Manonmaniam Sundaranar University,
Directorate of Distance & Continuing Education,
Tirunelveli - 627 012 Tamilnadu, India

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

M.Sc. Physics

Course Material

Quantum Mechanics - I

Prepared

By

Dr. V. Sabarinathan
Dr. S. Arunavathi
Assistant Professor
Department of Physics
Manonmaniam Sundaranar University
Tirunelveli - 12

QUANTUM MECHANICS – I

UNIT I:

BASIC FORMALISM

Interpretation of the wave function – Time dependent Schrodinger equation – Time independent Schrodinger equation – Stationary states – Ehrenfest's theorem -Linear vector space – Linear operator – Eigen functions and Eigen Values - Hermitian Operator – Postulates of Quantum Mechanics – Simultaneous measurability of observables – General Uncertainty relation

UNIT II:

ONE DIMENSIONAL AND THREEDIMENSIONAL ENERGY EIGEN VALUE PROBLEMS

Square – well potential with rigid walls – Square well potential with finite walls – Square potential barrier – Alpha emission – Bloch waves in a periodic potential - Kronig-penny square – well periodic potential – Linear harmonic oscillator: Operator method – Particle moving in a spherically symmetric potential – System of two interacting particles – Hydrogen atom – Rigid rotator

UNIT III:

GENERALFORMALISM

Dirac notation – Equations of motions – Schrodinger representation Heisenberg representation – Interaction representation – Coordinate representation – Momentum representation – Symmetries and conservation laws – Unitary transformation – Parity and time reversal

UNIT IV:

APPROXIMATION METHODS

Time independent perturbation theory for non-degenerate energy levels –Degenerate energy levels – Stark effect in Hydrogen atom – Ground and excited state – Variation method – Helium atom – WKB approximation – Connection formulae (no derivation) – WKB quantization – Application to simple harmonic oscillator.

UNIT V:

ANGULAR MOMENTUM

Eigen value spectrum of general angular momentum – Ladder operators and their algebra – Matrix representation – Spin angular momentum – Addition of angular momenta – CG Coefficients – Symmetry and anti – symmetry of wave functions – Construction of wave-functions and Pauli’s exclusion principle.

UNIT VI:

PROFESSIONAL COMPONENTS

Expert Lectures, Online Seminars - Webinars on Industrial Interactions/Visits, Competitive Examinations, Employable and Communication Skill Enhancement, Social Accountability and Patriotism

UNIT I:

BASIC FORMALISM

Interpretation of the wave function – Time dependent Schrodinger equation – Time independent Schrodinger equation – Stationary states – Ehrenfest's theorem -Linear vector space – Linear operator – Eigen functions and Eigen Values - Hermitian Operator – Postulates of Quantum Mechanics – Simultaneous measurability of observables – General Uncertainty relation

1.1 Introduction:

Two or more waves can traverse the same space independently of one another. Hence the total displacement at any point due to number of waves is simply the vector sum of the displacement produced by the individual waves.

This is known as the principle of superposition. The concept of superposition of states allows the construction of wave pockets.

Wave packet:

When the momentum of a particle is well defined, the wave can be of infinite extent. Therefore, a free particle moving along x-axis with a well defined momentum is described by an infinite plane wave

$$\Psi(x,t) = A_0 \exp(i (kx - \omega t)) \qquad \text{----------------(1)}$$

Where, the wave vector

$$K = \frac{2\pi}{\lambda}$$

And ω is the angular frequency.

In the case of electromagnetic field varies in space and time. Sound waves can be described by the pressure variation in space and time.

In other words, to describe wave motion, one requires a quantity which varies in space and time. In analogy with these, to describe matter waves associated with particles in motion, one requires a quantity which varies in space and time. This variable quantities is called the *wave function*, $\Psi(x,t)$, must be large in regions where the particle in likely to be found and small in the region where it is less likely to be found.

That is, the wave function of a particle in conformity with the uncertainty principle must be localized in a small region around it. The wave function of the matter wave which is confined to a small region of space as figure 1 is termed as a *wave pocket or wave group.*

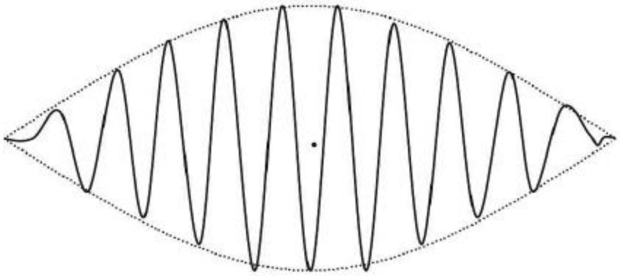


Figure 1 representation of wave packet

Mathematically, a wave packet can be constructed by the superposition of an infinite number of plane waves with slightly differing k value.

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k)\exp[ikx - i\omega(k)t]\, dk \qquad \text{---------------(2)}$$

As the particle is localized, we are interested in the superposition which leads to a wave group which travels without change of shape. This is possible when A(k) is zero everywhere except for the small range of k value

$$(k_0 - \frac{\Delta k}{2}) < k < (k_0 + \frac{\Delta k}{2}), \quad \text{where } \Delta k \ll k_0 \qquad \text{-----------------} \ (3)$$

ω(k) as a power series in (k - k_0) about k_0

$$\omega(k) = \omega(k_0) + (k - k_0)\left(\frac{d\omega}{dk}\right)_{k = k0} + \ldots\ldots \qquad \text{--------------------} \ (4)$$

Neglecting higher order terms and writing

$$\omega(k_0) = \omega_0 , \ \left(\frac{d\omega}{dk}\right)_{k = k0} = \frac{d\omega}{dk}$$

We have

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k)\exp[ikx - i\,\omega_0 t + i(k - k_0)\left(\frac{d\omega}{dk}\right) t\,]\, dk \qquad \text{-------------(5)}$$

Adding and subtracting i k_0x to the exponential,

$$\psi(x,t) = F(x,t) \exp[i\,(k_0x - \omega_0 t)] \qquad \text{-------------- -(6)}$$

Where

$$F(x,t) = \int_{-\infty}^{\infty} A(k) \exp[i(k-k_0)(\,x - \frac{d\omega}{dk}t\,]\, dk \qquad \text{-----------(7)}$$

The group velocity $\quad v_g = \frac{d\omega}{dk}$

The wave packet move with the group velocity v_g, the individual waves of the packet travels with the velocity v_p called phase velocity or wave velocity.

It can easily to proved that the group velocity of the wave packet v_g is the same as the velocity of the material particle. Consider the relation,

$$E = \hbar\omega \quad \text{and } p = \hbar k$$

The group velocity

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} \qquad \text{---------- (8)}$$

for a free non relativistic particle

$$E = \frac{p^2}{2m}$$

$$dE = \frac{p}{m} = v \qquad \text{------------ (9)}$$

for a relativistic particle,

$$E^2 = c^2p^2 + m_0{}^2c^4$$

Therefore,

$$\frac{dE}{dp} = \frac{c^2p}{E} = \frac{c^2\, m_0\;\; v/\sqrt{1-\frac{v^2}{c^2}}}{c^2\, m_0\;\; /\sqrt{1-\frac{v^2}{c^2}}} = v \qquad \text{------------- -(10)}$$

Thus, the velocity of a particle and the group velocity of the corresponding wave packet are the same. The phase velocity

$$v_p = \frac{\omega}{k} = \frac{E}{p} = \frac{c^2 m}{mv} = \frac{c^2}{v} \qquad \text{-------------------(11)}$$

It has no physical significance and is not a measurable quantity.

1.2 Time Dependent Schrodinger Equation

The wavelength l of the de-Broglie wave associated with a free particle of mass *m* moving along the x-axis with momentum p_x is given by,

$$\lambda = \frac{h}{p_x} \qquad \text{-------------------(12)}$$

The wave-vector *k* is related to the wavelength λ as,

$$K = \frac{2\pi}{\lambda} \qquad \text{--------------(13)}$$

From the above two equations, we get

$$p_x = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k \qquad \text{--------------(14)}$$

The kinetic energy *E* of the particle is related to the angular frequency *ω* of the wave associated with it as,

$$E = \hbar\omega \qquad \text{-------------------(15)}$$

Further, we have,

$$E = \frac{px^2}{2m} \qquad \text{-----------------------(16)}$$

So that Equations (14), (15) and (16) yield,

$$\omega = \frac{E}{\hbar} = \frac{px^2}{2\hbar m} = \frac{\hbar^2 k^2}{2\hbar m} = \frac{\hbar k^2}{2m} \qquad \text{-------------------(17)}$$

The wave function $\psi(r,t)$ which describes the free particle localized in the region of the *x*-axis is given by,

$$\psi(r,t) = \int_{-\infty}^{\infty} A(k) \exp[ikx - i\omega(k)t]\, dk \qquad \text{-----------(18)}$$

Using ω given by Equation (17), the above becomes

$$\psi(r,t) = \int_{-\infty}^{\infty} A(k) \exp[i(kx - \frac{\hbar k^2}{2m}t]\, dk \qquad \text{-----------(19)}$$

Differentiating Equation (19) with respect to time *t*, we get

$$\frac{\partial(\psi(x,t))}{\partial t} = \frac{i\hbar}{2m}\int k^2 \text{ A(k) exp [i (k x} - \frac{\hbar k^2}{2m}\text{t] dk}$$

Further, differentiation of Equation (18) with respect to *x* gives

$$\frac{\partial(\psi(x,t))}{\partial t} = \text{i}\int_{-\alpha}^{\alpha} A(k)\text{exp[i(kx} - \frac{\hbar k^2}{2m}\text{t] dk} \qquad \text{------------(20)}$$

Multiplying Equation (19) by *i ħ* we obtain

$$i\,\hbar\,\frac{\partial(\psi(x,t))}{\partial t} = \frac{\hbar^2}{2m}\int_{-\alpha}^{\alpha} k^2\, A(k)\text{exp[i(kx} - \frac{\hbar k^2}{2m}\text{t] dk} \qquad \text{------------ (21)}$$

In view of Equations (20) and (21) we obtain

$$i\,\hbar\,\frac{\partial(\psi(x,t))}{\partial t} = -\,\frac{\hbar^2}{2m}\,\frac{\partial^2(\psi(x,t))}{\partial t^2} \qquad \text{------------ (22)}$$

Equation (22) is the *one-dimensional time-dependent Schrödinger equation for a particle of mass m localized in the region of the x-axis and described by the wavefunction* $\psi(x,t)$.

Equation (22) can be extended to three dimensions in a straightforward manner. In three dimensions the wave function that describes the state of the particle is a function of position $\vec{r}$ in space and time *t*.

$$\psi(\vec{r},t) = \iiint A(k)\text{ exp[i k.}\,\vec{r} - \frac{\hbar k^2}{2m}\text{t] dk}_\text{x}\text{ dk}_\text{y}\text{ dk}_\text{z}$$

$$= \iiint A(k)\text{ exp[i(k}_\text{x}\text{.x+k}_\text{y}\text{.y+k}_\text{z.}\text{z)} - \frac{\hbar k^2}{2m}\text{t] dk}_\text{x}\text{ dk}_\text{y}\text{ dk}_\text{z} \qquad \text{----(23)}$$

Differentiating Equation (23) with respect to *t* we obtain

$$\frac{\partial(\psi(\vec{r},t))}{\partial t} = -\,\frac{i\hbar}{2m}\iiint k^2 A(k)\text{ exp[i(k}_\text{x}\text{.x+k}_\text{y}\text{.y+k}_\text{z.}\text{z)} - \frac{\hbar({k_x}^2+{k_y}^2\,{k_z}^2)}{2m}\text{t] dk}_\text{x}\text{ dk}_\text{y}\text{ dk}_\text{z}$$

The above gives,

$$i\,\hbar\,\frac{\partial(\psi(\vec{r},t))}{\partial t} = \text{i}\iiint k^2 A(k)\text{ exp[i(k}_\text{x}\text{.x+k}_\text{y}\text{.y+k}_\text{z.}\text{z)} - \frac{\hbar({k_x}^2+{k_y}^2\,{k_z}^2)}{2m}\text{t] dk}_\text{x}\text{ dk}_\text{y}\text{ dk}_\text{z} \qquad \text{---(24)}$$

Differentiating Equation (23) with respect to *x* we get,

$$\frac{\partial(\psi(\vec{r},t))}{\partial t} = \text{i}\iiint k_x A(k)\text{ exp[i(k}_\text{x}\text{.x+k}_\text{y}\text{.y+k}_\text{z.}\text{z)} - \frac{\hbar({k_x}^2+{k_y}^2\,{k_z}^2)}{2m}\text{t] dk}_\text{x}\text{ dk}_\text{y}\text{ dk}_\text{z}$$

The above gives on differentiating with respect to *x*,

$$\frac{\partial^2(\psi(\vec{r},t))}{\partial t^2} = - \iiint k_x{}^2 A(k) \exp[i(k_x.x+k_y.y+k_z.z) - \frac{\hbar(k_x{}^2+k_y{}^2\ k_z{}^2)}{2m}t]\, dk_x\, dk_y\, dk_z \qquad \text{-------(25)}$$

We similarly obtain

$$\frac{\partial^2(\psi(\vec{r},t))}{\partial t^2} = - \iiint k_y{}^2 A(k) \exp[i(k_x.x+k_y.y+k_z.z) - \frac{\hbar(k_x{}^2+k_y{}^2\ k_z{}^2)}{2m}t]\, dk_x\, dk_y\, dk_z \qquad \text{-------(26)}$$

$$\frac{\partial^2(\psi(\vec{r},t))}{\partial t^2} = - \iiint k_z{}^2 A(k) \exp[i(k_x.x+k_y.y+k_z.z) - \frac{\hbar(k_x{}^2+k_y{}^2\ k_z{}^2)}{2m}t]\, dk_x\, dk_y\, dk_z \qquad \text{-------(27)}$$

Adding Equations (25), (26) and (27), we get,

$$\frac{\partial^2(\psi(r,t))}{\partial t^2} = \iiint k^2 A(k) \exp[i(k_x.x+k_y.y+k_z.z) - \frac{\hbar(k_x{}^2+k_y{}^2\ k_z{}^2)}{2m}t]\, dk_x\, dk_y\, dk_z \qquad \text{-------(28)}$$

Equations (24) and (28) give,

$$i\,\hbar\ \frac{\partial(\psi(\vec{r},t))}{\partial t} = - \frac{\hbar^2}{2m}\nabla^2\,\psi(\vec{r},t) \qquad \text{--------------(29)}$$

Equation (29) is the three-dimensional time-dependent Schrödinger equation for a free particle described by the wave function $\psi(\vec{r},t)$. Equations (29) and (22) give the *causal development* or the *time evolution* of the wave functions describing the states of one-dimensional and three-dimensional motions of a *free* particle, respectively, *undisturbed by any measurement*.

1.3 Stationary state

The time-dependent states of a quantum system are the solutions of the general time-dependent Schrödinger equation,

$$\begin{aligned} i\,\hbar\ \frac{\partial(\psi(\vec{r},t))}{\partial t} &= - [\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)]\ \psi\ (\vec{r},t) \\ &= \hat{H}\ \ \psi\ (\vec{r},t) \qquad \text{--------------(30)} \end{aligned}$$

The operator $\hat{H}$ being the Hamiltonian for the system. The solution of the above equation when $\hat{H}$ is explicitly dependent on time is generally a difficult task and is treated most commonly by approximate methods.

For the moment, it will suffice to consider conservative systems, that is, systems for which $\hat{H}$ does not depend explicitly on time. If such is the case, the above equation becomes,

$$i\hbar \frac{\partial(\psi(\vec{r},t))}{\partial t} = [-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)]\,\psi(\vec{r},t) \qquad \text{------------ (31)}$$

Since the operator ($i\hbar \frac{\partial}{\partial t}$) on the left is independent of coordinates while the operator $[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]$ on the right is independent of time, it is reasonable to use, as a trial solution of Equation (31), one in the separated form:

$$\psi(\vec{r},t) = \psi(\vec{r})\ \mathrm{T(t)} \qquad \text{---------------- (32)}$$

Substituting Equation (30) in Equation (31) we get,

$$\psi(\vec{r})\ i\hbar \frac{dT(t)}{dt} = [-\frac{\hbar^2}{2m}\nabla^2 \psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r})]\,T(t)$$

Dividing throughout by $\psi(\vec{r})T(t)$, we get

$$\frac{1}{T(t)}\, i\hbar \frac{dT(t)}{dt} = \frac{1}{\psi(\vec{r})}[-\frac{\hbar^2}{2m}\nabla^2 \psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r})] \qquad \text{-------- (33)}$$

The left hand side of the above equation is a function of only time while the right hand side is a function of only coordinates. Hence for the above equation to hold, each side must be equal to some constant. Taking this constant as equal to E we obtain,

(a) $\frac{1}{T(t)}\, i\hbar \frac{dT(t)}{dt} = \mathrm{E}$ or

$$i\hbar \frac{dT(t)}{dt} = \mathrm{T(t)E} \qquad \text{-----(34)}$$

(b) $\frac{1}{\psi(\vec{r})}[-\frac{\hbar^2}{2m}\nabla^2 \psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r})] = \mathrm{E}$ or

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]\,\psi(\vec{r}) = \mathrm{E}\,\psi(\vec{r}) \qquad \text{----------(35)}$$

Solution of Equation (34) is given by,

$$\mathrm{T(t)} = \exp(-\frac{i}{\hbar}Et) \qquad \text{----------------(36)}$$

Therefore, equation (32)

$$\psi\,(\vec{r},t) \quad = \psi\,(\vec{r})\,\exp\left(-\frac{i}{\hbar}\,Et\right)$$

Equation (34) can be written as,

$$\widehat{H}\ \ \psi\,(\vec{r},t) = \mathrm{E}\,\psi\,(\vec{r}) \qquad \text{----------------- (37)}$$

Where,

$$\widehat{H}\ =\ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) = \widehat{p^2}\,/2\mathrm{m} + V(\vec{r}) \qquad \text{------------(38)}$$

$\widehat{H}$ - Operator corresponding to kinetic energy + operator corresponding to potential energy. or Operator corresponding to the total energy of the system.

Equation (37) is the energy eigen value equation and the constant is thus identified as the energy eigen value. In general, Equation (37) has a complete set of solutions $\psi_n(\vec{r}\,)$ such that,

$$\widehat{H}\,\psi_n(\vec{r}\,) = \mathrm{E}_\mathrm{n}\,\psi_n(\vec{r}\,) \qquad \text{-------------------- (39)}$$

E_n represent the possible results of energy measurement performed on the system. Including the time-dependent part, we have the wave function of the system,

$$\psi_n(\vec{r}\,,\mathrm{t}) = \psi_n(\vec{r}\,)\,\exp\left(-\frac{i}{\hbar}\,Et\right) \qquad \text{----------- -(40)}$$

Equation (40) gives the time-dependent states of the system.

The probability density, i.e., the probability of finding the particle, with energy eigen value E_n within unit volume about the position $\vec{r}$ at the instant *t* is given by,

$$P_n(\vec{r}\,,\mathrm{t}) = |\psi(r,t)|^2$$

$$= \psi_n{}^*\,(\vec{r})\,\exp\left(-\frac{i}{\hbar}\,Et\right)\psi_n{}^*\,(\vec{r})\,\exp\left(-\frac{i}{\hbar}\,Et\right)$$

$$= |\psi_n(\vec{r})|^2 \qquad \text{----------- -(41)}$$

We find that

$$P_n(\vec{r}\,,\mathrm{t})\ = \text{constant time} \qquad \text{------------- (42)}$$

The states described by wave function such as ψ_n(r,t) given by Equation (40) for which the probability density is constant in time are called stationary or steady states of the system.

