qquad - (21)$$

Eq^n (21) gives the lowest energy of the particle in a harmonic potential. Note that the lowest energy is not zero.

By the definition of the raising operator, higher energies can be obtained by applying the raising operator.

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

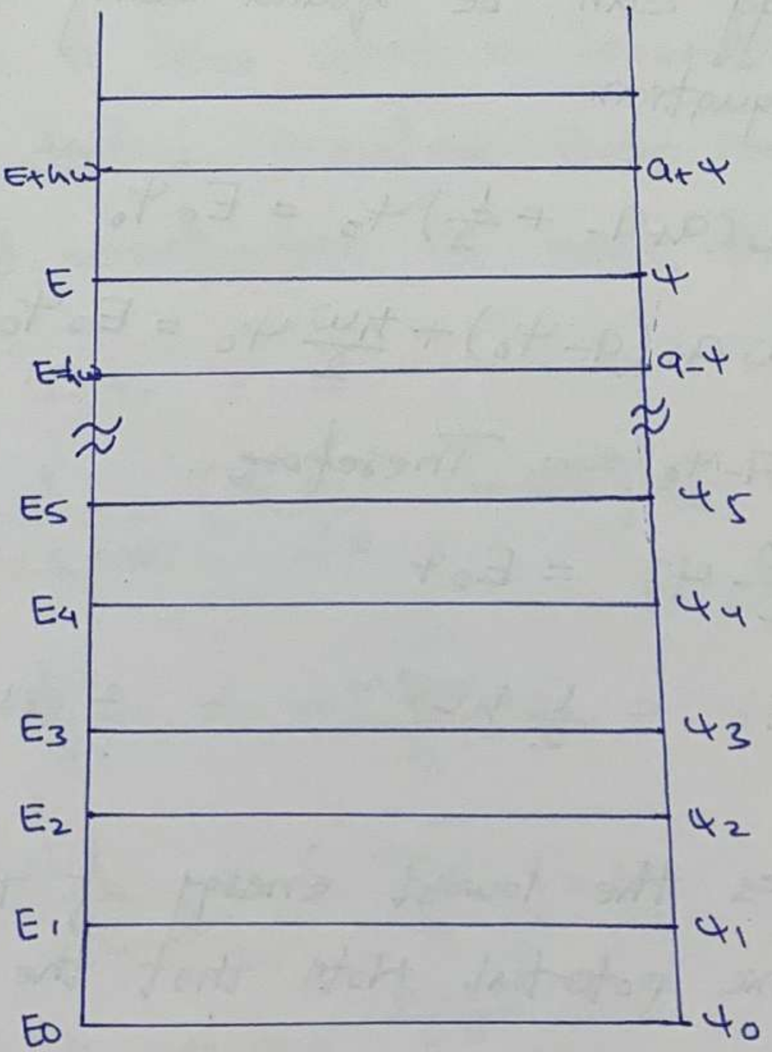
$$E_1 = \frac{1}{2}\hbar\omega + \hbar\omega$$

$$E_2 = \frac{1}{2}\hbar\omega + \hbar\omega + \hbar\omega$$

$$\vdots$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad -(22)$$

This solution procedure is called the ladder operator method due to the lowering or raising of energies in equal steps.



Series solution method:

The original Schrödinger equation for a particle in a harmonic potential is given as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi \qquad -(23)$$

We define a dimensionless variable α as

$$\alpha = \sqrt{\frac{m\omega}{\hbar}}\,x \qquad -(24)$$

Substitution of Eq^n (24) in Eq^n (23) gives

$$-\left(\frac{\hbar\omega}{2}\right)\frac{d^2\psi}{d\alpha^2} + \frac{1}{2}\alpha^2\hbar\omega\psi = E\psi \qquad -(25)$$

$$\Rightarrow \quad -\frac{d^2\psi}{d\alpha^2} + \alpha^2\psi = \left(\frac{2E}{\hbar\omega}\right)\psi$$

$$\Rightarrow \quad \frac{d^2\psi}{d\alpha^2} = (\alpha^2 - k)\psi \qquad -(26)$$

where $k = 2E/\hbar\omega$. We have two parameters in Eq^n (26), α and k. When α is very large (at large x), $\alpha^2 \gg k$.

$$\Rightarrow \frac{d^2\psi}{d\alpha^2} = \alpha^2\psi$$

$$\Rightarrow \psi = Ae^{-\alpha^2/2} + Be^{\alpha^2/2}$$

Since the wavefunction needs to be normalizable, $B = 0$. Therefore,

$$\psi = Ae^{-\alpha^2/2} \qquad -(27)$$

Eqⁿ (27) is applicable only at large α. Over the entire range, the wavefunction may be approximated as

$$\psi = h(\alpha)\, e^{-\alpha^2/2} \qquad -(28)$$

$$\Rightarrow \frac{d\psi}{d\alpha} = \frac{dh}{d\alpha} e^{-\alpha^2/2} - \alpha e^{-\alpha^2/2} h$$

$$\Rightarrow \frac{d\psi}{d\alpha} = \left(\frac{dh}{d\alpha} - \alpha h\right) e^{-\alpha^2/2}$$

$$\Rightarrow \frac{d^2\psi}{d\alpha^2} = \left(\frac{d^2h}{d\alpha^2} - \alpha\frac{dh}{d\alpha} - h\right) e^{-\alpha^2/2} + \left(\frac{dh}{d\alpha} - \alpha h\right)(-\alpha)\, e^{-\alpha^2/2}$$

$$\Rightarrow \frac{d^2\psi}{d\alpha^2} = \left\{\frac{d^2h}{d\alpha^2} - 2\alpha\frac{dh}{d\alpha} + (\alpha^2-1)h\right\} e^{-\alpha^2/2} \qquad -(29)$$

From the above equation, the Schrödinger equation becomes

$$\left\{\frac{d^2h}{d\alpha^2} - 2\alpha\frac{dh}{d\alpha} + (\alpha^2-1)h\right\} e^{-\alpha^2/2} = (\alpha^2-k)\, h\, e^{-\alpha^2/2}$$

$$\Rightarrow \frac{d^2h}{d\alpha^2} - 2\alpha\frac{dh}{d\alpha} + (k-1)h = 0 \qquad -(30)$$