Let us now consider an observable *A* for the system whose operator $\hat{A}$ does not depend on time explicitly. By definition, the expectation value of *A* in the stationary state described by the wave function $\psi_n(\vec{r}\,,\mathrm{t})$ is given by,

$$\langle A\rangle = \int_{-\infty}^{\infty} \psi_n{}^* \left(\overline{\vec{r},\vec{t}}\right)\hat{A}\, \psi_n(\vec{r}\,,\mathrm{t})\ \mathrm{d}^3(\vec{r})$$

$$= \int_{-\infty}^{\infty} \psi_n{}^* \left((\vec{r}\,)\right) \exp\left(-\frac{i}{\hbar}\, E_n t\right) \hat{A}\, \psi_n(\vec{r}\,) \exp\left(-\frac{i}{\hbar}\, E_n t\right) \mathrm{d}^3(\vec{r})$$

$$= \int_{-\infty}^{\infty} \psi_n{}^* \left((\vec{r}\,)\right)\hat{A}\, \psi_n(\vec{r}\,)\ \mathrm{d}^3(\vec{r}) \quad = \text{constant in time} \qquad \text{-----------(43)}$$

We find that the expectation value of an observable, which is not an explicit function of time, in any stationary state is constant in time. We know that the equation of continuity for probability is given by

$$\frac{\partial P(\vec{r}\,,\mathrm{t})}{\partial t} + \vec{\nabla}\,\vec{j}\,(\vec{r}\,,\mathrm{t}) \;=\; 0 \qquad \text{------------(44)}$$

For stationary states, probability density $P(\vec{r}\,,\mathrm{t})$ is independent of time so that $\frac{\partial P(\vec{r}\,,\mathrm{t})}{\partial t} = 0$. Clearly, for stationary states, the current density $j(\vec{r}\,,\mathrm{t})$, according to Equation (44), satisfies

$$\vec{\nabla}\,\vec{j}\,(\vec{r}\,,\mathrm{t}) \;=\; 0$$

$$\mathrm{Div}\quad \vec{j}\,(\vec{r}\,,\mathrm{t}) \;=\; 0 \qquad \text{-------------- (45)}$$

1.4 Time Independent Schrodinger equation

Consider a particle of mans *m* moving freely in space. Let $\psi\ (\vec{r},t)$ or y(*x*, *y*, *z*, *t*) B e the wave function for the de-Broglie wave associated with the particle at the location or (*x*, *y*, *z*) at the instant of time *t*.

In analogy with classical mechanics, the differential equation for the wavefunction can be written as,

$$\frac{\partial^2\psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial z^2} = \frac{1}{u^2}\ \frac{\partial^2\psi(x,y,z,t)}{\partial t^2}$$

where *u* in the wave velocity of the de-Broglie wave. The above equation can also be written as,

$$\frac{\partial^2\psi(x,y,z,t)}{\partial x^2} = \frac{1}{u^2}\ \frac{\partial^2\psi(x,y,z,t)}{\partial t^2}$$

$$\nabla^2\ (\psi(\vec{r},t)) = \frac{1}{u^2}\ \frac{\partial^2\psi(\vec{r},t)}{\partial t^2} \qquad \text{-----------(46)}$$

The solution of Equation (46) in its most general form is given by,

$$\psi(\vec{r},t) = \psi(\vec{r})\ \exp(-\mathrm{i}\omega \qquad \text{---------------(47)}$$

$$\omega = 2\pi\nu \qquad \text{-------------(48)}$$

ν being the frequency of the wave and $\psi(\vec{r})$ is a time-independent function and represents the amplitude of the wave at the location $\vec{r}$.

We get from Equation (47) an differentiation with respect to time *t*,

$$\frac{\partial(\psi(\vec{r},t))}{\partial t} = -\mathrm{i}\omega\, \psi(\vec{r})\exp\,(-\mathrm{i}\omega t)$$

Differentiating the above equation with respect to time *t* we get,

$$\frac{\partial^2(\psi(\vec{r},t))}{\partial t^2} = -\omega^2\, \psi(\vec{r})\exp\,(-\mathrm{i}\omega t) \qquad \text{--------------(49)}$$

Using Equation (49) in Equation (46) we get,

$$\nabla^2\,(\psi(\vec{r},t)) = -\frac{\omega^2}{u^2}\,\psi(\vec{r},t) \qquad \text{------------(50)}$$

We have,

$$\omega = 2\pi\nu = 2\pi\frac{u}{\lambda} \qquad \text{-------------(51)}$$

Where λ is the wavelength of the de-Broglie wave. Equation (51) gives,

$$\frac{\omega}{u} = \frac{2\pi}{\lambda} \qquad \text{---------(52)}$$

Use of Equation (52) in Equation (50) gives,

$$\nabla^2\,(\psi(\vec{r},t)) = -\frac{4\pi^2}{\lambda^2}\,\psi(\vec{r},t)$$

$$\nabla^2\,(\psi(\vec{r},t)) + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r},t) = 0$$

$$\nabla^2\,[(\psi(\vec{r})\exp(-\mathrm{i}\omega t)] + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r})\exp\,(-\mathrm{i}\omega t) = 0$$

$$\nabla^2\,(\psi(\vec{r}) + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r}) = 0 \qquad \text{-------------(53)}$$

It *v* the velocity of the particle, we have,

$$\lambda = \frac{h}{mv}$$

Substituting the above in Equation (53) we obtain,

$$\nabla^2\,\psi(\vec{r}) + \frac{4\pi^2 m^2 v^2}{h^2}\,\psi(\vec{r}) = 0$$

$$\nabla^2 \psi(\vec{r}) + \frac{m^2v^2}{h^2} \psi(\vec{r}) = 0 \qquad \text{--------------(54)}$$

If *E* be the total energy of the particle and *V* be its potential energy then we have the kinetic energy of the particle,

$$\frac{1}{2} \text{ m } v^2 = \text{E- V}$$

So that

$$m^2v^2 = 2\text{m (E - V)} \qquad \text{--------------(55)}$$

Substituting Equation (55) in Equation (54) we obtain,

$$\nabla^2 \psi(\vec{r}) + \frac{2m}{h^2} (\text{E - V}) \psi(\vec{r}) = 0 \qquad \text{---------------(56)}$$

Equation (56) is the time-independent Schrödinger equation for a particle of mass *m*, total energy *E* moving in a force field described by the potential energy function *V*.

For a freely moving particle in space, *V* = 0, so that Equation (56) reduces to,

$$\nabla^2 \psi(\vec{r}) + \frac{2m}{h^2} \text{ E } \psi(\vec{r}) = 0 \qquad \text{-------------(57)}$$

For one-dimensional motion localized in the region along the *x*-axis, Equation (56) gives

$$\frac{d^2(\psi(x))}{dt^2} + \frac{2m}{h^2} \text{ E } \psi(\vec{r}) = 0 \qquad \text{--------(58)}$$

1.5 Interpretation of the wave function

Probability interpretation

The wave function $\psi(r,t)$ has no physical existence since it can be complex. Also, it cannot be taken as a direct measure of the probability at (r,t) since the probability is real and nonnegative. However, $\psi(r,t)$ must in some way be an index of the presence of the particle at (r,t). A universally accepted statistical interpretation was suggested by Born in 1926. He interpreted the product of $\psi(r,t)$ and its complex conjugate ψ^* as the position probability density $P(r,t)$

$$P(r,t) = \psi^* \text{(r,t)} \psi(r,t) = |\psi(r,t)|^2 \qquad \text{----------------(59)}$$

The quantity $|\psi(r,t)|^2\, d\tau$ is then the probability of finding the system at time t in the small volume element $d\tau$ surrounding the point r.

Where $|\psi(r,t)|^2\, d\tau$ is integrated over the entire space one should get the total probability, which is unity. Therefore,

$$\int_{-\infty}^{\infty}|\psi(r,t)|^2\, d\tau = 1 \qquad \text{--------------------(60)}$$

The above equation to be define $\psi(r,t)$ must tend to zero sufficiently rapidly as r → $\pm\infty$ Hence, one can multiply $\psi(r,t)$ by a constat N, so that N ψ satisfies the condition in equation(60)

$$|N|^2 \int_{-\infty}^{\infty}|\psi(r,t)|^2\, d\tau = 1 \qquad \text{-----------------(61)}$$

The constant N is called the normalization constant and above equation is called normalization condition.

Probability Current density

The probability of finding a system, described by a wave function $\psi(r,t)$ in the finite volume V in space is given by $\int \psi * \psi \; d\tau$ and this changes as the wave function evolves time.

Consider the Schrodinger equation and its complex conjugate form,

$$i\hbar \frac{\partial\psi(r,t)}{\partial t} = [\, \frac{-h^2}{2m}\nabla^2 + V(r)]\, \psi \qquad \text{--------------(62)}$$

$$i\hbar \frac{\partial\psi*}{\partial t} = [\, \frac{-h^2}{2m}\nabla^2 + V(r)]\, \psi* \qquad \text{--------------(63)}$$

Here, the potential V is assumed to be real. Multiplying equation (62) by $\psi*$ and equation (63) by ψ from left and subtracting one from other

$$i\hbar\, (\psi^* \frac{\partial\psi}{\partial t} + \psi \frac{\partial\psi^*}{\partial t}) = \frac{-h^2}{2m}\, [\psi^*\nabla^2\ \psi - \psi\nabla^2\ \psi^*\ ]$$

$$\frac{\partial(\psi^*\psi)}{\partial t} = \frac{i\hbar}{2m}\, [\nabla.(\psi^*\nabla\ \psi - \psi\nabla\ \psi^*)\ ] \qquad \text{-----------------(64)}$$

Integrating, we get

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\psi^*\psi \;=\frac{i\hbar}{2m}\int_{-\infty}^{\infty}[\nabla.(\psi^*\nabla\;\psi-\psi\nabla\;\psi^*)\,]\,]\quad d\tau$$

$$=\quad\frac{i\hbar}{2m}\qquad[\nabla.(\psi^*\nabla\;\psi-\psi\nabla\;\psi^*]_{-\infty}^{\infty}\qquad\text{---------------- (65)}$$

ψ and ψ^* → 0 and $r\ \rightarrow\ \pm\infty$ the right - hand side of equation (65) vanishes. Then,

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\psi^*\psi\ =\ 0$$

$$\int_{-\infty}^{\infty}\psi^*\psi\ \ d\tau\ =\ \text{constant in time.}\qquad\text{-------------------(66)}$$

That is normalization integral is constant in time.

By defining a vector j(r,t) called the **probability current density.**

$$j(r,t)=\ \frac{i\hbar}{2m}\ (\psi^*\nabla\;\psi-\psi\nabla\;\psi^*)\qquad\text{-------------- (67)}$$

substitute in equation (17) we get

$$\frac{\partial P(r,t)}{\partial t}\ +\nabla\,.j(r,t)\ =\ 0\qquad\text{--------------------(68)}$$

The above equation is the equation of continuity for probability, which is analogous to the equation of continuity in hydrodynamics and electrodynamics.

Writing the integral form of equation (68) over a finite volume V and using Gauss theorem, we get

$$\frac{\partial}{\partial t}\int P(r,t)\ \ d\tau=\ \int\ \nabla\,.\,j\ \ d\tau\ =\ -\ \oint j.ds\qquad\text{-------------(69)}$$

Where s is the area of the enclosed volume V. this result, suggests that any decrease in probability in a region is accompanied by an outflow of probability across its surface.

Expectation Value

The definition of probability density immediately allows the calculation of the expectation value of the position vector of a particle. Consider a large number of measurements of the position vector r of a particle made when it is in a particular state. Ensure that the particle has the same wave function $\psi(r,t)$ before each measurement. The average of all the different values is the 'expectation vale' $\langle r\rangle$ of the position coordinate. As $|\psi(r,t)|^2$ represents the probability with which the value r occurs in the measurement, $\langle r\rangle$ can be written as

$$\langle r\rangle = \int \mathrm{r}\, \psi^* \psi\, \mathrm{d}\tau = \int \psi^* r\, \psi\, \mathrm{d}\tau \qquad \text{-------------(70)}$$

The expectation value of a function r may be written as

$$\langle f(r)\rangle = \int \psi^*(r,t) f(r)\, \psi(r,t)\, \mathrm{d}\tau \qquad \text{----------------(71)}$$

Left multiplying the time dependent - Schrödinger equation by ψ^* and integrating from -∞ to ∞, we get

$$\int_{-\infty}^{\infty} \psi^* (i\hbar \frac{\partial}{\partial t})\, \mathrm{d}\tau = \int_{-\infty}^{\infty} \psi^* (-\frac{\hbar^2}{2m}\nabla^2)\, \psi\, \mathrm{d}\tau + \int \psi^* V\, \psi\, \mathrm{d}\tau$$

Or

$$\langle i\hbar \frac{\partial}{\partial t}\rangle = \langle -\frac{\hbar^2}{2m}\nabla^2\rangle + \langle V\rangle \qquad \text{------------- (72)}$$

$$\langle E\rangle = \langle \frac{p^2}{2m}\rangle + \langle V\rangle \qquad \text{----------- (73)}$$

If the wave function is not normalized,

$$\langle A\rangle = \frac{\int \psi^* A_{0p} \psi\, \mathrm{d}\tau}{\int \psi^*\, \psi\, \mathrm{d}\tau} \qquad \text{---------(74)}$$

Since the space coordinates have been integrated out, the expectation value is a function of time only.

1.6 Ehrenfest's theorem

P. Ehrenfest in 1927 stated, in regard to the correspondence between the motion of a classical particle and the motion of a wave packet representing the particle, the following theorem.

The averages or the expectation values of the quantum mechanical variables satisfy the same equations of motion as the corresponding classical variables in the corresponding classical description. Specifically the theorem states that,

$$\frac{d}{dt}\ \langle x\rangle\ = \frac{l}{m}\,\langle p_x\rangle$$

$$\frac{d}{dt}\ \langle p_x\rangle\ = \langle -\ \frac{dV(x)}{dx}\rangle$$

provided that the wavefunction $\psi(x,\ t)$ with respect to which averages are computed satisfies the time-dependent Schrödinger equation

$$i\hbar\,\frac{\partial\psi(r,t)}{\partial t} = [\ \frac{\hbar^2}{2m}\ \frac{\partial^2}{\partial x^2} + V(r)]\ \psi(\mathrm{x,t})$$

$$i\hbar\,\frac{\partial\psi(r,t)}{\partial t}\ = \widehat{H}\ \psi(\mathrm{x,t})$$

1.7 Eigen functions and Eigen vectors

A particular class of operators is of primary interest in the mathematical formulation of quantum theory. These are the so-called linear operators.

Consider an operator $\hat{A}$ defined in a certain domain of definition. Let ψ_1 and ψ_2 be any two arbitrary functions defined in the domain of definition of $\hat{A}$.

If on operating on the sum of the functions ψ_1 and ψ_2 the operator $\hat{A}$ yields the same result as the sum of the operations on the two functions separately, then $\hat{A}$ is said to be linear operator. Thus, for the operator $\hat{A}$ to be linear we must have,

$$\hat{A}\ (\ \psi_1 +\ \psi_2) = \hat{A}\ \ \psi_1 + \hat{A}\ \ \psi_2 \qquad \text{----------------(1)}$$

For linear of $\hat{A}$ we must also have

$$\hat{A}(c\,\psi_1) = c\,\hat{A}\,\psi_1$$

$$\hat{A}(c\,\psi_2) = c\,\hat{A}\,\psi_2 \qquad \text{-------------(2)}$$

Where *c* is a number.

The properties of linear operator expressed by the Equations (1) and (2) will be useful in later developments of quantum mechanics.

1.8 Eigen functions and Eigen values of a Linear operator

Consider a linear operator $\hat{A}$ defined in a certain domain of definition. If ψ is any function defined in the domain of the definition of $\hat{A}$, then in general, we have,

$$\hat{A}\psi = \varphi \qquad \text{--------(3)}$$

However, for every linear operator $\hat{A}$, there exists a set of functions $\psi_1 , \psi_2 ,\ldots\ldots\ldots \psi_n$ such that,

$$\hat{A}\psi_1 = a_1\,\psi_1$$

$$\hat{A}\psi_2 = a_2\,\psi_2 \qquad \text{------(4)}$$

.

.

.

$$\hat{A}\psi_n = a_n\,\psi_n$$

Where a_1 , a_2 , ….., a_n are constant with respect to the variables of which ψ_I'(I = 1,2,3,..) are functions . the set of functions $\psi_1 , \psi_2 ,\ldots\ldots\ldots \psi_n$ are called eigen functions of the operator $\hat{A}$ and the constant a_1 , a_2 , ….., a_n are called the eigen values belonging to the eigen functions $\psi_1 , \psi_2 ,\ldots\ldots\ldots \psi_n$ respectively.

1.9 Hermitian Operator

The operators which play important role in quantum mechanics can be further specialized. They are not only linear, they are Hermitian. Before we define Hermitian operator, we need to define the **complex conjugate** of a linear operator $\hat{A}$. Let us suppose,

$$\hat{A}\psi = \varphi \qquad \text{------------(5)}$$

The operator denoted by $\hat{A}^*$ is called the complex conjugate of the operator $\hat{A}$ if, by the action of $\hat{A}^*$ on the function ψ^*(complex conjugate of the function y), we get the function φ^* (complex conjugate of the function f), i.e., we get,

$$\hat{A}^* \, \psi^* \; = \; \varphi^* \qquad \text{------------------(6)}$$

In the domain of definition V in which the operator $\hat{A}$ is defined, let u and v be two functions subject to identical boundary conditions.

The operator $\hat{A}$ is said to be Hermitian operator if it satisfies the condition,

$$\int u^* \;\hat{A}\, v \,\mathrm{d}\tau \;=\; \int \;(\hat{A}u)^*\, v\,\mathrm{d}\tau \;=\; \int \;\hat{A}^* u^*\, v\,\mathrm{d}\tau \qquad \text{--------(7)}$$

Alternatively, the Hermitian character of the linear operator $\hat{A}$ is made through the definition of **transpose** of the operator $\hat{A}$. The transpose of the operator $\hat{A}$ is denoted by $\hat{\hat{A}}$ and is defined according to the relation,

$$\int \; v(\,\hat{A}u) \;\mathrm{d}\tau \quad = \quad \int \; u(\,\hat{A}v) \;\mathrm{d}\tau \qquad \text{---------(8)}$$

The transposed operator $\widetilde{\widetilde{A^*}}$for the operator is, according to Equation(8), given by,

$$\int \; v(\widetilde{\widetilde{A^*}}\, u) \;\mathrm{d}\tau \quad = \quad \int \; u(\,\widetilde{\widetilde{A^*}} v) \;\mathrm{d}\tau \qquad \text{--------(9)}$$

It is usual to denote as $\widetilde{\widetilde{A^*}}$ (read as A-dagger) and is said to be the **Conjugate** to the operator $\hat{A}$. Now the operator $\hat{A}$ is called **Hermitian** or **self adjoint** if,

$$\hat{A} = \hat{A}^\dagger$$

We may note that in mathematics the terms adjoint, conjugate and associate operator are used for $\hat{A}_\dagger$.