Eqⁿ (30) is a second order ordinary differential equation but it is non-linear due to α in the coefficient of the second term. Such equations are solved using the series solution method. The solution is assumed to be of the form

$$h(\alpha) = a_0 + a_1\alpha + a_2\alpha^2 + \dots = \sum_{i=0}^{\infty} a_i \alpha^i$$

$$\Rightarrow \frac{dh}{d\alpha} = a_1 + 2a_2\alpha + 3a_3\alpha^2 + \dots = \sum_{i=0}^{\infty} i a_i \alpha^{i-1}$$

$$\Rightarrow \frac{d^2h}{d\alpha^2} = 2a_2 + 2.3a_3\alpha + 3.4a_4\alpha^2 + \dots$$

$$= (i+1)(i+2)a_{i+2}\alpha^i$$

$$\Rightarrow \sum_{i=0}^{\infty} \left\{(i+1)(i+2)a_{i+2} - 2ia_i + (k-1)a_i\right\}\alpha^i = 0$$

For the equation given above to be valid, every coefficient should be individually zero.

$$\Rightarrow (i+1)(i+2)a_{i+2} - 2ia_i + (k-1)a_i = 0$$

$$\Rightarrow \quad a_{i+2} = \left\{\frac{2i+1-k}{(i+1)(i+2)}\right\}a_i \qquad - (31)$$

Equations of the form shown in Eqⁿ (31) are calle recursion relations. Note that a knowledge of a will yield all even coefficients. Similarly, a knowledge of a_1 will yield all odd coefficients. When i very large, the recursion relation of Eqⁿ (31) ca be approximated as

$$a_{i+2} \approx \left(\frac{2}{i}\right)a_i \qquad - (32)$$

Since the wavefunction has been expressed as an infinite series and for the wavefunction to be physically realizable the series should not diverge, the series has to be truncated.

$$k = 2i + 1$$

For some n^{th} term, $k = 2n+1$

$$\Rightarrow \quad 2n + 1 = \frac{2E}{\hbar\omega}$$

$$\Rightarrow \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad -(33)$$

Note that again, we have ~~supp~~ supplied E by subscript n. Since the allowed values of k are $k = 2n+1$, the recursion relation gets modified to

$$a_{i+2} = \left\{ \frac{2i + 1 - (2n+1)}{(i+1)(i+2)} \right\} a_i$$

$$\Rightarrow \quad a_{i+2} = \left\{ \frac{2(i-n)}{(i+1)(i+2)} \right\} a_i \qquad -(34)$$

For the wavefunction with the lowest energy, a_1 must be zero thereby eliminating all the odd terms and for $i = 0$ and $n = 0$, $a_2 = 0$ i.e. there is only one term in the series.

$$h_0(\alpha) = a_0$$

$$\Rightarrow \psi_0(\alpha) = a_0 e^{-\alpha^2/2}$$

$$-(35)$$

For $n=1$ and $i=1$, $a_3=0$. If a_0 is taken as zero

$$\Rightarrow h_1(\alpha) = a_1\alpha$$

$$\Rightarrow \psi_1(\alpha) = a_1\alpha e^{-\alpha^2/2}$$

For $n=2$, $i=0$, $a_2=-2a_0$ and $i=2$, $a_4=0$

$$\Rightarrow h_2(\alpha) = a_0(1-2\alpha^2)$$

$$\Rightarrow \psi_2(\alpha) = a_0(1-2\alpha^2)\, e^{-\alpha^2/2}$$

All the above solutions can be generalized as Hermite polynomials defined by

$$H_n(x) = (-1)^n \exp(x^2)\left(\frac{d}{dx}\right)^n \left\{\exp(-x^2)\right\} \quad -(36)$$