1.10 Postulates of Quantum Mechanics

Postulate 1:

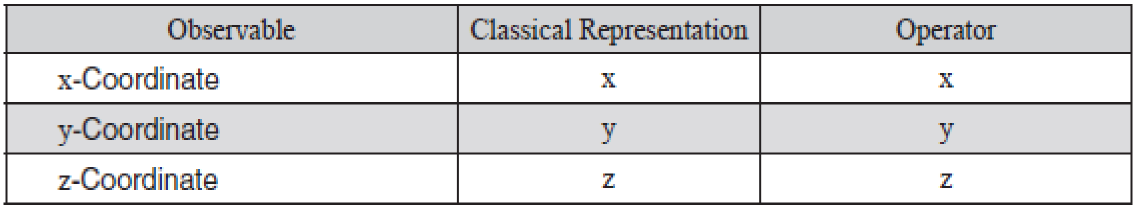
To every quantum mechanical state of a physical system of 's' degree of freedom, there corresponds a function y, called the **wave function**. In general, ψ is a complex-valued function of generalized coordinates q_1, q_2, ..., q_s and time 't'. The function y and its derivatives are single-valued, continuous and quadratically integrable over the entire domain of definition.

The representation in which the wave functions are functions of coordinates and time is called *coordinate representation,* while the representation in which the wave functions are functions of the momentum components and time is called the *momentum representation*. In order to extract physically meaningful information from wave functions, the second, third and fourth postulates have been made.

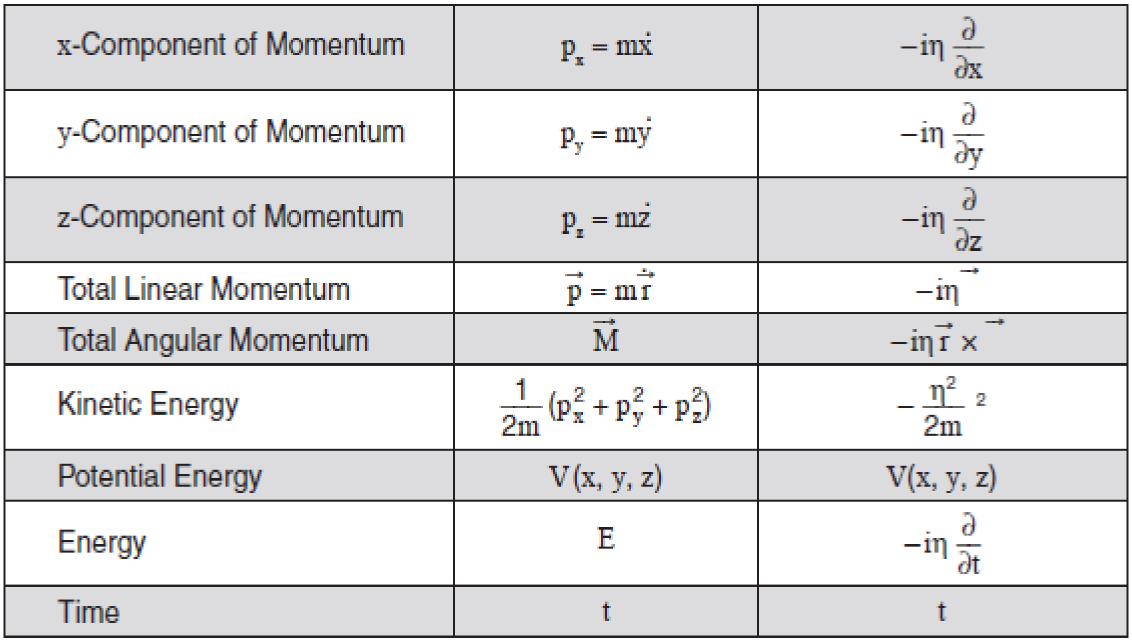
Postulate 2:

For every observable of a physical system, there corresponds a Hermitian operator.

In the Table below are given classical representations and corresponding quantum mechanical operators for the observables of a single particle.



Observable	Classical Representation	Operator
x-Coordinate	x	x
y-Coordinate	y	y
z-Coordinate	z	z



x-Component of Momentum	$p_x = m\dot{x}$	$-i\eta\frac{\partial}{\partial x}$
y-Component of Momentum	$p_y = m\dot{y}$	$-i\eta\frac{\partial}{\partial y}$
z-Component of Momentum	$p_z = m\dot{z}$	$-i\eta\frac{\partial}{\partial z}$
Total Linear Momentum	$\vec{p} = m\dot{\vec{r}}$	$-i\eta\vec{\ }$
Total Angular Momentum	$\vec{M}$	$-i\eta\vec{r}\times\vec{\ }$
Kinetic Energy	$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$	$-\frac{\eta^2}{2m}{}^{2}$
Potential Energy	$V(x, y, z)$	$V(x, y, z)$
Energy	E	$-i\eta\frac{\partial}{\partial t}$
Time	t	t

Postulate 3:

The only possible result of a precise measurement of an observable A whose corresponding operator is $\hat{A}$ are the eigen values a_n which are the solutions of the eigen value equation,

$$\hat{A}\psi_n = a_n\,\psi_n$$

Where ψ_n forms a *complete set* of functions called eigen function of $\hat{A}$. This means that any arbitrary state function can be expressed as a linear combination of the eigen functions.

Postulate 4:

When a system is in a state described by the wave function ψ, the expected mean or expectation value, of a series of measurement of an observable, say A, is

$$\langle A\rangle = \frac{\int \psi^* \,\hat{A}\psi\, d\tau}{\psi^*\,\psi\, d\tau}$$

where $\hat{A}$ is the operator corresponding to the observable A and the integration is carried over the entire domain of definition. It is usual to consider any state function, namely the wave function ψ to be normalized, i.e.,

$$\int \psi^* \psi \, d\tau = 1$$

With normalized wave function, Eq. (ii) gives

$$\langle A \rangle = \int \psi^* \hat{A}\psi \, d\tau$$

To study the development of the state of a quantum system, a fifth postulate has been introduced.

Postulate 5:

The state function $\psi(\vec{r}\,, t)$of a physical system are solutions of the differential equation

$$i\hbar \frac{\partial \psi(r,t)}{\partial t} = \widehat{H}\, \psi(\vec{r},t)$$

where the operator $\widehat{H}$ corresponds to the total energy of the physical system at time *t*. It is, in general, a function of the operators for$\vec{r}\,, \vec{p}$ and time *t*.

1.11 Uncertainty Principle

Heisenberg, in 1927, stated the uncertainty principle (also called indeterminacy principle) in the following two parts:

(i) Experiment cannot determine simultaneously the component of momentum say *px* of a particle and its corresponding coordinate position *x* with unlimited accuracy; instead, the precision of measurement is inherently limited by the measurement process itself, such that

$$\Delta p_x \, \Delta x \geq \frac{\hbar}{2} \qquad \text{--------(1)}$$

In the above, Δp_x is the uncertainty within which the momentum p_x is known and the position *x* in the same experiment is known within an accuracy D*x*. There are exactly similar relations for the other two components.

$$\Delta p_y \, \Delta y \geq \frac{\hbar}{2} \qquad \text{-------(2)}$$

$$\Delta p_z \, \Delta z \geq \frac{\hbar}{2} \qquad \text{----------(3)}$$

(ii) The uncertainties involved in simultaneous measurement of energy and time are given by,

$$\Delta E \, \Delta t \geq \frac{\hbar}{2}$$

The above relation means that an energy determination that has an uncertainty ΔE must occupy at least a time interval $\Delta E = \frac{\hbar}{2\Delta t}$. Alternatively, if a system is in a given state for not longer than Δt, the energy of the system in that state is uncertain, at least by an amount $\Delta E = \frac{\hbar}{2\Delta t}$.

UNIT II:

ONE DIMENSIONAL AND THREE DIMENSIONAL ENERGY EIGEN VALUE PROBLEMS

Square – well potential with rigid walls – Square well potential with finite walls – Square potential barrier – Alpha emission – Bloch waves in a periodic potential - Kronig-penny square – well periodic potential – Linear harmonic oscillator: Operator method – Particle moving in a spherically symmetric potential – System of two interacting particles – Hydrogen atom – Rigid rotator

2.1 Square – well potential with rigid walls

A symmetric infinite square well potential is defined as

$$V(x) = +\infty \quad \text{for } x < -a$$

$$= 0 \quad \text{for } -a \leq x \leq a$$

$$= +\infty \quad \text{for } x > -a$$

and is represented in the Figure (2)

Consider the motion of a particle of mass m in the one-dimensional potential described above

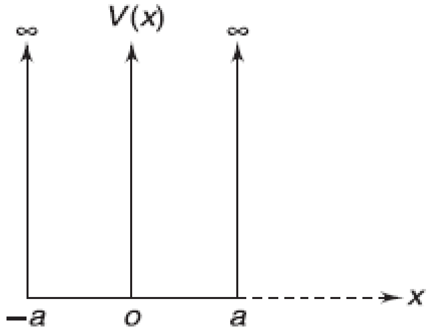


Figure 2 symmetric infinite square

If $\psi(x)$ is the wave function describing the state of the particle in the region $-a \leq x \leq a$ then it satisfies the time-independent Schrödinger equation,

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

$$\frac{d^2\psi(x)}{dx^2} + k^2 E\,\psi(x) = 0 \qquad \text{-----------(1)}$$

Where

$$k = \sqrt{\frac{2m}{\hbar^2} E} \qquad \text{----------(2)}$$

The most general solution of Equation (1) is given by,

$$\psi(x) = A \sin(kx) + B \cos(kx) \qquad \text{...(3)}$$

Where A and B are constants.

Since $V(x) = \infty$ for $x < -a$ and $x > a$, the wave functions in these two regions vanish giving,

$$\psi(\text{-a}) = 0 \text{ and } \psi(+a) = 0 \qquad \text{--------------(4)}$$

Using the conditions given by Equation (3) in Equation (4) we get

$$A \sin ka + B \cos ka = 0 \qquad \text{…………...(5)}$$

$$A \sin ka + B \cos ka = 0 \qquad \text{………… ...(6)}$$

For the above two equations to hold simultaneously we must have

$$A \sin ka = 0 \qquad \text{…… ...(7)}$$

and $$B \cos ka = 0 \qquad \text{-----------(8)}$$

In view of Equations (7) and (8) we may have $A = 0$ and $B = 0$ but these are physically unacceptable because $\psi(x)$ given by Equation (3) would then vanish.

Since B π 0, we have from Equation (8),

$$\cos ka = 0 = \cos \frac{n\pi}{2}, \qquad n = 1, 3, 5, ...$$

$$ka = \frac{n\pi}{2} \quad \text{or } k = \frac{n\pi}{2a} \qquad \text{-------------(9)}$$

Using Equation (1) in the above we obtain the energy eigen values

$$E_n = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} = \frac{n^2\hbar^2\pi^2}{8ma^2} \qquad n=1,3,5,\ldots \qquad \text{-----------(10)}$$

The energy eigen functions corresponding to the above energy eigen values are

$$\psi_n(x) = B \cos kx = \text{B} \cos\left(\frac{n\pi}{2a} x\right) \qquad n = 1, 3, 5 \qquad \text{-------(11)}$$

The condition given by Equation (6) gives

$$\sin ka = 0 = \sin n\pi \qquad (\text{since } A \neq 0)$$

or $ka = n\pi$ or $k = \frac{n\pi}{a}$; $n = 2, 4, 6$ --------(12)

Using the above value of k in Equation (2) we get the energy eigen values

$$E_n = \frac{\hbar^2}{2m} k^2 = \frac{n^2\hbar^2 \pi^2}{8ma^2} \qquad n= 2,4,6,\ldots \qquad \text{--------(13)}$$

The corresponding energy eigen functions are

$$\psi_n(x) = A \sin\left(\frac{n\pi}{2a}\right) \qquad n=2,4,6,\ldots.. \qquad \text{-----------(14)}$$

The normalization conditions of the wave functions,

$$\int_{-a}^{a} \psi n^*(x)\psi n(x) \, dx = 1$$

Lead to

$$A = \frac{1}{\sqrt{a}} \quad , \quad B = \frac{1}{\sqrt{a}} \qquad \text{--------------(15)}$$

We can thus write the set of energy eigen functions for the particle in the symmetric infinite square well potential as,

$$\psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a}\right) \qquad n=2,4,6,\ldots.. \qquad \text{-----------(16)}$$

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a}\right) \qquad n=1,3,5,\ldots.. \qquad \text{-----------(17)}$$

and the discrete set of energy eigen values as

$$E_n = \frac{n^2\hbar^2 \pi^2}{8ma^2} \qquad n= 2,4,6,\ldots \qquad \text{--------(18)}$$

2.2 Square well potential with finite walls

A symmetric square well potential of finite depth is described by potential function $V(x)$ of the form

$$V(x) = V_0 \text{ for } x < -a \qquad \text{(Region I)}$$

$$= 0 \text{ for } -a \leq x \leq a \qquad \text{(Region II)}$$

$$= V_0 \text{ for } x > a \qquad \text{(Region III)}$$

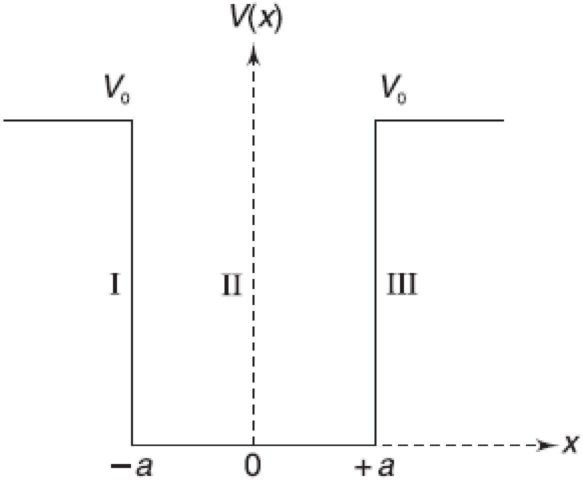


Figure 3 potential function

Consider the motion of a particle of mass m in the potential well described above. The Schrödinger equation in Regions I and III is,

$$- \frac{h^2}{2m} \frac{d^2(\psi(x))}{dt^2} + V_0 \, \psi(x) = E \, \psi(x)$$

$$\frac{d^2(\psi(x))}{dt^2} + \frac{2m}{h^2} (E - V_0) \, \psi(x) = 0 \qquad \text{----------------(1)}$$

In Region II the Schrödinger equation is

$$\frac{d^2(\psi(x))}{dt^2} + \frac{2m}{h^2} E \, \psi(x) = 0 \qquad \text{---------(2)}$$

which can be put in the form

$$\frac{d^2(\psi(x))}{dt^2} + k^2 \, E \, \psi(x) = 0 \qquad \text{---------(3)}$$

Where

$$k= \sqrt{\frac{2m}{\hbar^2} E} \qquad \text{------ (4)}$$

Let us consider the cases where: $E < V_0$, and $E > V_0$

Case $E < V_0$:

We may write Equation (2) in the form

$$\frac{d^2(\psi(x))}{dt^2} - \alpha^2 \psi(x) = 0 \qquad \text{---------(5)}$$

Where

$$\alpha = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)} \qquad \text{-----------(6)}$$

The most general solution of Equation (5) is

$$\psi(x) = A e^{+\alpha x} + B e^{-\alpha x} \qquad \text{-----------(7)}$$

A, B are constant

Specific solution in Region I

$$\psi_1(x)= A e^{+\alpha x} \qquad \text{----------(8)}$$

Specific solution in Region III

$$\psi_3(x)= A e^{-\alpha x} \qquad \text{------- (9)}$$

Solution of Equation (3) gives the wave function in region II

$$\psi_2(x) = C \sin (kx) + D \cos (kx) \qquad \text{----------- (10)}$$

$\psi_2(x)$ is either symmetric or anti symmetric about $x = 0$. The first term in Equation (10) is anti symmetric because sin (kx) = – sin (– kx). The second term is symmetric because cos (kx) = cos (– kx).

Case $E > V_0$:

The Schrodinger equation in Regions I and III is given by,

$$\frac{d^2(\psi(x))}{dt^2} + \frac{2m}{h^2} (E - V_0) \psi(x) = 0$$

Since E is greater than V_0, $\frac{2m}{h^2}$ (E - V_0) is a real positive quantity. As such the solution of the above equation is sinusoidal in nature. The probability density for the particle is distributed over all space in regions I and III. It is also distributed in Region II, i.e., within the well. Thus we do not get bound state for the particle.

2.3 Alpha emission

Radioactive nuclei disintegrate by the emission of alpha (a) particle which is the nucleus of a helium atom having charge of +2*e* and a mass 4 units.

An α-particle remains bound within the nucleus by a strong, attractive, short range nuclear force. This attractive nuclear force acts upto a distance which is approximately equal to the radius of the nucleus. When the α-particle comes out of the nucleus then it experiences a long range coulomb repulsive force due to the residual nucleus (the nucleus that remains after the emission of the α-particle). The variation of the potential energy of the α-particle with distance from the center of the nucleus is qualitatively as shown in the Figure 4.

If r_0 be the radius of the nucleus and *Ze* be the change of the residual nucleus then the coulomb potential energy of the α-particle just beyond the surface of the nucleus becomes $\frac{1}{4\pi\varepsilon_0}\ \frac{2Ze^2}{r_1}$. For the α-emitting nuclides this energy is several times larger than the energy of the α-particles.

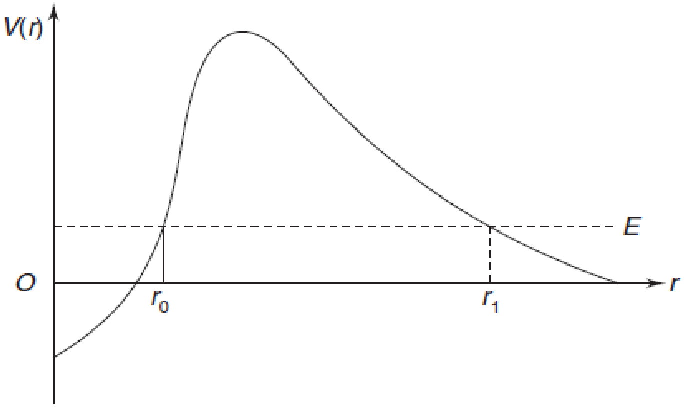


Figure 4 potential energy of the alpha particle

Let *E* be the energy of the α-particle emitted from the nucleus. Let the repulsive coulomb potential energy of the nucleus be equal to *E* at a distance r_1 from the center of the nucleus. We then have,

$$E = \frac{1}{4\pi\varepsilon_0}\ \frac{2Ze^2}{r_1} \qquad \text{------(1)}$$

$$r_1 = \frac{1}{4\pi\varepsilon_0}\ \frac{2Ze^2}{E} \qquad \text{-----(2)}$$

We may, for some qualitative understanding of the phenomenon of α-emission, consider the potential $V(r)$ in the region $r_0 \leq r \leq r_1$ as a one dimensional square potential barrier and use the result of the last section to write the transmission coefficient from the barrier as,

$$T = \frac{16\, E(V_0 - E)}{{V_0}^2} \exp\left(-\sqrt{\frac{8m}{V0}}(V_0 - E)\right)(r_1 - r_0) \qquad \text{------(3)}$$

$$V_0 = \frac{1}{4\pi\varepsilon_0} \frac{2Ze^2}{r_0} = \frac{1}{4\pi\varepsilon_0} \frac{2Ze^2}{r_1} \qquad \text{-------(4)}$$

A rigorous treatment yields the transmission coefficient to be,

$$T = \exp\left(-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2mV(r) - E}\right) dr$$

$$T = \exp\left(-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m\left(\frac{1}{4\pi\varepsilon_0} \frac{2Ze^2}{r} - E\right)}\right) dr \qquad \text{---------(5)}$$

The speed of an α-particle in a heavy nucleus has been estimated to be of the order of 10^7 ms^{-1}. Considering the nucleus's radius to be 10^{-14} m we find that the time taken by the α-particle to move once across the nucleus to be 10^{-21}. Clearly the α-particle strikes the coulomb barrier at the surface of the nucleus 10_{21} times per second. The probability that the α-particle crosses

the barrier and comes out of the nucleus per sec is,

$$P = T \times 10^{21}$$

The reciprocal of P gives the life time τ of the α-decaying nucleus, i.e.,

$$\tau = \frac{1}{P} = \frac{1}{T \times 10^{21}}$$

If λ be the disintegration constant of the nucleus we get,

$$\lambda = \frac{1}{\tau}$$

$$= T \times 10^{21}$$

$$= 10^{21} \exp\left(-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m\left(\frac{1}{4\pi\varepsilon_0} \frac{2Ze^2}{r} - E\right)}\right) dr$$

Taking its logarithm we get from the above,

$$\log \lambda = A + BE,$$

A and B Constants

which is the well-known Geiger-Nuttal law.