The first few Hermite polynomials, all of which are orthogonal, are

$$H_0(x) = 1$$

$$H_1(x) = 2x$$

$$H_2(x) = 4x^2-2$$

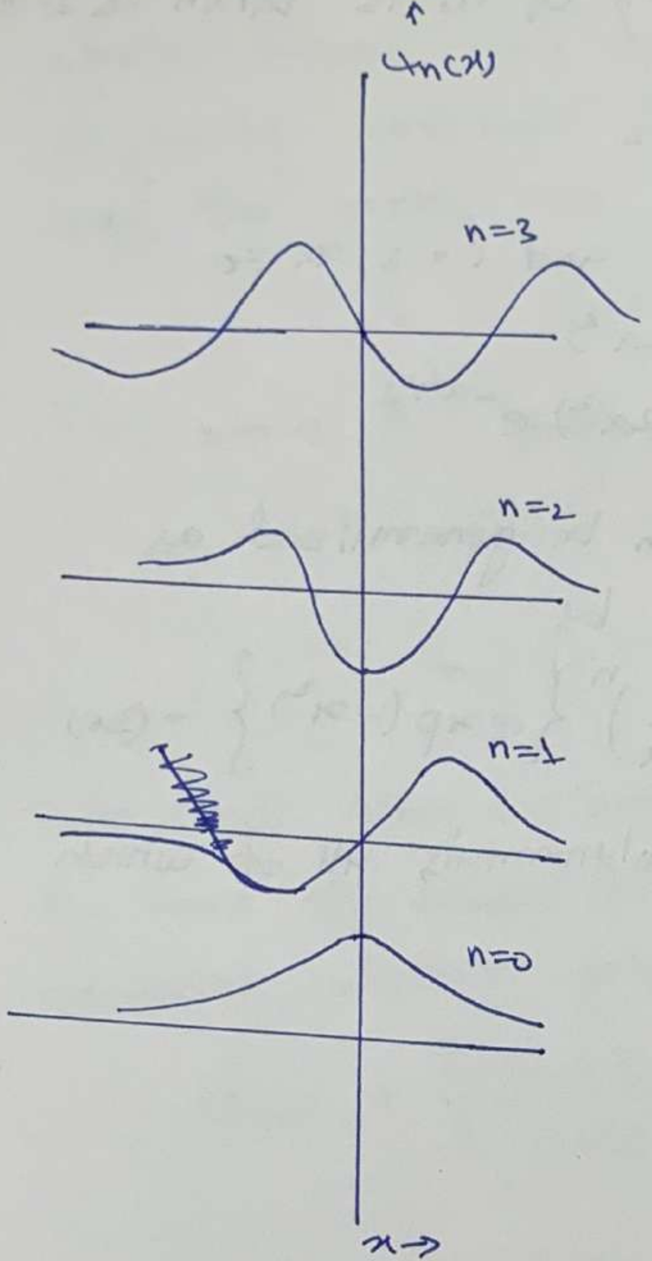
$$H_3(x) = 8x^3-12x$$

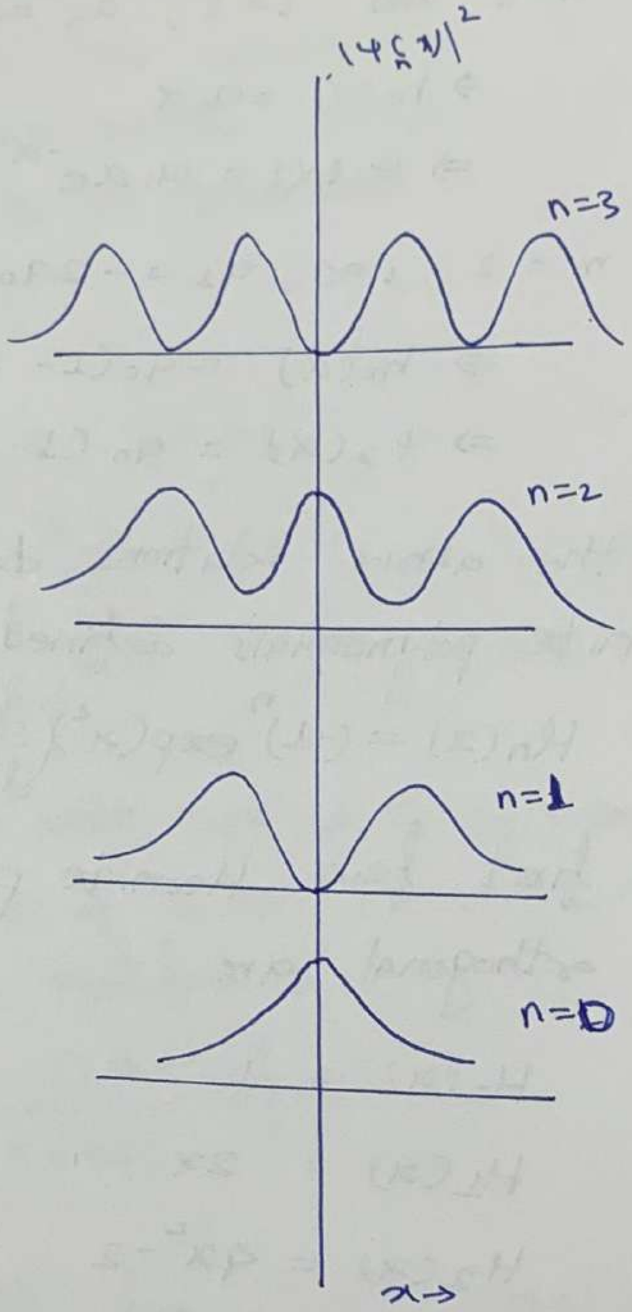
It is to be noted that the polynomials contain either all even powers or all odd powers.

The wavefunction after normalization can be written as

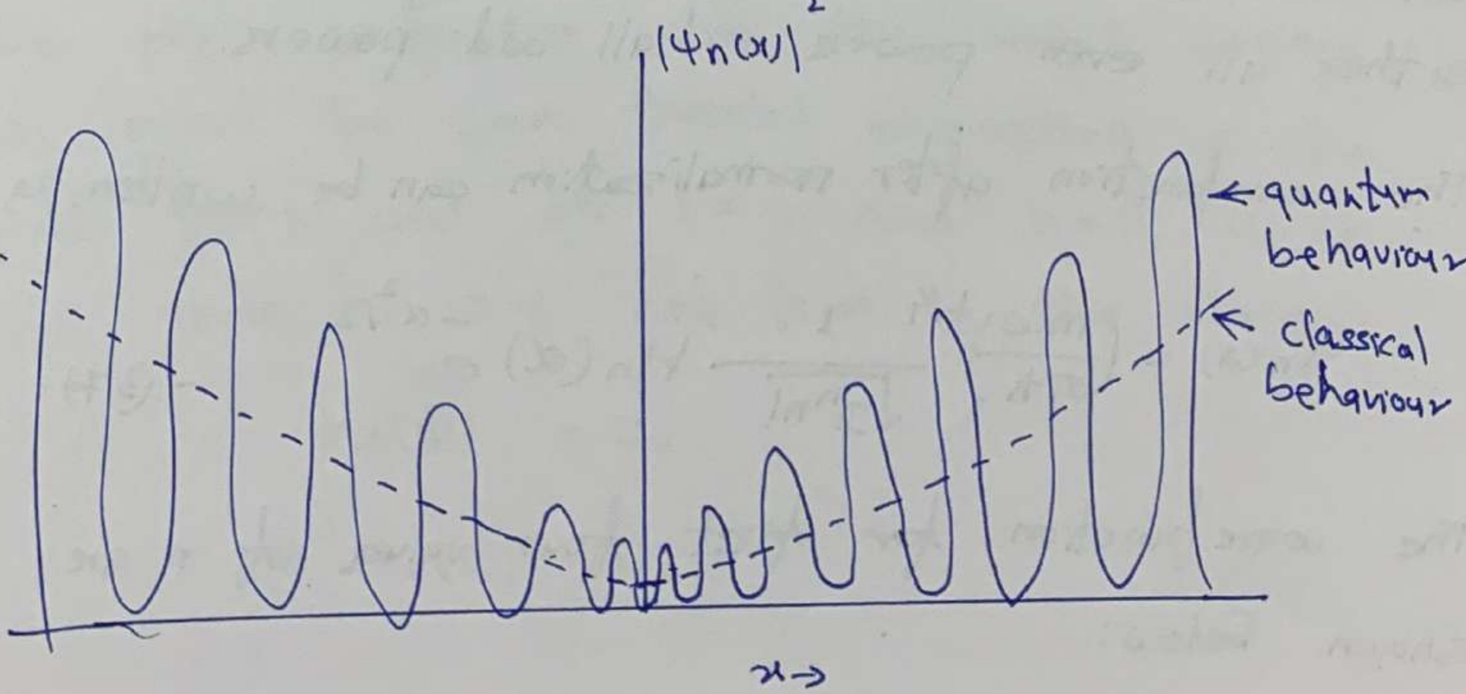
$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\alpha)\, e^{-\alpha^2/2} \quad -(37)$$

The wavefunction for first four values of n are shown below:



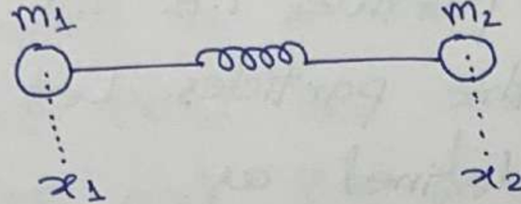


When n is very large



Two particles in harmonic oscillations :

Consider a system with two particles connected by a spring as shown below.