2.4 Block waves in a periodic potential

Consider the motion of an electron in a one-dimensional periodic potential. A one-dimensional metal crystal consisting of a number of stationary positive ions provides a periodic potential of period d. that is

$$V(x + nd) = V(x), \qquad n=0,1,2,\ldots\ldots \text{--------------(1)}$$

Consider a crystal lattice with N ions in the form of a closed loop. The Schrodinger equation at points x and (x+d) is then

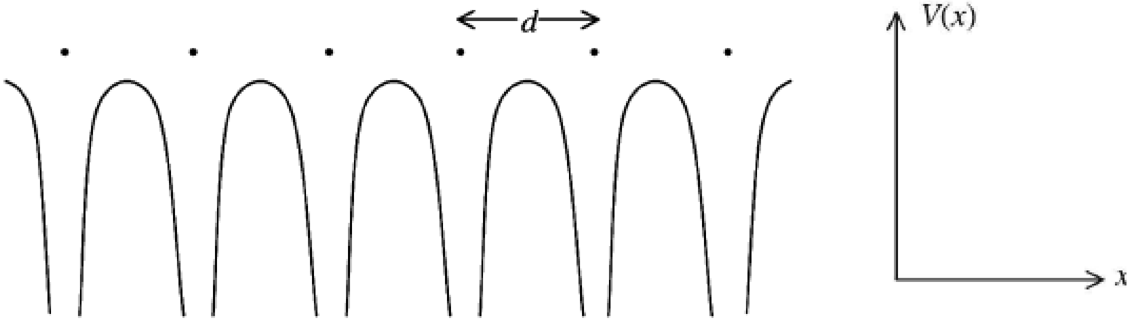


Figure 5 one-dimensional crystal lattice along with the periodic potential

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \qquad \text{------- -(2)}$$

$$\frac{d^2\psi(x+d)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x+d) = 0 \qquad \text{--------(3)}$$

Since $\psi(x)$ and $\psi(x+d)$ satisfy the same equation, the two can differ only by a multiplicative constant, say α.

$$\psi(x+d) = \alpha\,\psi(x)$$

And

$$\psi(x+Nd) = \alpha^N\,\psi(x) \qquad \text{-------(4)}$$

Since the lattice is in the form of a ring

$$\psi(x+Nd) = \alpha^N \psi(x) = \psi(x) \qquad \text{-------(5)}$$

Hence,

$$\alpha^N = 1 \text{ or } \alpha^N = \exp(2\pi i n) \qquad n = 0, 1, \ldots\ldots(N-1) \qquad \text{-------(6)}$$

Therefore,

$$\alpha = \exp(2\pi i n/N) \qquad n = 0,1,\ldots\ldots\ldots\ldots(N-1) \qquad \text{-------(7)}$$

It mean that

$$\psi(x) = e^{ikx} \; u(x) \qquad \text{------(8)}$$

Where

$$u(x+d) = u(x) \text{ and } k = \frac{2\pi n}{Nd} \qquad n = 0, \pm 1, \pm 2, \ldots\ldots \qquad \text{------(9)}$$

the justification of equation(8) can easily be done by replacing x by (x + d)

$$\psi(x+d) = e^{ik(x+d)} \; u(x+d)$$

$$= e^{ikd} \, e^{ikx} \; u(x+d)$$

$$= e^{ikd} \; \psi(x)$$

$$= \alpha \, \psi(x)$$

Which is equation(4),(8) with the condition in equation(9) is called Bloch theorem. That is the solution of schrodinger equation of a periodic potential will have the form of a plane wave modulated by a function having the periodicity of the lattice. Functions of the type as in equation(8) are sometimes referred to as Bloch function.

2.5 Kronig-Penny square-well periodic potential

In bloch theorem, we have considered a one-dimensional metal crystal consist of a number of positive ions providing a periodic potential. The approximation of the periodic potential in figure(5) is known as Kroning-Penney potential which is illustrated figure(6). The width of each well be a and that of each barrier be b. the period of the potential d = a + b. then

$$V\,[x + n(a+b)] = V(x + nd) = V(x) \qquad \text{---------(10)}$$

In the region 0 < x< a, V(x) = 0, and the Schrodinger equation takes the form

$$\frac{d^2\psi_1}{dx^2} + {k_1}^2\,\psi_1 = 0, \qquad {k_1}^2 = \frac{2m}{\hbar^2}\,E \qquad \text{-------(11)}$$

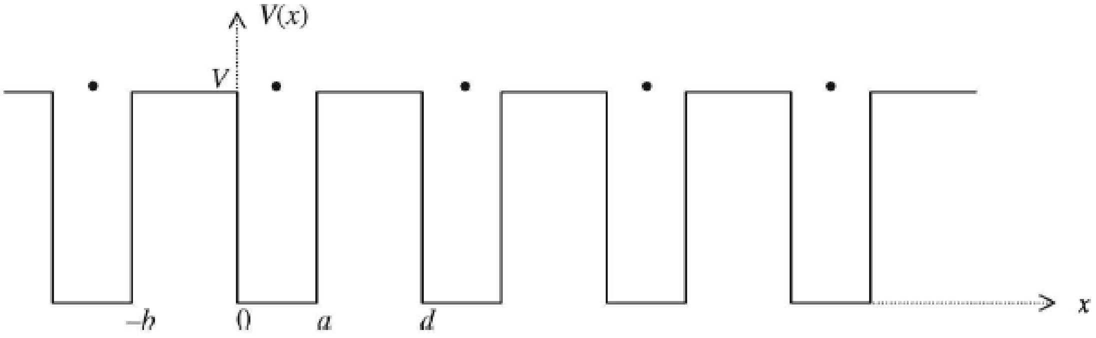


Figure 6 the Kroning-Penny periodic potential

In the region -b < x < 0, V(x) = V, then

$$\frac{d^2\psi_2}{dx^2} - {k_2}^2\,\psi_2 = 0,$$

$${k_2}^2 = \frac{2m}{\hbar^2}\,E \qquad , V>E \qquad \text{-------(12)}$$

According to Bloch theorem, the solution of equation (11) and (12) must be of the type

$$\psi_1 = e^{ikx}\;u_1(x) \qquad 0 < x < a \qquad \text{----------(13)}$$

$$\psi_2 = e^{ikx}\;u_2(x) \qquad -b < x < a \qquad \text{----------(14)}$$

Substituting of equation(13) in (11) and equation(14) in (12) gives

$$\frac{d^2u_1}{dx^2} + 2ik\,\frac{du_1}{dx} + ({k_1}^2 - k^2)\,u_1(x) = 0 \qquad \text{------- (15)}$$

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (k_2{}^2 - k^2)\, u_2(x) = 0 \qquad \text{------- (16)}$$

Equation (15) let us assume a solution of the form

$$u_1(x) = e^{mx} \qquad \text{-------(17)}$$

with this value of $u_1(x)$ equation(15) reduces to

$$m^2 + 2ikm + (k_1{}^2 - k^2) = 0, \quad 0 < x < a \qquad \text{------- (18)}$$

$$m = i\,(k_1 - k), \quad -i(k_1 + k)$$

hence the solution of equation(15) is

$$u_1(x) = A \exp[i(k_1 - k)x] + B \exp[-i(k_1 + k)x]\,, \quad 0 < x < a \qquad \text{------(19)}$$

in the same way

$$u_2(x) = A \exp[i(k_2 - k)x] + B \exp[-i(k_2 + k)x]\,, \quad -b < x < 0 \qquad \text{------(20)}$$

The wave function and their derivatives must be continuous at x = 0.

That is

$$u_1(x)\,|_{x=0} = u_2(x)\,|_{x=0} \text{ and}$$

$$\frac{du_1}{dx}\,|_{x=0} = \frac{du_2}{dx}\,|_{x=0} \qquad \text{-----(21)}$$

These conditions give

$$A + B = C + D \qquad \text{---------(22)}$$

$$i(k_1 - k) A - i(k_1 + k)B = C (k_2 - ik) - D(k_2 + k) \qquad \text{-------(23)}$$

As the potential is periodic, the value of the wave function at x = a must be equal to that at x = -b. hence,

$$u_1(x)\,|_{x=a} = u_2(x)\,|_{x=a} \text{ and}$$

$$\frac{du_1}{dx}\,|_{x=a} = \frac{du_2}{dx}\,|_{x=a} \qquad \text{-----(21)}$$

With the conditions in equation(16) and (17) we have

$$A \exp[i(k_1 - k)x] + B \exp[-i(k_1 + k)x] = (k_2 - ik)\, C \exp[-(k_2 - ik)b]$$

$$-(k_2 + ik)\, D \exp[(k_2 + ik)x] \quad \text{--------(22)}$$

And

$$i(k_1 - k) A \exp[i(k_1 - k)a] - i(k_1 + k) B \exp[-i(k_1 + k)a] = (k_2 - ik)\, C \exp[-(k_2 - ik)b] -(k_2$$

$$+ ik)\, D \exp[(k_2 + ik)x] \quad \text{----------(23)}$$

for nontrivial solution of equation (19) and (22,23),, the determinants of the coefficients of A, B, C and D should vanish. This gives the relation

$$\frac{{k_2}^2 - {k_1}^2}{2k_1\, k_2} \sinh(k_2 b) \sin(k_1 b) + \cosh(k_2 b) \cos(k_1 a) = \cos(kd) \quad \text{-----(24)}$$

As k_1 and k_2 are function of energy the left side is a function of energy.

The transcendental equation (24) can be solved graphically. For that, the left side of equation (24) is plotted as a function of E / V (continuous curve) and the limiting lines of $\cos(kd) = \pm 1$(broken lines) are also drawn. The energy ranges for which cos(kd) is between -1 and +1 are the allowed ones.

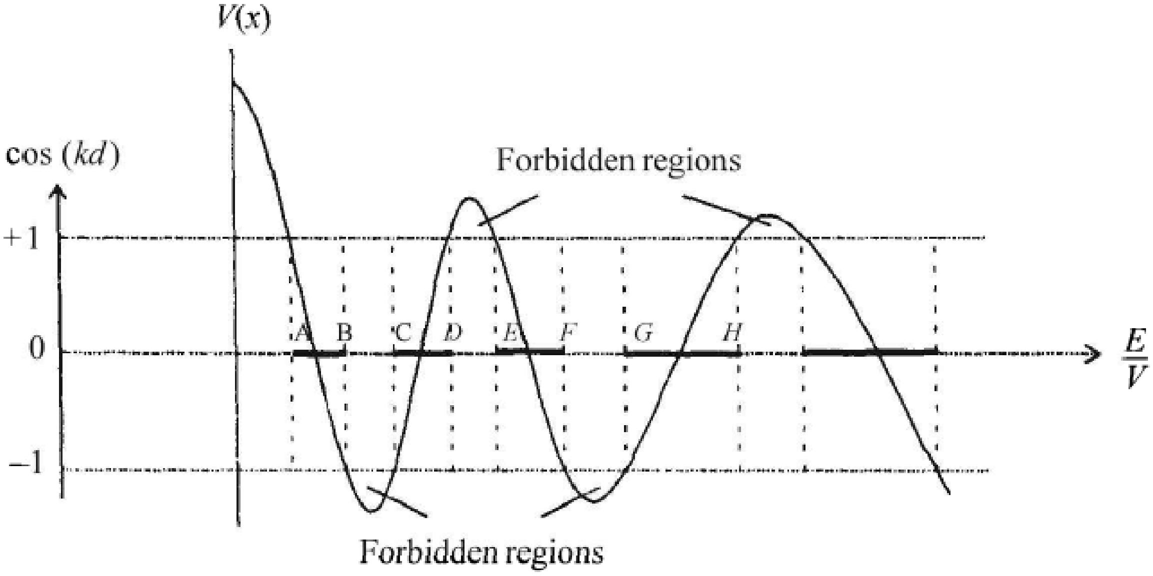


Figure 7 graphical evaluation of energy values in the Kronig-Penney model

2.6 Linear harmonic oscillator:

Operator method

The energy eigen value equation,

$$\widehat{H}\,\psi = \mathrm{E}\,\psi$$

One of the fundamental features of quantum mechanics is that operators $\hat{x} = x$ and $\hat{p}$ satisfy the commutation relation,

$$[\hat{x},\ \hat{p}\,] = i\hbar \qquad \text{-----------(1)}$$

In the following, we use this method to solve the energy eigen value problem for linear harmonic oscillator. As we shall see, the method allows us to find, with simplicity not only the expectation values of various physical quantities for the oscillator but also the energy eigen functions of the oscillator.

The Hamiltonian operator of a harmonic oscillator of mass *m* oscillating along the

x-axis under a force constant *k* is,

$$\widehat{H} = \frac{\widehat{p^2}}{2m} + \frac{1}{2}\,\mathrm{k}\,x^2 \qquad \text{------(2)}$$

Let us introduce two operators $\hat{a}$ and $\widehat{a^{\dagger}}$ according to,

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\,\mathrm{x} + \mathrm{i}\sqrt{\frac{1}{2m\omega_0\hbar}}\;\hat{p} \qquad \text{-----------(3)}$$

$$\widehat{a^{\dagger}} = \sqrt{\frac{m\omega_0}{2\hbar}}\,\mathrm{x} - \mathrm{i}\sqrt{\frac{1}{2m\omega_0\hbar}}\;\hat{p} \qquad \text{--------(4)}$$

In the above is $\widehat{a^{\dagger}}$ the Hermitian adjoint of $\hat{a}$ and ω_0 is the natural angular frequency of the oscillator. From Equations (3) and (4) we obtain

$$\hat{a}\;\widehat{a^{\dagger}} = \left(\sqrt{\frac{m\omega_0}{2\hbar}}\,\mathrm{x} + \mathrm{i}\sqrt{\frac{1}{2m\omega_0\hbar}}\;\hat{p}\right)\left(\sqrt{\frac{m\omega_0}{2\hbar}}\,\mathrm{x} - \mathrm{i}\sqrt{\frac{1}{2m\omega_0\hbar}}\;\hat{p}\right)$$

$$= \frac{m\omega_0}{2\hbar}\,x^2 + \frac{1}{2m\omega_0\hbar}\,\widehat{p^2} + \frac{i}{2\hbar}\,(\,\hat{p}\,x - x\,\hat{p})$$

Using Equation (1) in the above we obtain

$$\hat{a}\ \ \widehat{a^\dagger} = \frac{m\omega_0}{2\hbar}\, x^2 + \frac{1}{2m\omega_0\hbar}\,\widehat{p^2} + \frac{i}{2\hbar}\,(\text{-i}\,\hbar)$$

$$= \frac{1}{\omega_0\hbar}\left[\frac{\widehat{p^2}}{2m} + \frac{1}{2}m\omega_0\, x^2\right] + \frac{1}{2}$$

$$= \frac{\hat{H}}{\omega_0\hbar} + \frac{1}{2} \qquad \text{-----------(5)}$$

Similarly, we obtain

$$\widehat{a^\dagger}\ \ \hat{a} = \frac{\hat{H}}{\omega_0\hbar} - \frac{1}{2} \qquad \text{---------(6)}$$

Adding Equations (5) and (6) we obtain

$$2\ \ \frac{\hat{H}}{\omega_0\hbar} = \hat{a}\ \ \widehat{a^\dagger} + \widehat{a^\dagger}\ \ \hat{a}$$

$$\hat{H} = \frac{1}{2}\,\omega_0\hbar\,(\,\hat{a}\ \ \widehat{a^\dagger} + \widehat{a^\dagger}\ \ \hat{a}\ \,) \qquad \text{-------(7)}$$

Subtracting Equation (6) from Equation (5) we get

$$\hat{a}\ \ \widehat{a^\dagger} - \widehat{a^\dagger}\ \ \hat{a} = 1$$

Clearly, the operators $\hat{a}$ and $\widehat{a^\dagger}$ satisfy the commutation relation,

$$[\hat{a}\,,\widehat{a^\dagger}] = 1 \qquad \text{---------(8)}$$

We may also express the Hamiltonian operator $\hat{H}$as

$$\hat{H} = \omega_0\hbar\,(\,\widehat{a^\dagger}\ \ \hat{a} + \frac{1}{2}) \qquad \text{--------(9)}$$

2.7 Particle moving in a spherically symmetric potential

In spherically symmetric problem, the potential depends only on the distance of the particle from a fixed point. The time independent Schrodinger equation for such a system is

$$\nabla^2\,\Psi(\mathrm{r}) + \frac{2m}{\hbar^2}\,(\,\mathrm{E} - \mathrm{V}\,)\,\Psi(\mathrm{r}) = 0 \qquad \text{------(1)}$$

Since the potential is spherically symmetric, it is convenient to work in spherical polar coordinate, r, θ , φ $(0 \leq r \leq \infty, 0 \leq \theta \leq \pi, 0 \leq \varphi \leq 2\pi)$. Expressing equation (1) in polar coordinates, we get

$$\frac{1}{r^2}\ \frac{\partial}{\partial r}(r^2\ \frac{\partial\Psi}{\partial r}) + \frac{1}{r^2\ sin\theta}\ \ \frac{\partial}{\partial\theta}(sin\theta\ \frac{\partial\Psi}{\partial\theta})\ + \frac{1}{r^2\ sin2\theta}\frac{\partial^2\Psi}{\partial\varphi^2} + \frac{2m}{\hbar^2}\ (\mathrm{E} - \mathrm{V})\ \Psi = 0 \qquad \text{-------(2)}$$

Separation of the equation

Equation (2) can be separated into three equations by writing

$$\Psi\ (\mathrm{r}, \theta, \varphi) = \mathrm{R(r)}\ \theta(\theta)\ \emptyset(\ \varphi) \qquad \text{------(3)}$$

Substituting this for of Ψ in equation (2) and multiplying by

$$\frac{sin^2\theta}{R}\ \frac{\partial}{\partial r}(r^2\ \frac{\partial R}{\partial r}) + \frac{sin\theta}{\emptyset}\ \ \frac{\partial}{\partial\theta}(sin\theta\ \frac{\partial\varphi}{\partial\theta})\ + \frac{2m}{\hbar^2}\ (\ \mathrm{E} - \mathrm{V(r)}\ )\ r^2\ sin^2\theta = -\ \frac{1}{\emptyset}\frac{\partial^2\emptyset}{\partial\varphi^2} \qquad \text{--------(4)}$$

The left hand side of above equation is function of r and θ and the right side is a function of φ alone. This is possible when each side is a constant, say m^2. Then

$$\frac{d^2\emptyset(\varphi\ )}{\partial\varphi^2} = -\ m^2\ \emptyset(\ \varphi) \qquad \text{------(5)}$$

And

$$\frac{sin^2\theta}{R}\ \frac{\partial}{\partial r}(r^2\ \frac{\partial R}{\partial r}) + \frac{sin\theta}{\emptyset}\ \ \frac{\partial}{\partial\theta}(sin\theta\ \frac{\partial\varphi}{\partial\theta})\ + \frac{2m}{\hbar^2}\ (\ \mathrm{E} - \mathrm{V(r)}\ )\ r^2\ sin^2\theta = \mathrm{m}^2 \qquad \text{-------- (6)}$$

Dividing both sides of equation (6) by $sin^2\theta$ and rearranging, we get

$$\frac{1}{R}\ \frac{\partial}{\partial r}(r^2\ \frac{\partial R}{\partial r}) + + \frac{2m}{\hbar^2}\ (\ \mathrm{E} - \mathrm{V}\ )\ r^2\ = \frac{1}{\emptyset sin\theta}\ \ \frac{d}{d\theta}(sin\theta\ \frac{\partial\varphi}{\partial\theta})\ + \frac{m^2}{sin\ ^2\ \theta}$$

This is possible when both sides are equal to a constant, say λ consequently, we get the θ equation and the radial equation:

$$\frac{1}{sin\theta}\ \ \frac{d}{d\theta}(sin\theta\ \frac{\partial\varphi}{\partial\theta})\ +\ (\lambda\ -\ \frac{m^2}{sin\ ^2\ \theta})\ \ \varphi\ =\ 0 \qquad \text{--------(7)}$$

And

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\ \frac{\partial R}{\partial r}) + \frac{2m}{\hbar^2}\ (\ \mathrm{E} - \mathrm{V(r)}\ )\mathrm{R}\ -\ \frac{\lambda}{r^2}\ \mathrm{R}\ =\ 0 \qquad \text{-------(8)}$$

Thus the three-dimensional wave equation (2) is separated into three one-dimensional equations (5), (7) and (8).

Solution of φ equation

The solution of equation (5) is straightforward and is given by

$$\emptyset(\ ) = \mathrm{A}\ e^{\pm im\varphi}$$

For $\emptyset$ to be single valued,

$$\emptyset(\varphi) = \emptyset(\varphi + 2\pi).$$

Therefore,

$$\mathrm{A}\, e^{\pm im\varphi} = \mathrm{A}\, e^{\pm im(\varphi+2\pi)} \qquad \text{or}$$

$$e^{\pm im2\pi} = 1$$

This is possible only if m = 0,1,2,…. The quantum number m is called the magnetic quantum number. The normalization condition gives,

$$1 = \int_0^{2\pi} \varphi^* \varphi \, d\varphi = |\mathrm{A}|^2 \int_0^{2\pi} d\varphi$$

Then

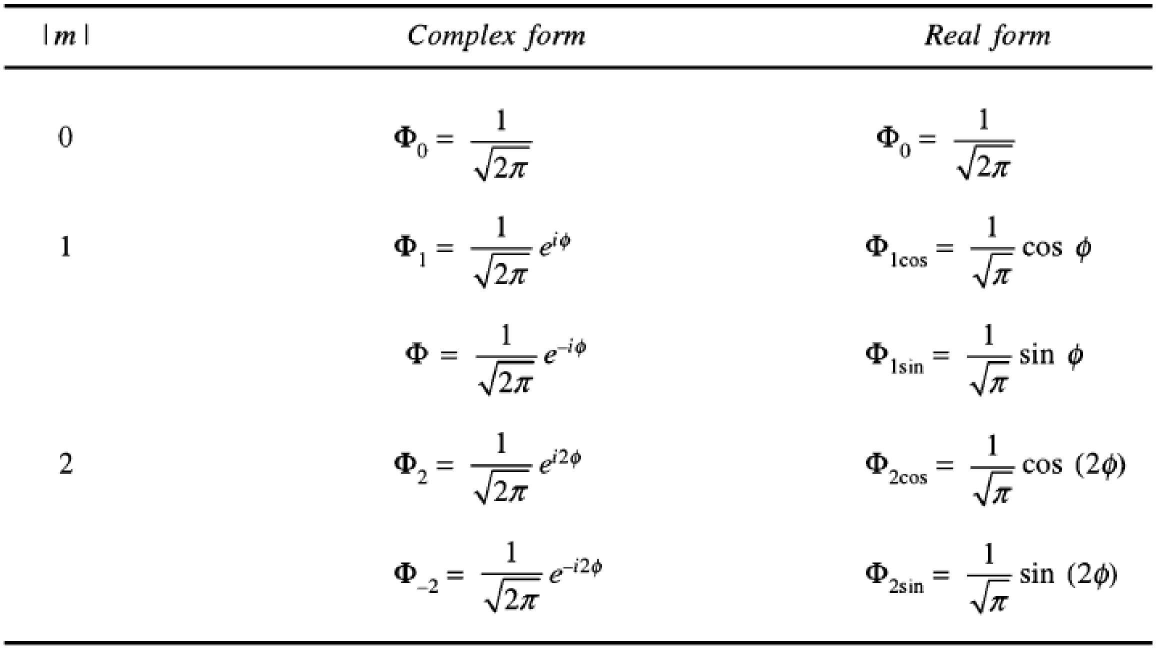
$$|\mathrm{A}|^2 \, 2\pi = 1 \quad \text{or} \quad \mathrm{A} = \frac{1}{\sqrt{2\pi}}$$

Except for an arbitrary phase factor which can be taken as zero. The normalized solution is then

$$\emptyset = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \qquad m = 0, \pm 1, \pm 2, \ldots.. \qquad \text{------ (9)}$$

Some of the normalized $\emptyset(\varphi)$ are given in below table. As sin (|m| φ) and cos (|m| φ) are also solutions of equation (5) the real form of the solutions are also listed in table.

Table 1 few- normalized functions



$\lvert m \rvert$	*Complex form*	*Real form*
0	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$
1	$\Phi_1 = \frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\Phi_{1\cos} = \frac{1}{\sqrt{\pi}} \cos\ \phi$
	$\Phi = \frac{1}{\sqrt{2\pi}} e^{-i\phi}$	$\Phi_{1\sin} = \frac{1}{\sqrt{\pi}} \sin\ \phi$
2	$\Phi_2 = \frac{1}{\sqrt{2\pi}} e^{i2\phi}$	$\Phi_{2\cos} = \frac{1}{\sqrt{\pi}} \cos\ (2\phi)$
	$\Phi_{-2} = \frac{1}{\sqrt{2\pi}} e^{-i2\phi}$	$\Phi_{2\sin} = \frac{1}{\sqrt{\pi}} \sin\ (2\phi)$

Solution of the θ equation

To solve the θ equation, a new variable z = cos θ is introduced. On differentiating we get

$$dz = -\sin\theta\ d\theta$$

we may also write

$$\frac{d}{d\theta} = -\sin\theta \frac{d}{dz} = -\ (1-z^2)^{1/2} \frac{d}{dz}$$

In terms of z, equation (7) is

$$\frac{d}{dz}\left[\ (1 - z^2)\ \frac{\partial\varphi(z)}{\partial\theta}\right) + \left(\lambda - \frac{m^2}{(1-z^2)}\right)\ \varphi(z) = 0 \qquad \text{--------(10)}$$

Which is associated Legendre equation. Equation (10) has poles at z = $\pm$ 1. For physically acceptable solution,

$$\lambda = l\,(l+1) \qquad l = 0,1,2\ldots\ldots \qquad M = 0, \pm1, \pm2, \ldots..$$

The solution of equation(10) is Legendre polynomial $P_l(z)$ for m=0, and the associated Legendre polynomials $P_l^{|m|}(z)$ for m$\neq$ 0. The normalized solution is then

$$\varphi(\theta) = N_{lm} P_l^{|m|}(z) \qquad \text{--------- (11)}$$

Where N_{lm} is the normalization constant. The normalization condition is

$$| N_{lm} |^2 \int_{-1}^{+1} P_k^{|m|}(z)\, P_l^{|m|}(z)\, dz = 1$$

The orthogonality relation for associated Legendre polynomials

$$\int_{-1}^{+1} P_k^{|m|}(z)\, P_l^{|m|}(z)\, dz = \frac{2(l+|m|)!}{(2l+1)(l+|m|)!}\, \delta_{lk} \qquad \text{-------(12)}$$

Leads to

$$\emptyset_l^m(\theta) = \varepsilon \sqrt{\frac{(2l+1)(l+|m|)!}{2(l+|m|)!}}\, P_l^m (\cos\theta) \qquad \text{------(13)}$$

Where $\varepsilon = (-1)^m$ for $m > 0$ and

$\varepsilon = 1$ for $m \leq 0$ as per the established phase convention.

2.8 System of two interacting particles

Consider the motion of a particle in a potential field. However, there are situations wherein we have two interacting particles moving in a three-dimensional space. The wave equation of such a system can be reduced into two one-particle equations, one representing the translational motion of the center of mass and the other the relative motion of the two particles.

Hamiltonian operator

The position vectors and masses of the two particles are shown in figure. The radius vector of the center of mass

$$R = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \qquad \text{-------(1)}$$

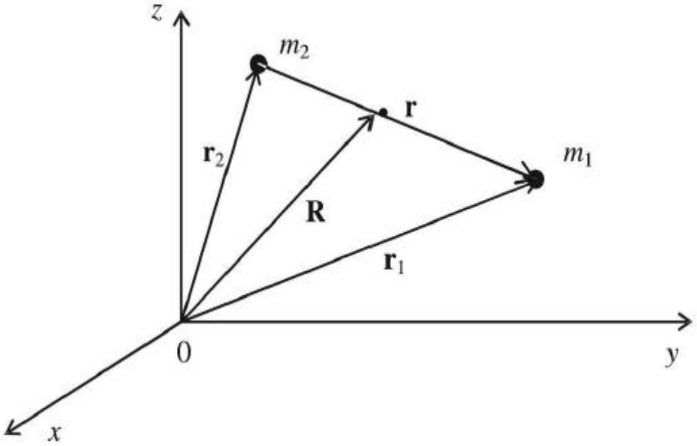


Figure 8 System of two interacting particles

The relative position vector is given by

$$r = r_1 - r_2 \qquad \text{------------(2)}$$

from equation(1) and (2) we have

$$r_1 = R + \frac{m_2\, r}{m_1 + m_2}$$

$$r_2 = R - \frac{m_1\, r}{m_1 + m_2} \qquad \text{--------(3)}$$

The momenta of the two particles can be written as

$$p_1 = m_1\, \dot{r_1} = m_1\, \dot{R} + \mu\, \dot{r_1}$$

$$p_2 = m_2\, \dot{r_2} = m_2\, \dot{R} + \mu\, \dot{r_2} \qquad \text{--------(4)}$$

where

$$\mu = \frac{m_1\, m_{12}}{m_1 + m_2} \qquad \text{---------(5)}$$

Is called the reduced mass of the particles. Assuming the potential to be dependent only on the distance between the two particles, the Hamiltonian of the system is

$$H = \frac{{p_1}^2}{2m_1} + \frac{{p_2}^2}{2m_2} + V(r) \qquad \text{--------(6)}$$

Substitute the value of p_1 and p_2

$$H = \frac{1}{2}(m_1 + m_2)\, \dot{R} + \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \mu^2 \dot{r}^2 + V(r)$$

$$= \frac{1}{2M} {p_R}^2 + \frac{1}{2\mu} {p_r}^2 + V(r) \qquad \text{------(7)}$$

Where M $= m_1 + m_2$ = M $\dot{R}$ and $p_r = \mu$ r. replacing the dynamical variables by the corresponding operators and writing

$${\nabla_R}^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \text{ and}$$

$${\nabla_r}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{------(8)}$$

$$H = -\frac{\hbar^2}{2M} {\nabla_R}^2 - \frac{\hbar^2}{2\mu} {\nabla_r}^2 + V(r) \qquad \text{--------(9)}$$

The time-independent Schrodinger equation is then

$$\left[-\frac{\hbar^2}{2M} {\nabla_R}^2 - \frac{\hbar^2}{2\mu} {\nabla_r}^2 + V(r)\right] \psi_T(R,r) = E_T\; \psi_T(R,r) \qquad \text{---------(10)}$$

Wave equation for Relative motion

Equation (10) can be separated into two equations by writing

$$\psi_T(\mathrm{R,r}) = \chi(\mathrm{R})\, \psi(\mathrm{R}) \qquad \text{-----------(11)}$$

With this for of ψ_T(R,r) , equation(10) reduces to

$$-\frac{\hbar^2}{2M} \nabla_R{}^2 \chi(\mathrm{R}) = \frac{\hbar^2}{2\mu} \frac{1}{\psi(\mathrm{r})} \nabla_r{}^2 \psi(\mathrm{r}) + E_T - V \qquad \text{-----------(12)}$$

For the validity of equation (12) each side must be equal to constant, say E_t,

$$-\frac{\hbar^2}{2M} \nabla_R{}^2 \chi(\mathrm{R}) = E_t\, \chi(\mathrm{R}) \qquad \text{--------(13)}$$

And

$$-\frac{\hbar^2}{2\mu} \nabla_r{}^2 \psi(\mathrm{r}) + V(\mathrm{r})\, \psi(\mathrm{r}) = (E_T - E_t)\, \psi(\mathrm{r}) \qquad \text{---------(14)}$$

As equation (13) is the same as a free-particles equation of mass M, it describes the translational motion of the system in space. Equation (14) is the same as the Schrodinger equation of a particle of mass μ moving in a fields of potential V(r) and represents the relatives motion of the two particles. The energy for the relative is

$$E_T - E_t = E.$$

In the coordinate system in which the center of mass is at rest, $E_t = 0$ and then E is the total energy of the system. Thus, the Schrodinger equation for relative motion is,

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(\mathrm{r}) + V(\mathrm{r})\, \psi(\mathrm{r}) = E\, \psi(\mathrm{r})$$

2.9 Hydrogen atom

Theory of hydrogen atom is of fundamental importance as it provides the basis for the theory of many electron systems. Also, this is the only atom for which exact solution of the Schrodinger equation is possible. Consider hydrogen like atom which consists of a nucleus of chare Ze and an electron of charge -e separated by a distance r. The potential is Coulombic and is given by

$$V(\mathrm{r}) = -\frac{kZe^2}{r} \qquad \text{-------(1)}$$

The time-independent Schrodinger equation for relative motion is given by

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{kZe^2}{r}\right) \psi(\mathrm{r}) = E\, \psi(\mathrm{r}) \qquad \text{------(2)}$$

Radial equation

Expressing equation (2) in spherical polar coordinates(r,θ, φ) and separating the variables

$$\Psi\,(r, \theta, \varphi) = R(r)\,\theta(\theta)\,\emptyset(\varphi) \qquad \text{------(3)}$$

We get the radial equation

$$\frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial \Psi}{\partial r}\right) + \left[\,E - \frac{l(l+1)\hbar^2}{2I} + \frac{kZe^2}{r}\,\right] R = 0 \qquad \text{------(4)}$$

the solution of the angular part is the spherical harmonics, $Y_{lm}\,(\theta, \varphi)$.

To solve equation(4) let us introduce a variable ρ and a constant λ defined by

$$\rho = \sqrt{\frac{-8\mu E}{\hbar^2}}\,r, \qquad \lambda = \frac{kZe^2}{\hbar^2}\sqrt{\frac{\mu}{-2E}} \qquad \text{---------(5)}$$

As E negative for bound states, ρ and a constant λ are real quantities. In terms of the new variables equation(3) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\,-\frac{1}{4} - \frac{l(l+1)}{\rho^2}\right] R = 0 \qquad \text{----------(6)}$$

Solution of radial equation

Its asymptotic solution can be investigated first. When $\rho \rightarrow \infty$, equation(6) reduces to

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}\,R = 0$$

Its solutions are

$$R = e^{-\rho/2} \text{ and } \rho/2$$

Out of these two solutions, only $e^{-\rho/2}$ is acceptable since $e^{-\rho/2} \rightarrow \infty$. The exact solution of equation(6) be

$$R(\rho) = e^{-\rho/2}\,F(\rho) \qquad \text{-------------(7)}$$

Substitution of equation(7) in equation(6) gives the differential equation satisfies by F(ρ) as

$$\rho^2\frac{d^2F}{d\rho^2} + \rho\,(2 - \rho)\frac{dF}{d\rho} + [\,\rho\,\lambda - l(l+1) - \rho\,]\,F(\rho) = 0 \qquad \text{---------(8)}$$

When $\rho = 0$, we get

l(l+1) F(0) = 0 or

F(0) = 0, $\quad l \neq 0 \quad$ -----------(9)

Therefore if we try a power series solution for F(ρ) it must not contain a constant term. Hence,

$$F(\rho) = \sum_{k=0}^{\infty} a_k\,\rho^{c+k} \qquad \text{---------(10)}$$

With this value of F(ρ) equation(8) reduces to

$\sum_{k=0}^{\infty} a_k\,(\lambda - 1 - c - k)\rho^{c+k+1} \; + \; \sum_{k=0}^{\infty} a_k (c^2 + 2ck + k^2 + c + k - l^2 - l)\rho^{c+k} \; = \; 0$ --(11)

Equation(11) is valid for all values of ρ only if the coefficient of each power of ρ vanishes separately. Equating the coefficient of ρ^c to zero, we have

$$a_0(c^2 + c - l^2 - l) = 0$$

Or

$$c^2 + c - l^2 - l = 0 \qquad (\text{as } a_0 \neq 0)$$

$$(c-l)(c+l+1) = 0$$

therefore ,

$$c = l, \quad c = -(l+1) \qquad \text{------(12)}$$

if , c = -(l + 1) the first term in F(ρ) would be a_0 / ρ^{l+1} which tends to infinity as $\rho \to 0$. Hence, c = l is the only acceptable value. Setting the coefficient of ρ^{l+k+1} in equation(11) to zero, we obtain

$$a_{k+1} = \frac{(l+k+1-\lambda)}{(k+1)(k+2l+2)} \qquad \text{---------(13)}$$

This recursion relation allows us to determine the coefficients a_1, a_2, a_3,…. In terms of a_0 which is quite arbitrary. For large values of k, we get from equation (13)

$$\frac{a_{k+1}}{a_k} = \frac{1}{k}$$

In the expansion

$$e^{\rho} = \sum_{k=0}^{\infty} \frac{1}{k!}\rho^k = \sum_{k=0}^{\infty} A_k\,\rho^k$$

$$\frac{A_{k+1}}{A_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1} \xrightarrow[k\to\infty]{} \frac{1}{k}$$

Hence, as k → ∞, the series for F(ρ) behaves like $\rho^l\, e^{\rho/2}$ and

$$R(\rho) = e^{-\rho/2}\rho^l\, e^{\rho/2}$$

This value of R(ρ) is not aceptable and therefore the series must break off after a certain value of k, say n’. then equation(13)

$$l + n' + 1 - \lambda = 0, \qquad n' = 0,1,2,\ldots \qquad \text{--------(14)}$$

Energy eigen values

Defining a new quantum number n by

$$N = l + n' + 1 = \lambda = \frac{kZe^2}{\hbar^2}\sqrt{\frac{\mu}{-2E}}$$

Squaring and simplifying

$$E_n = \frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2\, 2\hbar^2 n^2}$$

$$= -\frac{\mu Z^2 e^4}{32\epsilon_0\,\pi^2\,\hbar^2 n^2}, \qquad n = 1,2,3\ldots.. \qquad \text{-------(15)}$$

Since n’ and l are integers including zero.

$$n = 1,2,\ldots.. \qquad \text{----------(16)}$$

as n ≥ l + 1, the highest possible value of l is n – 1. Thus

$$l = 0,1,2,\ldots\ldots(n-1) \qquad \text{--------(17)}$$

The new quantum number n is called the principal quantum number which determines the energy.