The classical equations of motion of the two particles can be written as

$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - l_0) \qquad -(1)$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - l_0) \qquad -(2)$$

where l_0 is the equilibrium (or undistorted) length of the spring. By adding Eq^n (1) and (2) we get

$$\frac{d^2}{dx^2}(m_1 x_1 + m_2 x_2) = 0$$

$$\Rightarrow (m_1 + m_2)\frac{d^2}{dx^2}\left(\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}\right) = 0$$

$$\Rightarrow M\frac{d^2 X}{dx^2} = 0 \qquad -(3)$$

where $M = m_1 + m_2$ and $X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$

X denotes the coordinates of the centre of mass of the system.

The motion of the system described above depends upon the relative motion between the two particles i.e. on the relative separation of the particles. Let the relative coordinate be defined as

$$x = x_2 - x_1 - l_0$$

From Equations (1) and (2),

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = \frac{-k}{m_2}(x_2 - x_1 - l_0)$$

$$-\frac{k}{m_1}(x_2 - x_1 - l_0)$$

$$\Rightarrow \frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - l_0)$$

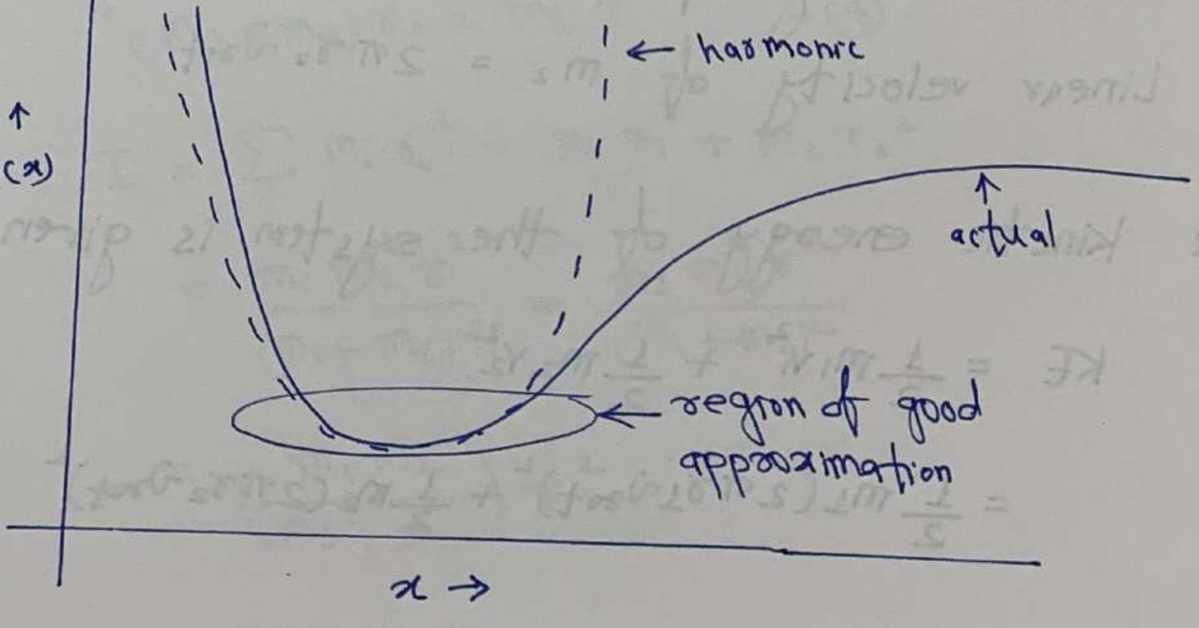
We define reduced centre of mass as

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\Rightarrow \quad \frac{d^2x}{dt^2} = \frac{-kx}{\mu}$$

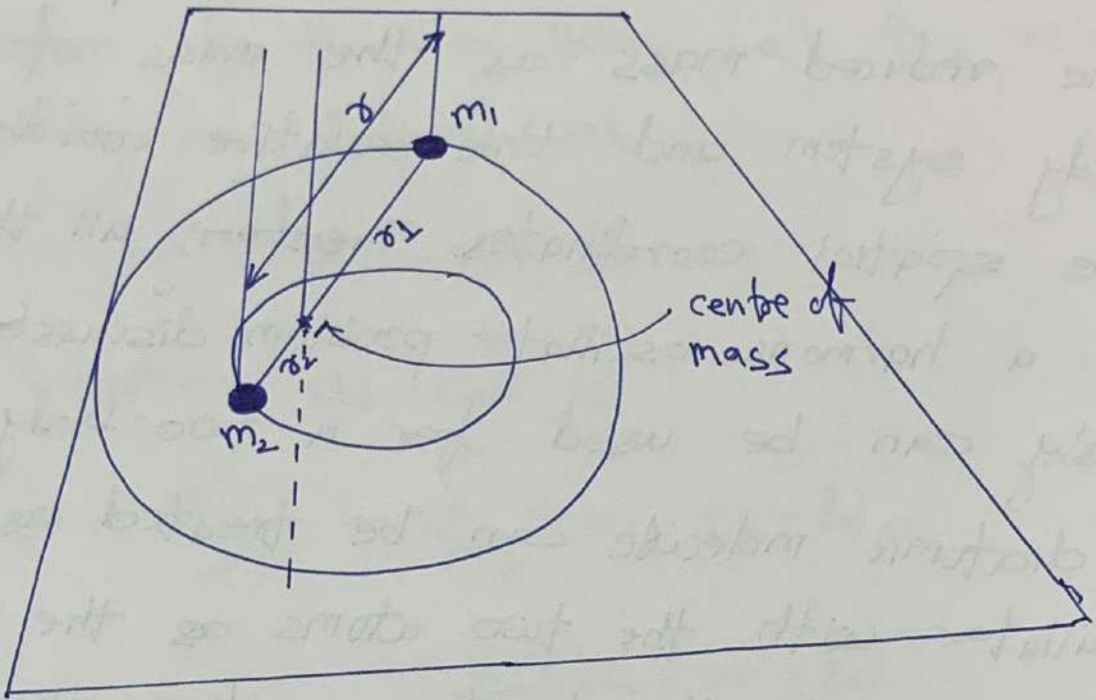
$$\Rightarrow \quad \mu\frac{d^2x}{dt^2} + kx = 0 \qquad -(4)$$

It can be noted that Eq^n (4) is exactly the same as that for a harmonic oscillator of with only one particle of mass μ and of the spring constant which is same as that for the original two-body system. Therefore, the two-body problem in a harmonic potential can be treated as a one-body problem with the reduced mass as the mass of one-body system and the relative coordinates as the spatial coordinates. Therefore, all the results of a harmonic oscillator problem discussed previously can be used for a two-body problem. A diatomic molecule can be treated as an oscillator with the two atoms as the two masses and the bond connecting them as the spring. The harmonic approximation works well for small amplitudes of vibration of the molecule.



A two-particle rigid rigid rotator :

Consider a system consisting of two masses m_1 and m_2 at fixed distances r_1 and r_2 from their centre of mass. The system is shown below.



The masses rotate about the center of mass at a frequency of ν_{rot} cycles per second. Therefore,

Linear velocity of m_1 = $2\pi r_1 \nu_{rot}$

Linear velocity of m_2 = $2\pi r_2 \nu_{rot}$

The kinetic energy of the system is given as

$$KE = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

$$= \frac{1}{2} m_1 (2\pi r_1 \nu_{rot})^2 + \frac{1}{2} m_2 (2\pi r_2 \nu_{rot})^2$$

$$\Rightarrow KE = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$$

$$= \frac{1}{2}(m_1 r_1^2 + m_2 r_2^2)\omega^2$$

$$= \frac{1}{2} I \omega^2$$

where I is the moment of inertia of the system.

$$I = \sum_i m_i r_i^2 \qquad - (5)$$

The moment about the center of mass must be zero.

$$\Rightarrow m_1 r_1 = m_2 r_2 \qquad - (6)$$

Now consider $(m_1 + m_2) r_1$.

$$(m_1 + m_2) r_1 = m_1 r_1 + m_2 r_1$$

$$= m_2 r_2 + m_2 r_1$$

$$= m_2 (r_1 + r_2)$$

$$\Rightarrow (m_1 + m_2) r_1 = m_2 r \qquad - (7)$$

Similarly,

$$(m_1 + m_2) r_2 = m_1 r \qquad - (8)$$

$$\Rightarrow \quad I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2$$

$$= \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

$$= \left(\frac{m_1 m_2}{m_1 + m_2}\right) r^2$$

Using the definition of reduced mass, we get

$$I = \mu r^2 \qquad -(9)$$

Therefore it can be seen that a two-body rigid rotator problem can be solved as a one-body problem using the reduced mass of the system and using the distance between the masses for calculating the moment of inertia.

Solution of a two-particle problem as a one body problem:

Consider two particles located at (x_1, y_1, z_1) and (x_2, y_2, z_2), respectively. The potential energy of the system is assumed to be a function of only the relative coordinates $x_2 - x_1$, $y_2 - y_1$ and $z_2 - z_1$. We denote the relative coordinates as

$$x = x_2 - x_1$$

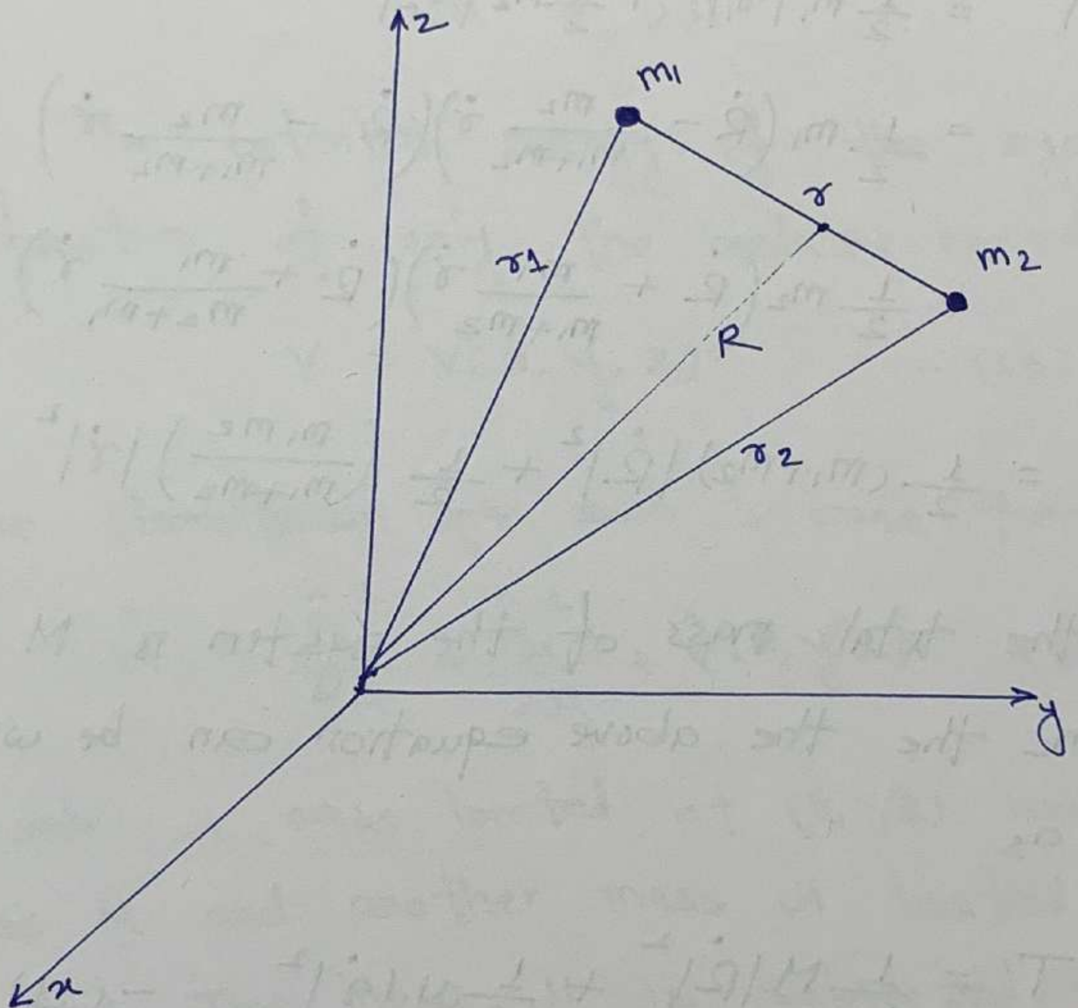
$$y = y_2 - y_1$$

$$z = z_2 - z_1$$

The center of mass in this case is defined as:

$$(X, Y, Z) = \left(\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}, \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} \right) \quad - (10)$$

The vectors corresponding to the two masses and the center of mass are shown below.