Radial wave functions

The above restriction in energy makes the series for

$$F(\rho) = \rho^l\, L(\rho) \qquad \text{------------(18)}$$

Equation(8) reduces to

$$\rho\frac{d^2L(\rho)}{d\rho^2} + (2l+2-\rho)\frac{dL(\rho)}{d\rho} + (n-l-1)\,L(\rho) = 0 \qquad \text{------(19)}$$

The associate Laguerre polynomial of order p and degree (q - p), denoted as $L_q^p(\rho)$, satisfies the equation

$$\rho\frac{d^2L_q^p(\rho)}{d\rho^2} + (p+1-\rho)\frac{dL_q^p(\rho)}{d\rho} + (q-p)\,L_q^p(\rho) = 0 \qquad \text{------(20)}$$

Equation (19) and (20) are identical if L(ρ) is taken as $L_{n+l}^{2l+1}(\rho)$. hence

$$R_{nl}(r) = N\, e^{-\rho/2}\rho^l\, L_{n+l}^{2l+1}(\rho) \qquad \text{----------(21)}$$

The normalization integral

$$\int_0^\infty R_{nl}^2(r) r^2\, dr = 1$$

Allows the determination of the constant N. hence

$$\frac{n^3\hbar^6}{8\mu^3\, Z^3\, k^3\, e^6}\,|N|^2\,\frac{2n[(n+l)!]^3}{(n-l-1)!} \;=\; 1$$

Or

$$|N| \;=\; \pm\,\{(\frac{2Z\mu k e^2}{n\hbar^2})\;\frac{(n-l-1)!}{2n[(n+l)!]^3}\}^{1/2} \qquad \text{-----------(22)}$$

Thus, the normalized radial wave functions are

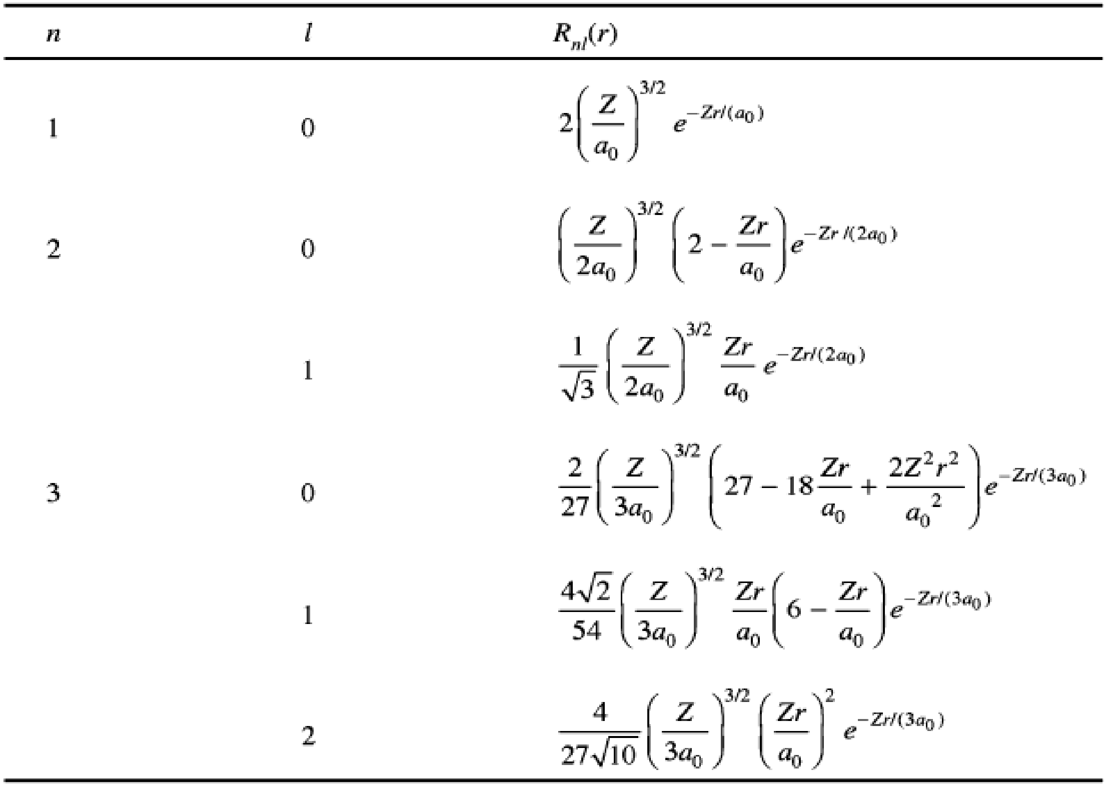
$$R_{nl}\,(r) \;=\; -\,\{(\frac{2Z}{na_H})^3\;\frac{(n-l-1)!}{2n[(n+l)!]^3}\}^{1/2}\, e^{-\rho/2}\rho^l\, L_{n+l}^{2l+1}(\rho) \qquad \text{--------(23)}$$

Where

$$a_H \;= \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \qquad \text{--------(24)}$$

The negative sign is selected to make R_{10} positive. As μ is approximately equal to the electron mass, $a_H \;=\; a_0$ the Bohr radius. Some of the radial wave function are given in the table. It may be noted that at the origin the wave functions R_{10}, R_{20}, R_{30} are finite whereas R_{21}, R_{31}, R_{32} are zero.

Table 2 the first-six radial wave functions of a Hydrogen-like atom



n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/(a_0)}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/(2a_0)}$
	1	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}\, e^{-Zr/(2a_0)}$
3	0	$\frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+\frac{2Z^2r^2}{a_0{}^2}\right)e^{-Zr/(3a_0)}$
	1	$\frac{4\sqrt{2}}{54}\left(\frac{Z}{3a_0}\right)^{3/2}\frac{Zr}{a_0}\left(6-\frac{Zr}{a_0}\right)e^{-Zr/(3a_0)}$
	2	$\frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/(3a_0)}$

2.10 Rigid rotator

A rigid rotator consists of two masses m_1 and m_2 separated by a fixed distance r. consider the rotation of the system about an axis passing through the center of mass and perpendicular to the plane containing the two masses. For free rotation, the potential V(r) = 0. As r is fixed, the wave function will depend only on the angles θ and φ. In spherical polar coordinates, the Schrodinger equation for relative motion reduces to

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2\,sin\theta}\,\frac{\partial}{\partial\theta}(sin\theta\,\frac{\partial}{\partial\theta}) + \frac{1}{r^2\,sin2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]\psi(\theta,\varphi) = E\,\psi(\theta,\varphi) \qquad \text{-------(1)}$$

Or

$$\frac{1}{sin\theta}\,\frac{d}{d\theta}(sin\theta\,\frac{\partial}{\partial\theta}) + \frac{1}{sin^2\theta}\,\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2\mu r^2 E}{\hbar^2}\,\psi(\theta,\varphi) = 0 \qquad \text{---------(2)}$$

Writing

$$\frac{2\mu r^2 E}{\hbar^2} = \frac{2IE}{\hbar^2} = \lambda \qquad \text{--------(3)}$$

And

$$\psi(\theta,\varphi) = \vartheta(\theta)\emptyset(\varphi) \qquad \text{---------(4)}$$

Equation(2) reduces to the following two equations:

$$\frac{d^2\emptyset(\varphi)}{d\varphi^2} = -m^2\,\emptyset(\varphi) \qquad \text{----------(5)}$$

And

$$\frac{1}{sin\theta}\,\frac{d}{d\theta}(sin\theta\,\frac{\partial\emptyset}{\partial\theta}) + (\lambda - \frac{m^2}{sin^2\theta})\,\vartheta(\theta) = 0 \qquad \text{--------(6)}$$

Where I = μr^2 is the moment of inertia of the rotator and m^2 is a constant. Hence, the rigid rotator wave functions are the spherical harmonics $Y_{lm}(\theta, \varphi)$. From the solution, it follows that $\lambda = l(l+1)$. From equation(3) the energy eigenvalues are

$$E_l = \frac{l(l+1)\hbar^2}{2I} \qquad l = 0,1,2,\ldots. \qquad (7)$$

This constitutes a set of quantized energy levels with $\frac{l(l+1)\hbar^2}{2I}$ separation between any two consecutive levels. (l is the quantum number of the lower state). Since (2l+1) values of m are possible for a given value of l, each state is (2l+1) – fold degenerate.

UNIT III:

GENERALFORMALISM

Dirac notation – Equations of motions – Schrodinger representation - Heisenberg representation – Interaction representation – Coordinate representation – Momentum representation – Symmetries and conservation laws – Unitary transformation – Parity and time reversal

3.1 DIRAC'S BRA KET VECTORS

In Dirac's formulation, quantum mechanics is developed without using any specific representation and instead it uses the concept of vectors in a space that may have a finite or an infinite dimension.

Wavefunction as Vector; Ket Vector

With each state of a dynamical system is associated a ket vector. A general ket is denoted by the symbol $| >$. The ket vectors with labels inside such as $|a>$, $|b>$, etc., designate particular states. The state ket is postulated to contain complete information about the physical state. The ket vector space is a linear vector space by which we mean that if C_1 and C_2 are two complex numbers and $|a>$ and $|b>$ are two ket vectors in a given space, the linear combination,

$$|a> = C_1 |a> + C_2 |b>$$

is also a ket vector in the space of $|a>$ and $|b>$ and represents a state of the system.

Scalar Product, Bra Vector

With each ket $|a>$, a complex number f is associated. The set of numbers associated with different $|a>$'s is a linear function of $|a>$. This means that the number associated with $(|a_1> + |a_2>)$, where $|a_1>$ and $|a_2>$ are two kets, is the sum of the numbers associated with $|a_1>$ and $|a_2>$ separately. Similarly, the number associated with $C|a>$, where C is a complex number, is C times the number associated with $|a>$. The above results may be written as,

$$f(|a_1> + |a_2>) = f(|a_1>) + f(|a_2>)$$

$$f\,(C\,|a>) = C\,f\ \ |\,a>$$

The number *f* associated with all the kets in ket space may be visualized as defining a vector in another space (dual space) denoted, following Dirac, by the symbol <*f* │ . and called the *bra* vector.

3.2 Schrodinger representation

In physics, the Schrödinger picture, also termed as the Schrödinger representation is a formulation of quantum mechanics in which the state vectors evolve in time, but the operators (observables and others) are constant with respect to time. This differs from the Heisenberg picture which keeps the states constant while the observables evolve in time, and from the interaction picture in which both the states and the observables evolve in time. The Schrödinger and Heisenberg pictures are related as active and passive transformations and commutation relations between operators are preserved in the passage between the two pictures.

In the Schrödinger picture, the state of a system evolves with time. The evolution for a closed quantum system is brought about by a unitary operator, the time evolution operator.

For time evolution from a state vector $|\psi(t_0)\rangle$ at time t_0 to a state vector $|\psi(\mathrm{t})\rangle$ at time *t*, the time-evolution operator is commonly written $U(t, t_0)$ and one has,

$$|\psi(\mathrm{t})\rangle = \mathrm{U}(\mathrm{t}, \mathrm{t}_0)\,|\psi(t_0)\rangle$$

In the case where the Hamiltonian of the system does not vary with time, the time-evolution operator has the form,

$$\mathrm{U}(\mathrm{t}, \mathrm{t}_0) = \exp(-\mathrm{i}\mathrm{H}(\mathrm{t} - \mathrm{t}_0) / \hbar\ )$$

Where the exponent is evaluated via its Taylor series.

The Schrödinger picture is useful when dealing with a time-independent Hamiltonian *H*; that is,

$$\partial_t \mathrm{H} = 0.$$

In elementary quantum mechanics, the state of a quantum-mechanical system is represented by a complex-valued wavefunction ψ(*x*, *t*). More abstractly, the state may be represented as a state vector, or ket $|\psi\rangle$. This ket is an element of a Hilbert space, a vector space containing all possible states of the system. A quantum-mechanical operator is a function which takes a ket $|\psi\rangle$ and returns some other $|\psi'\rangle$.

The differences between the Schrödinger and Heisenberg pictures of quantum mechanics revolve around how to deal with systems that evolve in time: the time dependent nature of the system must be carried by some combination of the state vectors and the operators. For example, a quantum harmonic oscillator may be in a state $|\psi\rangle$ for which the expectation value of the momentum, $\langle\psi \;|\hat{p}|\psi\rangle$ oscillates sinusoidally in time. One can then ask whether this sinusoidal oscillation should be reflected in the state vector $|\psi\rangle$, the momentum operator $\hat{p}$, or both. All three of these choices are valid; the first gives the Schrödinger picture, the second the Heisenberg picture, and the third the interaction picture.

The Time Evolution Operator

The time-evolution operator $U(t, t_0)$ is defined as the operator which acts on the ket at time t_0 to produce the ket at some other time t:

$$|\,\psi(\mathrm{t})\rangle \;=\; U(t, t_0)\,|\psi(t_0)\rangle$$

For Bras, we instead have

$$|\,\psi(\mathrm{t})\rangle \;=\; \langle\psi(t_0)\;|\,U^{\dagger}(t, t_0)$$

Properties

Unitarity:

The time evolution operator must be unitary. This is because we demand that the norm of the state ket must not change with time. That is,

$$\langle\psi(t_0)|\;\psi(\mathrm{t})\rangle \;=\; \langle\psi(t_0)\;|\,U^{\dagger}(t, t_0)\,U(t, t_0)\,|\psi(t_0)\rangle$$

$$=\;\langle\psi(t_0)|\;\psi(t_0)\rangle$$

Therefore,

$$U^{\dagger}(t, t_0)\,U(t, t_0) \;=\; \mathrm{I}$$

Identity:

When $t = t_0$, U is the identity operator, since

$$\psi(t_0)\rangle = U(t, t_0)\;|\;\psi(\mathrm{t})\rangle$$

Closure:

Time evolution from t_0 to t may be viewed as a two-step time evolution, first from t_0 to an intermediate time t_1, and then from t_1 to the final time t. Therefore

$$U(t, t_0) \;= U(t, t_1)\;\;U(\,t_1, t_0)$$

3.3 Heisenberg representation

In physics, the Heisenberg picture, also called the Heisenberg representation, is a formulation given by Werner Heisenberg in 1925, of quantum mechanics in which the operators (observables and others) incorporate a dependency on time, but the state vectors are time-independent, an arbitrary fixed basis rigidly underlying the theory.

It stands in contrast to the Schrödinger picture in which the operators are constant, instead, and the states evolve in time. The two pictures only differ by a basis change with respect to time-dependency, which corresponds to the difference between active and passive transformations. The Heisenberg picture is the formulation of matrix mechanics in an arbitrary basis, in which the Hamiltonian is not necessarily diagonal. It further serves to define a third hybrid picture, the interaction picture.

In the Heisenberg picture of quantum mechanics the state vectors, $|\psi(t)$, do not change with time, while observables *A* satisfy,

$$\frac{d}{dt}\mathrm{A(t)} = \frac{i}{\hbar}[\mathrm{H, A(t)}] + \left(\frac{\partial A}{\partial t}\right)_H$$

Where *H* is the Hamiltonian and [•,•] denotes the commutator of two operators (in this case *H* and *A*). Taking expectation values automatically yields the Ehrenfest theorem, featured in the correspondence principle. By the Stone–von Neumann theorem, the Heisenberg picture and the Schrödinger picture are unitarily equivalent, just a basis change in Hilbert space. In some sense, the Heisenberg picture is more natural and convenient than the equivalent Schrödinger picture, especially for relativistic theories. Lorentz invariance is manifest in the Heisenberg picture, since the state vectors do not single out the *time* or space.

This approach also has a more direct similarity to classical physics: by simply replacing the commutator above by the Poisson bracket, the Heisenberg equation reduces to an equation in Hamiltonian mechanics.

3.4 Interaction representation

In quantum mechanics, the interaction picture, also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture. While the other two pictures either the state vector or the operators carry time dependence, the interaction picture carry both the part of the time dependence of observables (probability amplitudes). The interaction picture is advantageous since it consider the changes to the wave functions and observables due to interactions. Most field-theoretical calculations typically use the interaction representation because they provide the solution to the various Schrödinger equations as the solution to the free-particle problem and also for some unknown interaction parts.

Equations that include operators at different times, which hold in the interaction picture, do not necessarily hold either in the Schrödinger picture or in the Heisenberg picture. This is because time dependent unitary transformations relate operators in one picture to the analogous operators in the others. Operators and state vectors in the interaction picture are related by a change of basis (unitary transformation) to those same operators and state vectors in the Schrödinger picture.

To switch into the interaction picture, we divide the Schrödinger picture Hamiltonian into two parts:

$$H_s = H_{0,s} + H_{1,s}$$

Any possible choice of parts will yield a valid interaction picture; but in order for the interaction picture to be useful in simplifying the analysis of a problem, the parts will typically be chosen so that $H_{0,s}$ is well understood and exactly solvable, while $H_{1,s}$ contains some harder-to-analyze perturbation to this system.

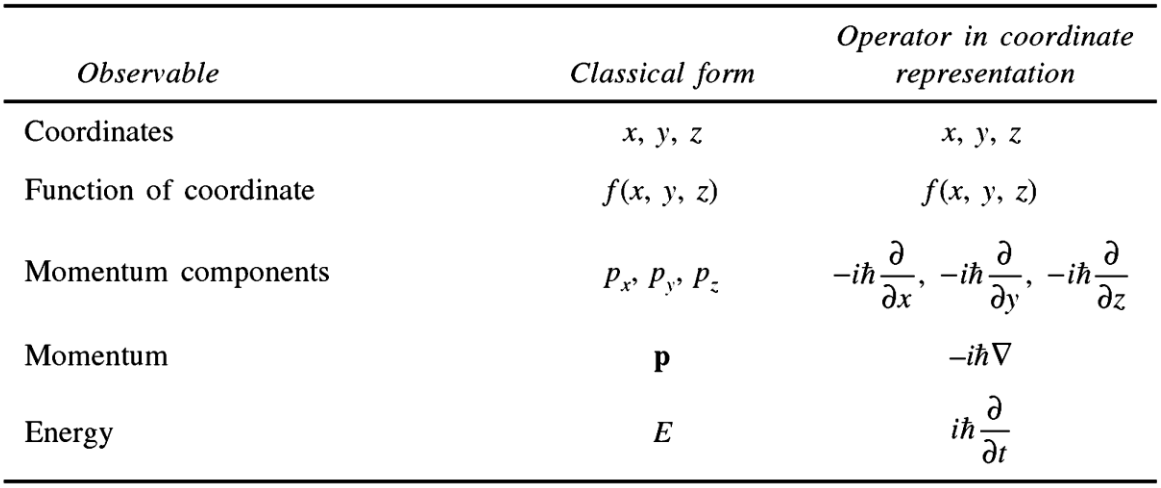
If the Hamiltonian has explicit time-dependence (for example, if the quantum system interacts with an applied external electric field that varies in time), it will usually be advantageous to include the explicitly time-dependent terms with $H_{1's}$, leaving $H0_{0's}$ time-independent. We proceed assuming that this is the case. If there is a context in which it makes sense to have $H_{0's}$ be time-dependent, then one can proceed by replacing

$$\exp(\pm iH_{0,s}\, t/\hbar)$$

by the corresponding time-evolution operator in the definitions below.