$$r = r_2 - r_1$$

$$R = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2}$$

Solution of the above two equations simultaneously for r_1 and r_2 yields

$$r_1 = R - \left(\frac{m_2}{m_1+m_2}\right) r$$

$$r_2 = R + \left(\frac{m_1}{m_1+m_2}\right) r$$

The total kinetic energy of the system is given as

$$T = \frac{1}{2} m_1 |\dot{r}_1|^2 + \frac{1}{2} m_2 |\dot{r}_2|^2$$

$$= \frac{1}{2} m_1 \left(\dot{R} - \frac{m_2}{m_1+m_2} \dot{r}\right)\left(\dot{R} - \frac{m_2}{m_1+m_2} \dot{r}\right)$$

$$+ \frac{1}{2} m_2 \left(\dot{R} + \frac{m_1}{m_1+m_2} \dot{r}\right)\left(\dot{R} + \frac{m_1}{m_2+m_1} \dot{r}\right)$$

$$\Rightarrow T = \frac{1}{2} (m_1+m_2) |\dot{R}|^2 + \frac{1}{2} \left(\frac{m_1 m_2}{m_1+m_2}\right) |\dot{r}|^2$$

If the total mass of the system is $M = m_1 + m_2$ the the above equation can be written as

$$T = \frac{1}{2} M |\dot{R}|^2 + \frac{1}{2} \mu |\dot{r}|^2 \qquad -(11)$$

The above equation shows that the kinetic energy of the two-body system is the sum of contributions coming from the motion of the center of mass (the first term on RHS) and the relative motion of the masses (second term on RHS).

The momentum of the system, in an analogous manner, be split into the momentum of the centre of mass and the momentum due to the relative motion of particles.

$$T = \frac{|P_M|^2}{2M} + \frac{|P_\mu|^2}{2\mu} \quad - (12)$$

The potential energy of the system is a function of only the relative coordinates.

$$V = V(x, y, z) \quad - (13)$$

The Hamiltonian for such a case then becomes

$$\hat{H} = \frac{\hat{P}_M^2}{2M} + \frac{\hat{P}_\mu^2}{2\mu} + \hat{V}(x, y, z) \quad -(14)$$

Consider a mass located at (X, Y, Z) having a mass M and another mass μ located at (x, y, z). The mass μ is subjected to a potential V(x, y, z) and the mass M is subjected to zero potential. There is no interaction between the masses M and μ. The Hamiltonian for such a system is exactly given by Eq^n (14). Therefore, we have obtained an equation for two independent particles.

Particle 1: Mass $= M = m_1 + m_2$

coordinates $= (X, Y, Z)$, given by Eq^n (10)

Potential $= 0$

$$\Rightarrow \hat{H} = \frac{\hat{P}_M^2}{2M} ; \quad \frac{\hat{P}_M^2}{2M} \psi_M = E_M \psi_M$$

Particle 2: Mass $= \mu = \frac{m_1 m_2}{M}$

coordinates $= (x, y, z)$

$= (x_2 - x_1, y_2 - y_1, z_2 - z_1)$

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

$$\Rightarrow \hat{H} = \frac{P_\mu^2}{2\mu} + V$$

$$\Rightarrow \left\{ \left(\frac{\hat{P}_\mu^2}{2\mu} \right) + \hat{V} \right\} \psi_\mu = E_\mu \psi_\mu$$

The total energy of the system is $E = E_M + E_\mu$. E_μ is the interaction energy of the particles.

Energy levels of a rigid rotator:

As discussed before, the rigid rotator two-body problem can be reduced to a one-body problem using the following.

Mass = reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$

Moment of inertia $I = \mu r^2$; $r = r_1 + r_2$.

The angular momentum of the system is given as

$$L = I\omega$$

and the kinetic energy of the system is given as

$$K = \frac{L^2}{2I}$$

In the absence of an external potential, the Hamiltonian becomes

$$\hat{H} = \hat{K} = \frac{-\hbar^2}{2\mu}\nabla^2 \qquad -(15)$$

Since we have reduced the system to a one-particle system, and the system has a natural centre of symmetry, we use spherical coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left(\frac{1}{r^2\sin^2\theta}\right)\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad -(16)$$

For a rigid rotator, $r =$ constant. Hence the radial derivatives vanish. Using separation of variables the problem may be solved.

$$\frac{-\hbar^2}{2I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right\}Y(\theta,\phi)$$

$$= EY(\theta,\phi)$$

$$\Rightarrow \quad \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}+(\beta\sin^2\theta)Y=0 \quad -(17)$$

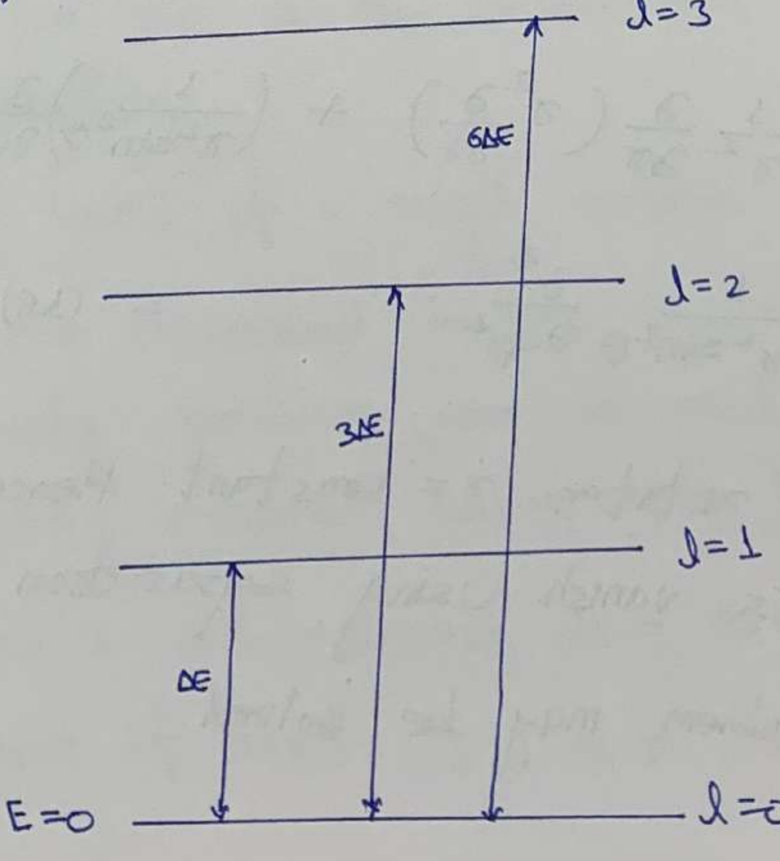
where $\beta = \frac{2IE}{\hbar^2}$. Following the method adopted for solution of a particle in a spherically symmetric potential, we get the requirement for β.

$$\beta = l(l+1) \quad ; l \in N$$

$$\Rightarrow E = \frac{\hbar^2 l(l+1)}{2I} \quad ; l = 0,1,2\ldots, N$$

$-(18)$

From the above Eq^n, it is seen that the energy levels of a rigid rotater are also quantized.