3.5 Coordinate representation

Some of the important operators associated with observables in the coordinate representation are given in table



Observable	Classical form	Operator in coordinate representation
Coordinates	x, y, z	x, y, z
Function of coordinate	$f(x, y, z)$	$f(x, y, z)$
Momentum components	p_x, p_y, p_z	$-i\hbar\frac{\partial}{\partial x},\ -i\hbar\frac{\partial}{\partial y},\ -i\hbar\frac{\partial}{\partial z}$
Momentum	$\mathbf{p}$	$-i\hbar\nabla$
Energy	E	$i\hbar\frac{\partial}{\partial t}$

Figure 9 Classical observables and their quantum mechanical operators

3.6 Momentum representation

The wave function is a function of the coordinates and time. In such a case, we have the coordinate or position representation. In certain case, it is convenient to work in the momentum representation in which the state function of a system φ (p,t) is take as a function of momentum and time. In the coordinate representation, the operator for the coordinate r is simply r and the operator p is -i $\hbar\nabla$. However, in the momentum representation, the momentum p is represented by the operator p itself and the coordinate is represented by a differential operator. Since p = k $\hbar$. The momentum space is equivalent to a k space in which the operator for k is k itself. Relations in the momentum representation equivalent to the ones in the coordinate representation can be easily be derived.

$$\langle p\rangle = \int_{-\infty}^{\infty}\psi^*(x,t)\left(-i\hbar\frac{d}{dx}\right)\psi(x,t)\,\mathrm{dx}$$

$$= \frac{-i\hbar}{2\hbar\pi}\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}\varphi^*(p,t)\,\exp\left(\frac{-ipx}{\hbar}\right)\mathrm{dp}\int_{-\infty}^{\infty}\frac{\partial}{\partial x}\varphi(p',t)\exp\left(\frac{-ip'x}{\hbar}\right)\mathrm{dp'}$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty}\varphi^*(p,t)\,\mathrm{dp}\int_{-\infty}^{\infty}\frac{\partial}{\partial x}\varphi(p',t)\mathrm{dp'}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left(\frac{i}{\hbar}(p'-p)x\right)dx$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty} \varphi^* \ (p,t) \text{ dp} \int_{-\infty}^{\infty} \frac{\partial}{\partial x}\ \varphi(p',t)p'\hbar\delta(p'-p)\text{dp'}$$

$$= \int_{-\infty}^{\infty} |\varphi\ (p,t)|^2 \text{ p dp}$$

Thus the operator for momentum in the momentum space is p itself.

3.7 Conservation laws

Conservation of momentum

The unitary infinitesimal operator is given by

$$U_T = I - \frac{i\rho.p}{\hbar}$$

It follows immediately

$$H' = U_T\, H\, U_T^{\dagger}$$

$$= (I - \frac{i\rho.p}{\hbar})\, H\, (I + \frac{i\rho.p}{\hbar})$$

$$= H - \frac{i\rho}{\hbar}[p, H]$$

Hence, invariance of the Hamiltonian under translation in space requires that the linear momentum operator p must commute with H. this implies that the linear momentum of the system is conserved. Thus, the conservation of linear momentum of physical system is a consequence of the translational invariance of the Hamiltonian of the system. the above equation holds good only for isolated systems wherein H does not contain a potential energy term which is usually a function of r.

Conservation of energy

For an infinitesimal time translation τ in a similar way

$$\psi'\ (x,t) = \Psi\ (x,t+\tau) = \Psi\ (x,t) + \tau\frac{\partial\Psi}{\partial t}$$

$$= \Psi\ (x,t) + \frac{i}{\hbar}\tau\ (-i\,\hbar\frac{\partial}{\partial t})\ \Psi\ (x,t)$$

$$= [\,1 + i\,\tau\,(-\frac{H}{\hbar})]\ \Psi\ (x,t) \qquad \text{--------(1)}$$

The Unitary operator corresponding to infinitesimal displacement τ in time of the system is given by

$$U = I - \frac{i}{\hbar}\tau H \qquad \text{------(2)}$$

Where H is the Hamiltonian which is independent of time. The invariance of the Hamiltonian under translation in the requires that

$$H' = UHU^{\dagger} = H \qquad \text{or}$$

$$UH = HU \qquad \text{------(3)}$$

It is obvious from the form of U that it commutes with H as it is independent of time. The time independent of H means that the total energy of the system is conserved. Thus, the total energy of the system is conserved if the system is invariant under translation in time. If H depends on time, it will not be invariant under translation in time.

Conservation of angular momentum

The unitary operator corresponding to an infinitesimal rotation θ about an arbitrary axis n is given by

$$U_R(n, \theta) = I + \frac{i\theta}{\hbar} n.J \qquad \text{------(1)}$$

Where J is the total angular momentum. For H to be invariant under the transformation, H' must equal to H.

$$H' = U_R H U_R{}^{\dagger}$$

$$= (I + \frac{i\theta}{\hbar} n.J)\, H\, (I - \frac{i\theta}{\hbar} n.J)$$

$$= H + \frac{i\theta}{\hbar} n.[J, H] \qquad \text{--------(2)}$$

This is the condition for invariance of H requires that

$$[J, H] = 0.$$

Thus, conservation of total angular momentum is a consequence of the rotational invariance of the system.

3.8 Time reversal

Discrete transformation is one in which the time is reversed, $t' = -t$. denoting the wave function after time reversal ψ' (r, t'), we have

$$\psi' (r, t') = T\,\Psi (r,t), \qquad t' = -t \qquad \text{------(1)}$$

Where T is the operator that effects the transformation. Let A be a time-independent operator associated with an observable and A' be its transform. Consider the equation

$$A\,\Psi = \varphi \qquad \text{--------(2)}$$

Then

$$\varphi' = TA\,\Psi$$

$$= TAT^{-1}\,T\,\Psi$$

$$= (TAT^{-1})\,T\,\Psi$$

$$= (TAT^{-1})\,\psi'$$

$$\varphi' = A'\psi'$$

Where

$$A' = TAT^{-1} \qquad \text{-----------(3)}$$

we shall now investigate the effect of the operator T on observables. To be in conformity with the time-reversal invariance in classical mechanics, we require that the position operator r be left unchanged and the momentum operator shall change sign under time reversal.

Mathematically,

$$r' = T\,r\,T^{-1} = r$$

$$p' = T\,p\,T^{-1} = -p$$

$$L' = T\,L\,T^{-1} = -L \qquad \text{------(4)}$$

we now evaluate the fundamental commutation relation $[\,x', p_x{}']$

$$[\,x', p_x{}'] = [\,T\,x\,T^{-1}\ ,T\ p_x\,T^{-1}\,]$$

by virtue of equation (4)

$$T\,x\,T^{-1} = x \text{ and}$$

$$T\ p_x\ T^{-1} = -p_x$$

Therefore

$$[\ x', p_x'] = [x, -p_x] = -i\,\hbar \qquad \text{------(5)}$$

The value of $[\ x', p_x']$ commutator can also be written as

$$[\ x', p_x'] = T\ [x, p_x]\ T^{-1} = T(i\,\hbar)\ T^{-1} \qquad \text{------(6)}$$

From equation (5) and (6)

$$T\ (i\,\hbar)\ T^{-1} = -i\,\hbar \qquad \text{---------(7)}$$

which is possible only if T operating on any number changes it into its complex conjugate.

UNIT IV:

APPROXIMATION METHODS

Time independent perturbation theory for non-degenerate energy levels –Degenerate energy levels – Stark effect in Hydrogen atom – Ground and excited state – Variation method – Helium atom – WKB approximation – Connection formulae (no derivation) – WKB quantization – Application to simple harmonic oscillator.

4.1 Time independent perturbation theory

Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence. The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small in-homogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.

First Order Corrections

Consider an unperturbed Hamiltonian, H_0, which is also assumed to have no time dependence. It has known energy levels and eigen states, arising from the time independent Schrödinger equation of the form:

$$H_0 \mid n^{(0)}\rangle = E_n{}^{(0)} \mid n^{(0)}\rangle \qquad n = 1,2,3,\ldots.$$

For simplicity, assume that the energies are discrete. The (0) superscripts denote that these quantities are associated with the unperturbed system. Note the use of bra–ket notation.

Now introduce a perturbation to the Hamiltonian. Let V be a Hamiltonian representing a weak physical disturbance, such as a potential energy produced by an external field. Thus, V is formally a Hermitian operator. Let λ be a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation). The perturbed Hamiltonian is represented as,

$$H = H_0 + \lambda V$$

The energy levels and eigen states of the perturbed Hamiltonian are again given by the Schrödinger equation:

$$(H_0 + \lambda V) | n\rangle = E_n | n\rangle$$

The objective is to express E_n and $| n\rangle$ in terms of the energy levels and eigen states of the old Hamiltonian. If the perturbation is sufficiently weak, we can write them as a (Maclaurin) power series in λ:

$$E_n = E_n{}^{(0)} + \lambda E_n{}^{(1)} + \lambda^2 E_n{}^{(2)} + \cdots ...$$

$$| n\rangle = | n^{(0)}\rangle + \lambda | n^{(1)}\rangle + \lambda^2 | n^{(2)}\rangle \text{ ……….}$$

Where,

$$E_n{}^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}|_{\lambda=0}$$

$$| n^{(k)}\rangle = \frac{1}{k!}\frac{d^k | n\rangle}{d\lambda^k}|_{\lambda=0}$$

When $k = 0$, these reduce to the unperturbed values, which are the **first term** in each series. Since the perturbation is weak, the energy levels and eigenstates should not deviate too much from their unperturbed values, and the terms should rapidly become smaller as we go to higher order. Substituting the power series expansion into the Schrödinger equation, we obtain,

$$(H_0 + \lambda V)(| n^{(0)}\rangle + \lambda | n^{(1)}\rangle + \lambda^2 | n^{(2)}\rangle\ldots) = (E_n{}^{(0)} + \lambda E_n{}^{(1)} + \lambda^2 E_n{}^{(2)} + \cdots ...)$$

$$(n^{(0)}\rangle + \lambda | n^{(1)}\rangle + \lambda^2 | n^{(2)}\rangle \text{ ..})$$

Expanding this equation and comparing coefficients of each power of λ results in an infinite series of simultaneous equations. The zeroth-order equation is simply the Schrödinger equation for the unperturbed system. The first order equation is,

$$H_0 | n^{(1)}\rangle + V | n^{(0)}\rangle = E_n{}^{(0)} | n^{(1)}\rangle + E_n{}^{(1)} | n^{(0)}\rangle$$

Operating through by $| n^{(0)}\rangle$, the first term on the left-hand side cancels the first term on the right-hand side as per the unperturbed Hamiltonian is Hermitian. This leads to the first order energy shift:

$$E_n{}^{(1)} = \langle n^{(0)}| V | n^{(0)}\rangle$$

This is simply the expectation value of the perturbation Hamiltonian while the system is in the unperturbed state.

4.2 The Stark Effect for *n* = 2 Hydrogen

The Stark effect for the $n = 2$ states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of E_0. That is

$$H_0\, \varphi_{2lm} = E_0\, \varphi_{2lm}$$

The degenerate states are ϕ_{200}, ϕ211, ϕ210 and ϕ21(−1).

The perturbation due to an electric field in the z direction is $H_1 = + e\varepsilon z$.

So the first order degenerate state perturbation theory equation is,

$$\sum \alpha_i \left\langle \varphi^{(j)} \middle| H_0 + e\varepsilon z \middle| \varphi^{(i)} \right\rangle = (E_0 + E^{(0)})\alpha_j$$

This is essentially a 4 x 4 matrix eigenvalue equation. There are 4 eigenvalues , $(E_0 + E^{(1)})$ distinguished by the index n .

Because of the exact degeneracy ($H_0\, \varphi^{(j)} = E_0\, \varphi^{(j)}$) then H_0, E_0 can be eliminated from the equation.

$$\sum \alpha_i \left\langle E_0\, \delta_{ij} \middle| e\varepsilon z \middle| \varphi^{(i)} \right\rangle = (E_0 + E^{(1)})\alpha_j$$

$$E_0\ \alpha_i \quad + \quad \sum \alpha_i \left\langle \varphi^{(j)} \middle| e\varepsilon z \middle| \varphi^{(i)} \right\rangle = E_0\alpha_j + E^{(1)}\alpha_j$$

$$\sum \alpha_i \left\langle \varphi^{(j)} \middle| e\varepsilon z \middle| \varphi^{(i)} \right\rangle = E^{(1)}\alpha_j$$

This is just the eigen value equation for H_1 which we can write in (pseudo) matrix form as follows,

$$(H_1)\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)}\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

Now, in fact, most of the matrix elements of H_1 are zero. We can define that because

$$[L_z, z] = 0 ,$$

hence all the matrix elements between states of unequal are zero. Another way of saying this is that the operator *z* does not ‘change’ .

The equation that is labelled with the basis states to define the order is.

$$\begin{array}{c} \phi_{200} \\ \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{array} \begin{pmatrix} 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

We can see by inspection that the eigenfunctions of this operator are ϕ211, ϕ21−1, and $\frac{1}{\sqrt{2}}\,(\varphi_{200} \pm \varphi_{210})$with eigenvalues (of H_1) of 0, 0, and $\pm\,\gamma$.

$$\gamma \;=\; e\varepsilon \int (2a_0)^{-3/2}\,(1-\frac{r}{2a_0})\,\exp(-\frac{r}{2a_0})\,Y_{00}\,(2a_0)^{-3/2}\,\frac{1}{\sqrt{3}}\,(\frac{r}{a_0})\,\exp(\frac{r}{2a_0})\,Y_{10}\,d^3r$$

$$\begin{aligned}
&= 2e\mathcal{E}\,(2a_0)^{-3}\,\frac{1}{\sqrt{3}} \int r^3 d^3 r \left(1 - \frac{r}{2a_0}\right)\left(\frac{r}{a_0}\right) e^{-r/a_0} \int \frac{1}{\sqrt{4\pi}} \cos\theta Y_{10}\, d\Omega \\
&= 2eE(2)^{-3}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}} \int_0^\infty \left(\frac{r^4}{a_0^4} - \frac{r^5}{2a_0^5}\right) e^{-r/a_0}\, dr \\
&= \frac{a_0 e\mathcal{E}}{12}\left[\int_0^\infty x^4 e^{-x} dx - \frac{1}{2}\int_0^\infty x^5 e^{-x} dx\right] \\
&= \frac{a_0 e\mathcal{E}}{12}\left[4\cdot 3\cdot 2\cdot 1 - \frac{5\cdot 4\cdot 3\cdot 2\cdot 1}{2}\right] \\
&= \frac{a_0 e\mathcal{E}}{12}(-36) \\
&= -3e\mathcal{E}a_0 \qquad \Rightarrow \qquad E^{(1)} = \mp 3e\mathcal{E}a_0
\end{aligned}$$

This is first order in the electric field, as we would expect in first order (degenerate) perturbation theory.

If the states are not exactly degenerate, we have to leave in the diagonal terms of H_0. Assume that the energies of the two (mixed) states are $E_0 \pm \Delta$, where Δ comes from some other perturbation, like the hydrogen fine structure. The ϕ211 and ϕ21 (−1) are still not mixed by the electric field.

$$\begin{pmatrix} E_0 - \Delta & \gamma \\ \gamma & E_0 + \Delta \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

$$E = E_0 \pm \sqrt{\gamma^2 + \Delta^2}$$

This is correct in both limits, $\Delta \gg \gamma$, and $\gamma \gg \Delta$. It is also correct when the two corrections are of the same order.

4.3 Variation method

The variational method is the key approximate method/technique typically used in quantum mechanics. The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.

The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.

Basically the ‘trial wave function’ for the problem consists of some adjustable parameters called termed as the ‘variational parameters’. These parameters are adjusted until the energy of the trial wave function is minimized. The resulting trial wave function and its corresponding energy are variational method approximations to the exact wave function and energy.

Suppose we are given a Hilbert space and a Hermitian operator over it called the Hamiltonian, *H*. Ignoring complications about continuous spectra, consider the discrete spectrum of *H* and the corresponding eigen spaces of each eigen value :

$$\langle \Psi_{\lambda 1} | \Psi_{\lambda 2} \rangle = \delta_{\lambda 1 \lambda 2}$$

Where, δ_{ij} is the Kronecker delta,

$$\delta_{ij} = 0 \text{ if } i \neq j,$$

$$= 0 \text{ if } i = j.$$

And the Hamiltonian is related to » through the typical eigen value relation

$$\hat{H} \; |\Psi_\lambda\rangle = \lambda \; |\Psi_\lambda\rangle$$

Physical states are normalized, meaning that their norm is equal to 1. Once again ignoring complications involved with a continuous spectrum of *H*, suppose it is bounded from below and that its greatest lower bound is E_0. Suppose also that we know the corresponding state |Èé’. The expectation value of *H* is then,

$$\begin{aligned}\langle \psi \mid H \mid \psi \rangle &= \sum_{\lambda_1,\lambda_2 \in \mathrm{Spec}(H)} \langle \psi | \psi_{\lambda_1} \rangle \langle \psi_{\lambda_1} | H | \psi_{\lambda_2} \rangle \langle \psi_{\lambda_2} | \psi \rangle \\ &= \sum_{\lambda \in \mathrm{Spec}(H)} \lambda |\langle \psi_\lambda \mid \psi \rangle|^2 \geq \sum_{\lambda \in \mathrm{Spec}(H)} E_0 |\langle \psi_\lambda \mid \psi \rangle|^2 = E_0\end{aligned}$$

UNIT V:

ANGULAR MOMENTUM

Eigenvalue spectrum of general angular momentum – Ladder operators and their algebra – Matrix representation – Spin angular momentum – Addition of angular momenta – CG Coefficients – Symmetry and anti – symmetry of wave functions – Construction of wave-functions and Pauli's exclusion principle.

5.1 Eigenvalue spectrum of general angular momentum

Let us first consider the angular momentum classically. For this, let us consider a particle of mass *m* moving along a path *AB* about some fixed point *O* as shown in the Figure . Let at some instant of time, the particle be at the position *P*. The position *P* of the particle with respect to the point *O* is defined by the position vector $\overrightarrow{OP}$or $\vec{r}$. Let the linear momentum of the particle at the position *P* be $\vec{p}$. The direction of $\vec{p}$. is along the tangent to the path *AB* at *P*.