Many-body Schrödinger equation :

Atoms and molecules are in general many-body systems. For example benzene has 6 C atoms, 6 H atoms and 42 electrons, which correspond to these atoms. Each nucleus of the molecule is considered to be a body and so is each electron. Hence, benzene is a 54-body system. We will write the Schrödinger equation for such systems now.

Consider a molecule having N electrons and M nuclei. For such a system, the Schrödinger equation in the most generalized form is

$$\hat{H}\Psi_i(x_1, x_2 \ldots, x_N, R_1, R_2 \ldots, R_M)$$

$$= E_i \Psi_i (x_1, x_2, \ldots, x_N, R_1, R_2, \ldots, R_M) - (19)$$

$x_i \rightarrow$ coordinates of electrons

$R_i \rightarrow$ coordinates of nuclei

It is to be noted that the wavefunction contains a subscript because the equation is linear giving rise to multiple solutions

The Hamiltonian operator for such a case is (in atomic units) is written as

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_A}{R_{AB}} \quad - (20)$$

It can be seen that the equation is simplified by making several constants (e.g. $\hbar$) equal to unity. The energy hence obtained is in a unit called Hartree. 1 Ha = 627.5 kcal/mol. Various terms on the RHS have the following significance.

1st term: K.E. of electrons

2nd term: K.E. of nuclei

3rd term: electron-nuclei attraction potential

4th term: electron-electron repulsion potential

5th term: nucleus-nucleus repulsion potential

Molecular partition functions

We saw by solving the Schrödinger equation under different potentials, it is possible to model molecular systems and find the corresponding energies. The energy of a molecule is the summation of the contributions arising from different energies and hence, corresponding "molecular partition functions" can be evaluated. The molecular degrees of freedom can be identified as translational, rotational, vibrational and electronic. We now develop expressions for these individual molecular partition functions.

Translational partition function :

We have solved the particle in a 3-D box problem from which the following expression for the energy of the system was obtained.

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \quad -(1)$$

For a monoatomic gas, rotation and vibration of atoms is not possible. Eq^n (1) can be identified as the translational energy of the particle as the particle is free to translate inside the box. Hence, the translational partition function can be written as

$$Z_{trans} = \sum_{n_x, n_y, n_z} e^{-\beta E_{n_x n_y n_z}} \quad - (2)$$

$$\Rightarrow Z_{trans} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp\left\{ -\frac{\beta h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right\}$$

$$\Rightarrow Z_{trans} = \sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2 n_x^2}{8ma^2} \right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{\beta h^2 n_y^2}{8ma^2} \right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{\beta h^2 n_z^2}{8ma^2} \right)$$

Applying symmetry we get

$$Z_{trans} = \left[\sum_{n=1}^{\infty} \exp\left(\frac{-\beta h^2 n^2}{8ma^2} \right) \right]^3 \quad - (3)$$

Since the above equation contains a summation over all values of 'n' and for a large number of particles translational states are closely spaced, we can replace the summation with an integral.

$$Z_{trans} = \left[\int_0^{\infty} \exp\left(\frac{-\beta h^2 n^2}{8ma^2} \right) dn \right]^3 \quad - (4)$$

The integral is an integral of a Gaussian function and

$$\int_0^\infty e^{-\alpha n^2}\, dn = \sqrt{\frac{\pi}{4\alpha}}$$

$$Z_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \qquad -(5)$$

where $V = a^3$ = volume of the box. It can be seen from Eqⁿ (5) that $Z_{trans} = Z_{trans}(V, T)$.

Using Eqⁿ (5), we can determine the average translational energy of the system.

$$\langle E_{trans}\rangle = k_B T^2 \left(\frac{\partial \ln Z_{trans}}{\partial T}\right)_V$$

$$= k_B T^2 \left[\frac{\partial}{\partial T}\left(\frac{3}{2}\ln T + \text{terms independent of } T\right)\right]_V$$

$$\Rightarrow \langle E_{trans}\rangle = \frac{3}{2} k_B T \qquad -(6)$$

If we solve the above equation in 1-D then we obtain $\langle E_{trans}\rangle = \frac{1}{2} k_B T$. Hence each degree of freedom contributes $\frac{1}{2} k_B T$ amount of energy to the system. This is called the principle of equipartition of energy.

Electronic partition function :

The electronic partition function can be written as the following sum.

$$Z_{ele} = \sum_i g_{ei} e^{-\beta E_{ei}} \quad - (5)$$

g_{ei} in Eq^n (5) is the degeneracy and E_{ei} is the energy of i^{th} electronic level. The ground-state energy of the system is calulated by solving the electronic Hamiltonian following the elaborate computational chemistry schemes. If the ground state energy is set arbitrarily to zero the $E_{e1} = 0$.

$$\Rightarrow Z_{ele} = g_{e1} + g_{e2} e^{-\beta E_{e2}} + \cdots \quad - (6)$$

From the above equation, it is clear that $Z_{ele} = Z_{ele}(T)$.

$$\beta E_{ele} \approx \frac{10^4}{T}$$

Therefore, the contributions of higher excited states to the electronic partition function is negligible. Hence, at ordinary temperatures, most of the systems are at ground state of electronic energy.

Now consider a monoatomic gas made up of non-interacting particles. For such a gas the contribution to the energy will come only from translation and electronic states

$$Z_{trans}(V,T) = \left(\frac{2\pi m K_B T}{h^2}\right)^{3/2} V$$

$$Z_{ele}(T) \approx g_{e1} + g_{e2} e^{-\beta E_{e2}}$$

$$\Rightarrow Z(V,T) = \frac{1}{N!}\left(Z_{trans} Z_{ele}\right)^N \quad - (7)$$

We will understand the origin of N! in the denominator a little later.

$$\langle P \rangle = K_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{N,T}$$

$$\Rightarrow \langle P \rangle = K_B T N \frac{\partial}{\partial V}\left(Z_{trans} Z_{ele}\right)_{N,T}$$

$$= N K_B T \frac{\partial}{\partial V}\left(\ln V + \underset{\text{of } V}{\text{terms independent}}\right)_{N,T}$$

$$\Rightarrow \langle P \rangle = \frac{N K_B T}{V}$$

$$\Rightarrow \langle P \rangle V = N K_B T \quad - (8)$$

Hence, the ideal gas equation is followed when the particles are non-interacting.

Now we try to understand the reason behind N! in Eq^n (7). Atoms and molecules in general are not distinguishable. Hence, the partition function is no more a simple product of individual partition functions. For non-interacting indistinguishable particles,

$$E_{ijk\ldots} = E_i + E_j + E_k + \cdots \qquad -(9)$$

Note that we are no more using any superscript for the identification of particles. The partition function for such a system would be

$$Z(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta(E_i+E_j+E_k+\cdots)} \qquad -(10)$$

The particles can either be bosons (with integral spins) or fermions (with half-integral spins). No two fermions can occupy the same single particle quantum states. Therefore, in case of fermions, i, j, k... are not independent of one another. Hence, the summation cannot be over all possible i, j, k... Consider for example the case of two non-interacting fermions each with states having energies E_1, E_2, E_3 and E_4. The allowed total energies are:

$E_1 + E_2$ $\quad$ $E_2 + E_3$

$E_1 + E_3$ $\quad$ $E_2 + E_4$

$E_1 + E_4$ $\quad$ $E_3 + E_4$

Hence, there will be only six terms in the summation for obtaining the partition function. The aforementioned restriction does not apply to bosons. Still, the summation is not over all possible i, j, k... Consider a 4-particle system. Four possible energy states are

$E_1 + E_2 + E_2 + E_2$

$E_2 + E_1 + E_2 + E_2$

$E_2 + E_2 + E_1 + E_2$

$E_2 + E_2 + E_2 + E_1$

While none of the above summations is valid for fermions, all four summations are acceptable in case of bosons. However, since the particles are indistinguishable, we have only one energy state of $E_1 + 2E_2$.

Hence the total number of accessible energy states is just one and not four! Therefore, for an N-particle system, a permutation N! will give the same energy and for a system with large N, it is very likely that all the particles are in different quantum states. Therefore,

$$Z(N, V, T) = \frac{1}{N!} Z_i(V, T)^N \quad -(11)$$

The accuracy of Eq^n (11) requires satisfying an approximation that the number of accessible quantum states is much larger than the number of particles in the system. Consider the translational partition function.

$$Z_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

The above equation is often represented as

$$Z_{trans} = \frac{V}{\Lambda^3} \quad -(12)$$

where Λ = de Broglie thermal wavelength.

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \qquad - (13)$$

The de Broglie thermal wavelength specifies the length scale over which a particle has thermal effects and it is a function of temperature and mass of the particle. For an ideal gas, two particles are far apart. Hence, the number of particles is very small when compared to the total number of accessible translational quantum states.

$$\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \gg N$$

$$\Rightarrow \quad \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} \ll 1 \qquad - (14)$$

$$\text{or} \quad \frac{N\Lambda^3}{V} \ll 1 \qquad - (15)$$

When the above inequality is satisfied then the approximation of Eq^n (11) holds true. All ideal gases and some liquids at their boiling points satisfy this condition and are said to follow Boltzmann statistics.

Diatomic molecules :

The total energy of a diatomic molecule can be written as

$$E = E_{trans} + E_{rot} + E_{vib} + E_{ele} \quad - (16)$$

The partition function is given as

$$Z = \frac{1}{N!}\left(Z_{trans} Z_{rot} Z_{vib} Z_{ele}\right)^N \quad - (17)$$

If m_1 and m_2 are the masses of the two nuclei then

$$Z_{trans}(V, T) = \left(\frac{2\pi (m_1 + m_2) k_B T}{h^2}\right)^{3/2} V$$

For vibration of the molecule under harmonic approximation,

$$E_{vib} = (n + \tfrac{1}{2})\hbar\omega$$

$$\Rightarrow Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta E_{vib}}$$

$$= \sum_{n=0}^{\infty} e^{-\beta (n + \frac{1}{2})\hbar\omega}$$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}$$

The summation in the above equation is of the form $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

$$\Rightarrow \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$\Rightarrow Z_{vib}(T) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \quad - (18)$$

The quantity $\hbar\omega/k_B$ is called the vibrational temperature, denoted by θ_{vib}

$$Z_{vib}(T) = \frac{e^{-\theta_{vib}/2T}}{1 - e^{-\theta_{vib}/T}} \quad - (19)$$

At temperatures significantly above the vibration temperature, the contribution of the vibrational energy to the total energy of the system is significant. The average vibrational energy can be obtained as follows :

$$\langle E_{vib} \rangle = N k_B T^2 \frac{d}{dT} \ln(Z_{vib})$$

$$= N k_B T^2 \left(\frac{\theta_{vib}}{2} + \frac{\theta_{vib}}{e^{\theta_{vib}/T} - 1} \right) \quad -(20)$$

Since the partition function is an exponentially decaying function of θ_{vib}, essentially all the molecules are in ground vibrational state.

For the rotation of the molecule,

$$E = \frac{\hbar^2 l(l+1)}{2I} \quad ; \; l \in \mathbb{N}$$

Each energy level has a degeneracy of

$$g_l = 2l + 1$$

$$\Rightarrow Z_{rot}(T) = \sum_{l=0}^{\infty} (2l+1) e^{-\beta\hbar^2 l(l+1)/2I} \quad - (21)$$

Similar to vibrational temperature, we can define rotational temperature.

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

$$\Rightarrow Z_{rot}(T) = \sum_{l=0}^{\infty} (2l+1) e^{-\theta_{rot} l(l+1)/T} \quad -(22)$$

θ_{rot}/T is a small number at ordinary temperatures as a result of which the rotational quantum states are closely packed. Hence,

$$Z_{rot}(T) = \int_0^{\infty} (2l+1) e^{-\theta_{rot} l(l+1)/T} \, dl \quad -(23)$$

Let $l(l+1) = x \Rightarrow (2l+1)\,dl = dx$

$$\Rightarrow Z_{rot}(T) = \int_0^{\infty} e^{-\theta_{rot} x/T} \, dx$$

$$= \frac{T}{\theta_{rot}}$$

$$\Rightarrow Z_{rot}(T) \quad - (24)$$

$$\langle E_{rot} \rangle = Nk_BT^2 \frac{d \ln Z_{rot}}{dT} = Nk_BT \quad -(25)$$