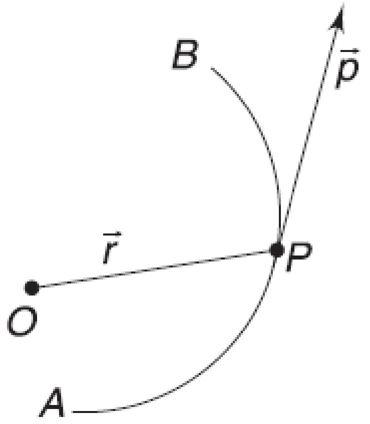


Figure 10 angular momentum

Classically, the angular momentum (which is a vector quantity) of the particle about the point *O* when it is at *P* is defined as

$$\vec{L} = \vec{r} \; X \; \vec{p} \qquad \text{----------(1)}$$

With the point *O* as the origin, let us consider a rectangular coordinate system (*XYZ*). If *x*, *y*, *z* be the coordinates of the point *P* then

$$\vec{r} \; = \hat{\imath}\text{x} + \hat{\jmath}\text{y} + \hat{k}\text{z} \qquad \text{----------(2)}$$

Further, if p_x, p_y and p_z be respectively the components of along *X*, and *Z* axes then

$$\vec{p} = \hat{\imath}\, p_x + \hat{\jmath}\, p_y + \hat{k}\, p_z \qquad \text{----------(3)}$$

If L_x, L_y and L_z be respectively the X, Y and Z components of , then using equations (7.80) and (2) in Equation (1), we get

$$\hat{\imath}\, L_x + \hat{\jmath}\, L_y + \hat{k}\, L_z = \begin{pmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

Evaluating the right hand side of the above equation and comparing the coefficients of $\hat{\imath}$, $\hat{\jmath}$ and $\hat{k}$ on both sides we obtain

$$L_x = \mathrm{y}\, p_z - \mathrm{z}\, p_y \qquad \text{-------(4)}$$

$$L_y = \mathrm{z}\, p_x - \mathrm{x}\, p_z \qquad \text{-------------(5)}$$

$$L_z = \mathrm{x}\, p_y - \mathrm{y}\, p_x \qquad \text{---------(6)}$$

Quantum Mechanical Description of Angular Momentum

In order to treat angular momentum quantum mechanically, we replace the physical quantities L_x, L_y, L_z, x, y, z, p_x, p_y and p_z by corresponding linear Hermitian operators,

$$\mathrm{x} \rightarrow \hat{x} = \mathrm{x}$$

$$\mathrm{y} \rightarrow \hat{y} = \mathrm{y}$$

$$\mathrm{z} \rightarrow \hat{z} = \mathrm{z}$$

$$p_x \rightarrow \widehat{p_x} = -\mathrm{i}\hbar \frac{\partial}{\partial x}$$

$$p_y \rightarrow \widehat{p_y} = -\mathrm{i}\hbar \frac{\partial}{\partial y}$$

$$p_z \rightarrow \widehat{p_z} = -\mathrm{i}\hbar \frac{\partial}{\partial z} \qquad \text{--------(7)}$$

Substituting the above in Equations (1), (4), (5) and (6) we obtain the quantum mechanical operators corresponding to the quantities $\vec{L}$, L_x, L_y, L_z as

$$\vec{L} = -\mathrm{i}\hbar\, \vec{r} \times \vec{\nabla} \qquad \text{----------(8)}$$

$$\widehat{L_x} = -\mathrm{i}\hbar \left(\mathrm{y}\frac{\partial}{\partial z} - z\, \frac{\partial}{\partial y} \right) \qquad \text{--------(9)}$$

$$\widehat{L_y} = -\mathrm{i}\hbar \left(\mathrm{z}\frac{\partial}{\partial x} - x\, \frac{\partial}{\partial z} \right) \qquad \text{--------(9)}$$

$$\widehat{L_x} = -\mathrm{i}\hbar \left(\mathrm{x}\frac{\partial}{\partial y} - y\, \frac{\partial}{\partial x} \right) \qquad \text{--------(9)}$$

5.2 Ladder Operators

Instead of $\widehat{L_x}$, and $\widehat{L_y}$ it is often convenient and more instructive to use their complex combinations $\widehat{L_x} \pm i\widehat{L_y}$

The operator

$$\widehat{L_+} = \widehat{L_x} + i\widehat{L_y} \qquad \text{-----------(10)}$$

is called the step-up operator.

The operator

$$\widehat{L_-} = \widehat{L_x} + i\widehat{L_y} \qquad \text{-----------(11)}$$

is called the step-down operator.

We find

$$\widehat{L_z}\ \widehat{L_+} = \widehat{L_z}(\widehat{L_x} + i\widehat{L_y}) = \widehat{L_z}\widehat{L_x} + i\widehat{L_z}\widehat{L_y} \qquad \text{--------(12)}$$

Using the commutation relations Equation (12) becomes

$$\widehat{L_z}\ \widehat{L_+} = \widehat{L_x}\widehat{L_z} + i\widehat{L_y} + i(\widehat{L_y}\widehat{L_z} - i\widehat{L_x})$$

$$= (\widehat{L_x} + i\widehat{L_y})\widehat{L_z} + (\widehat{L_x} + i\widehat{L_y})$$

$$= \widehat{L_+}\ \widehat{L_z} + \widehat{L_+}$$

Or

$$\widehat{L_z}\ \widehat{L_+} = \widehat{L_+}\ (\widehat{L_z} + 1) \qquad \text{---------(13)}$$

Similarly, we obtain

$$\widehat{L_z}\ \widehat{L_-} = \widehat{L_-}\ (\widehat{L_z} + 1) \qquad \text{---------(14)}$$

5.3 Algebra – Matrix representation

(i) **Sum** of two linear operators and , i.e., ($\widehat{\alpha_1} + \widehat{\alpha_2}$) is defined according to

$$(\widehat{\alpha_1} + \widehat{\alpha_2})\,|a\rangle = \widehat{\alpha_1}\,|a\rangle + \widehat{\alpha_2}\,|a\rangle \qquad \text{-------(1)}$$

(ii) **Product** of two linear operators a_1 and , i.e., ($\widehat{\alpha_1}\ \widehat{\alpha_2}$) is defined according to

$$(\widehat{\alpha_1}\ \widehat{\alpha_2}\ )\,|a\rangle = \widehat{\alpha_1}\,(\widehat{\alpha_2}\ )\,|a\rangle \qquad \text{--------(2)}$$

From Equation (2) it is possible to define powers of a linear operator. We further find the following relations to hold

$$(\widehat{\alpha_1}+\widehat{\alpha_2})\,|a\rangle = (\widehat{\alpha_2}+\widehat{\alpha_1})\,|a\rangle \qquad \text{------(3)}$$

$$[(\widehat{\alpha_1}+\widehat{\alpha_2})+\widehat{\alpha_3}]\,|a\rangle = [\widehat{\alpha_1}+(\widehat{\alpha_2}+\widehat{\alpha_3})]\,a\rangle \qquad \text{--------(4)}$$

$$[\widehat{\alpha_1}(\widehat{\alpha_2}+\widehat{\alpha_2})]\,|a\rangle = \widehat{\alpha_1}\,\widehat{\alpha_2}\,|a\rangle + \widehat{\alpha_1}\,\widehat{\alpha_3}\,|a\rangle \qquad \text{-------(5)}$$

iii) **Commutator** of two linear operators $\widehat{\alpha_1}$ and $\widehat{\alpha_2}$ is written as $[\widehat{\alpha_1}, \widehat{\alpha_2}]$ and is defined as

$$[\widehat{\alpha_1}, \widehat{\alpha_2}] = \widehat{\alpha_1}\,\widehat{\alpha_2} - \widehat{\alpha_2}\,\widehat{\alpha_1} \qquad \text{.....(6)}$$

The operator $\widehat{\alpha_1}$ and $\widehat{\alpha_2}$ are said to be *non-commutative* if

$$\widehat{\alpha_1}\,\widehat{\alpha_2} \neq \widehat{\alpha_2}\,\widehat{\alpha_1},$$

$$\text{i.e., } [\widehat{\alpha_1}, \widehat{\alpha_2}] \neq 0 \qquad \text{...(7)}$$

We may note that the above properties hold with matrices.

It is seen that the algebra of *N*-dimensional square matrices is the same as the algebra of linear operators.

We may further note that the algebra of quantum mechanics is a noncommutative algebra.

Multiplication by a constant is linear operation. A constant operator commutes with all linear operators.

(iv) **Inverse of an Operator:** If two linear operators $\widehat{\alpha_1}$ and $\widehat{\alpha_2}$ satisfy the equation

$$\widehat{\alpha_1}\,\widehat{\alpha_2} = \widehat{\alpha_2}\,\widehat{\alpha_1} = \text{(Identity operator)} \qquad \text{...(8)}$$

then $\widehat{\alpha_2}$ is said to be the *inverse* of $\widehat{\alpha_1}$ and vice-versa, provided the inverse exists and we write

$$\widehat{\alpha_2} = \widehat{\alpha_1}^{-1}, \quad \widehat{\alpha_1} = \widehat{\alpha_2}^{-1} \qquad \text{----------(9)}$$

The inverse of a product of operators $(\widehat{\alpha_1}, \widehat{\alpha_2}, \widehat{\alpha_2})$ is

$$(\widehat{\alpha_1}\,\widehat{\alpha_2}\,\widehat{\alpha_2})^{-1} = \widehat{\alpha_3}^{-1}\,\widehat{\alpha_2}^{-1}\,\widehat{\alpha_1}^{-1} \qquad \text{...(10)}$$

As mentioned earlier, the above properties of linear operators are common to finite square matrices. This fact allows us to *represent operators by matrices*.

5.4 Spin angular momentum

To account for the multiplicity of atomic states, Uhlenbeck and Goudsmit proposed in 1925 that an electron in an atom possesses an intrinsic angular momentum in addition to orbital angular momentum. This intrinsic angular momentum S is called spin angular momentum whose projection on the z-axis can have the values $s_z = m_s \hbar$, $m_s = \pm ½$. The maximum measurable component of spin angular momentum in units of $\hbar$ is called the spin of the particle and is usually denoted by s. they also suggested that the spin angular momentum gives rise to an intrinsic magnetic moment μ_s given by

$$\mu_s = -\frac{e}{m} s \qquad \text{------------(1)}$$

Assuming that all the stable and unstable particles to have spin angular momentum S, we expect its components S_x, S_y, and S_z to obey the general commutation relation and S^2 and S_z to have the eigenvalues $s(s+1)\hbar^2$ and $m_s \hbar$, $m_s = -s, -s+1, \ldots\ldots..2$ respectively.

5.5 Addition of angular momentum

Addition of angular momenta is very important in the study of atomic spectra, structure of nuclei, etc. consider two non interacting systems having angular momenta J_1 and J_2 and eigen kets $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ respectively,\.

$$j_1{}^2 |j_1 m_1\rangle = j_1(j_1 + 1)\hbar^2 |j_1 m_1\rangle \qquad \text{-------(1)}$$

$$J_{1z} |j_1 m_1\rangle = m_1 \hbar |j_1 m_1\rangle \qquad \text{-------(2)}$$

And

$$j_2{}^2 |j_2 m_2\rangle = j_2(j_2 + 1)\hbar^2 |j_2 m_2\rangle \qquad \text{-------(3)}$$

$$J_{2z} |j_2 m_2\rangle = m_2 \hbar |j_2 m_2\rangle \qquad \text{-------(4)}$$

Where $m_1 = j_1, j_1 - 1, \ldots, -j_1$ $\qquad m_2 = j_2, j_2 - 1, \ldots, -j_2$

Since the two systems are non interacting

$$[j_1, j_2] = 0 \text{ and } [j_1{}^2, j_2{}^2] = 0 \qquad \text{----(5)}$$

And therefore the operators $j_1{}^2$, J_{1z}, $j_2{}^2$, J_{2z} form a complete set with simultaneous eigen kets $|j_1 m_1, j_2 m_2\rangle$, which is a product of $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$. For given values of j_1 and j_2

$$|j_1 m_1, j_2 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle = |m_1\, m_2\rangle \qquad \text{-------(6)}$$

Since m_1 and m_2 can respectively have $(2j_1 + 1)$ and $(2j_2 + 1)$ orientation, the subspace with define values of j_1 and j_2 will have $(2j_1 + 1)\ (2j_2 + 1)$ dimensions.

5.6 Clebsh – Gordan Coefficients

for the total angular momentum vector

$$J = J_1 + J_2$$

$$J \times J = i\hbar J \qquad \text{------------(7)}$$

Also it follows that

$$[j^2, j_z] = 0, \quad [j^2, {j_1}^2] = [j^2, {j_2}^2] = 0 \qquad \text{------(8)}$$

The orthogonal eigenkets of j^2 and j_z be $|j\ m\rangle$. the completeness of the known kets $|m_1\ m_2\rangle$ allows us to express the unknown kets $|\ j\ m\rangle$ as a linear combination of $|m_1\ m_2\rangle$.

$$|\ j\ m\rangle = \sum_{m1,m2} C_{jmm1m2}\ |m_1\ m_2\rangle \qquad \text{-----(9)}$$

The coefficient of this linear combination are called Clebsh-Gordan coefficient or wigner coefficient or vector coupling coefficients. Multiplying equation(9) with the bra $\langle m_1 m_2|$, we get

$$\langle jm| = \sum_{m1,m2} |m_1\ m_2\rangle\ \langle m_1 m_2|\ j\ m\rangle \qquad \text{--------(10)}$$

The parameters J_1 and J_2 are not explicitly in the coefficients as we are working for definite values of j_1 and j_2. In the strict sense the coefficients would be $\langle j_1 m_1, j_2 m_2 |\ j1, j2\ jm\rangle$

The inverse of equation(10) is given by

$$|m_1\ m_2\rangle = \sum_{jm} |\ jm\rangle\ \langle jm|\ m_1 m_2\rangle \qquad \text{--------(11)}$$

Where the summation over m is from -j to j is from $|j_1 - j_2|$ to $j_1 + j_2$. The unitary character of Clebsh - Gordan coefficients in expressed by the equations

$$\sum_{j,m} \langle m_1 m_2|\ j\ m\rangle\ \langle jm|\ m_1'\ m_2'\rangle = \langle m_1 m_2|\ m_1'\ m_2'\rangle$$

$$= \delta\ m_1 m_1'\ \delta\ m_2 m_2' \qquad \text{---------(12)}$$

And $$\sum_{m1m2} \langle jm|\ m_1 m_2\rangle\ \langle m_1 m_2|\ j'\ m'\rangle = \langle jm|\ j'\ m'\rangle$$

$$= \delta\ jj'\ \delta\ mm' \qquad \text{---------(12)}$$

Where $$\langle jm|\ m_1 m_2\rangle = \langle jm|\ m_1 m_2\rangle^*$$

5.7 Symmetric and Anti symmetric Wave functions

A wave function is symmetric if the interchange of any pair of particles among its arguments leaves it unchanged. If the interchange of any pair of particles change the sign of ψ, it is said to be antisymmetric. Any physically acceptable wave function representing two identical particles must be either symmetric or anti symmetric with respect to an interchange of the particles. Generalizing, the principle of indistinguishability requires that the wave function must be either symmetric or anti symmetric with respect to the interchange of any pair of particles.

Let the wave function ψ(1,2,…,n,t) is symmetric at a particular time t. H ψ is then symmetric since H is symmetric in its arguments. The schrodinger equation states that.

$$i\hbar \frac{\partial}{\partial t} \psi\,(1,2,\ldots,n,t) = H\,(1,2,\ldots,n,t)\ \psi(1,2,\ldots,n,t) \qquad \text{--------(1)}$$

since H ψ is symmetric, $\frac{\partial}{\partial t}\psi$ is also symmetric. Then the wave function at an infinitesimally latter time t + dt given by $\psi + \frac{\partial}{\partial t}\psi$ is also symmetric. This procedure can be continued to cover large time intervals. In similar fashion, if ψ is antisymmetric at any time, it is always antisymmetric. Thus, a wave function which is symmetric continues to be symmetric and a wave function which is anti symmetric continues to be anti symmetric. In other words, the symmetry character of a wave function does not change with time.

5.8 Pauli principle

Consider a system of non interacting indistinguishable particles. The Hamiltonian of such a system can be written as

$$H(1,2,\ldots,n) = H(1) + H(2) + \ldots\ldots H(n) \qquad \text{-------(1)}$$

The approximate energy eigen function will be a simple product of one particle eigen functions. If $u_a(1)$, $u_b(2)$, …… $u_n(n)$, are the n one-particle eigen functions, then

$$\psi\,(1,2,\ldots,n,) = u_a(1), u_b(2), \ldots\ldots u_n(n), \qquad \text{--------(2)}$$

$$E = E_a + E_b + E_c \ \ldots\ldots\ldots E_n \qquad \text{-----(3)}$$

Where $u_a(1)$, $u_b(2)$, …… $u_n(n)$ and E_a, E_b, E_c ….. E_n satisfy the relation:

$$H(1)\,u_a(1) = E_a\,u_a(1),$$

$$H(2)\, u_b(2) = E_b\, u_b(2), \qquad \text{-------(4)}$$

Our assumption that state u_a is occupied by particle 1, u_b by particle 2 and so on is not correct since the particles are indistinguishable. All that we can say is that one particle is in the state u_a , a second is in u_b and so on. Thus for a system consisting of two particles, the possible eigenfunctions are $u_a(1)\, u_b(2)$ and $u_a(2)\, u_b(2)$. The symmetric and anti symmetric combinations are:

$$\Psi_s = u_a(1)\, u_b(2) + u_a(2)\, u_b(2). \qquad \text{-------(5)}$$

$$\Psi_{as} = u_a(1)\, u_b(2) - u_a(2)\, u_b(2).$$

$$= \begin{vmatrix} u_a(1) & u_a(2) \\ u_b(1) & u_b(1) \end{vmatrix} \qquad \text{-------(6)}$$

If both particles are put in the same state say u_a then

$$\Psi_s = u_a(1)\, u_a(2) + u_a(1)\, u_a(2)$$

$$= 2\quad u_a(1)\, u_a(2) \qquad \text{--------(7)}$$

$$\Psi_{as} = u_a(1)\, u_a(2) - u_a(2)\, u_a(2). \quad = 0 \qquad \text{----------(8)}$$

The symmetry or anti symmetry of a state function is an important law of nature and experiments have shown that the particular state of symmetry of a system is related to the spin of the identical particles. Pauli demonstrated that:

(i) Systems of identical particles with half-off-integer spins(spin ½, 3/2,….) are described by anti symmetric wave functions. Such particles obey Fermi-Dirac statistics and are called fermions.

(ii) Systems of identical particles with inter spins(spin 0,1,2,…) are described by symmetric wave function. Such particles obey Bose-einstein statistics and are called bosons.

Equation(8) show that the antisymmetric wave function vanishes when two identical particles have the same set of coordinates. In other words, two identical fermions cannot occupy the same state. This is one form of Pauli's exclusion principle. As the spin of electron is 1/2 , the pauli principle is commonly defined as" no two electrons can have the same set of quantum numbers".

Generalizing for an n-particle system, the normalized anti symmetric combination can be written as

$$\Psi_{as}\ (1,2,\ldots.\mathrm{n})\ = \frac{1}{\sqrt{n!}}\begin{bmatrix} u_a(1) & \cdots & u_a(\mathrm{n}) \\ \vdots & \ddots & \vdots \\ u_n(1) & \cdots & u_n(\mathrm{n}) \end{bmatrix}$$

The factor $\frac{1}{\sqrt{n!}}$ Is the normalization constant and the determinant is called slater determinant.