UNIT-1

Fundamental Concepts in Quantum Mechanics: The Stern-Gerlach Experiment ,Kets, Bras and Operators

Structure of the Unit

1.0 Objectives

- To illustrate fundamental concepts of quantum mechanics by using the Stern Gerlach experiment
- Principle of superposition of states
- Ket vectors, Bra vectors and operators
- What is an eigenstate?
- What is an observable in quantum mechanics?

1.1 Introduction

When we attempt to apply classical mechanics and electrodynamics to explain atomic phenomena, they lead to results which are in obvious conflict with experiment. There is a sharp contradiction between theory and experiment. This is very clearly seen from the contradiction obtained on applying ordinary electrodynamics to a model of an atom in which the electrodynamics to a model of an atom in which the electrons move round the nucleus in classical orbits. This indicates that phenomena occurring in particles of very small mass at very small distances demand a fundamental modifications of the basic physical concepts and laws. Here in this unit the basic formalism of quantum mechanics is presented with the example of the Stern –Gerlach experiment in the back of our minds.

1.2 Localized Wave Packets

Construction of a theory applicable to atomic phenomena that is, phenomena occurring in particles of very small mass at very small distances-demands a fundamental modification of the basic physical concepts and laws. In quantum mechanics there is no such concept as the path of a particle. This forms the content of what is called the uncertainty principle, one of the fundamental principles of quantum mechanics, discovered by W. Heisenberg in 1927.In that it rejects the ordinary ideas by classical mechanics, the uncertainty principle might be said to be negative in content.

It is possible to imagine configurations of waves that are very localized. (A clap of thunder is an example of a superposition of waves leading to an effect localized in time at a given location).Such localized "wave packets' can be achieved by superposing waves with different frequencies in a special way, so that they interfere with each other almost completely outside of a given spatial region.

Consider the function

$$f(x) = \int dk\, g(k) e^{+ikx}$$

Let us choose $g(k) = e^{-\alpha(k-k_0)^2}$,therefore

$$f(x) = \int dk\, e^{-\alpha(k-k_0)^2 + ikx}$$

Let $k - k_0 = k'$

Then $$f(x) = \int dk\, e^{-\alpha k'^2} . e^{i(k'+k_0)x}$$

$$= e^{ik_0 x} \int dk'\, e^{-\alpha k'^2} . e^{ik'x}$$

$$f(x) = \sqrt{\frac{\pi}{\alpha}}\, e^{ik_0 x} e^{-\frac{x^2}{4\alpha}}$$

$$|f(x)|^2 = \frac{\pi}{\alpha}\, e^{-\frac{x^2}{2\alpha}}$$

$$\Delta k\, \Delta x \sim \frac{2}{\sqrt{2\alpha}}\, 2\sqrt{2\alpha} = 4$$

$$\Delta x \Delta k \underset{\sim}{>} 0$$

Propagation Wave Packets:

$$f(x,t) = \int_{-\infty}^{\infty} g(k) e^{ik(x-ct)} dk = f(x - ct)$$

$$= \int_{-\infty}^{\infty} dk\, g(k) e^{i[kx - w(k)t]}$$

Expanding $w(k)$ by Taylor's expansion

$$w(k) = w(k_0) + (k - k_0)\left(\frac{\partial w}{\partial k}\right)_{k_0} + \frac{1}{2}(k - k_0)^2 \left(\frac{\partial^2 w}{\partial k^2}\right)_{k_0} + \ldots$$

Denoting $\left(\frac{\partial w}{\partial k}\right)_{k_0}$ by v_g , and $\left(\frac{\partial^2 w}{\partial k^2}\right)_{k_0}$ by β, we find

$$f(x,t) = e^{i[k_0 x - w(k_0)t]} \int_{-\infty}^{\infty} dk'\, e^{-\alpha k'^2} e^{ik'(x - v_g t)} . e^{-ik'^2 \beta t} \qquad \text{where } k' = k - k_0 .$$

or $$f(x,t)=\left[e^{i[k_0x-w(k_0)t]}\right]\int_{-\infty}^{\infty}dk'\,e^{ik'(x-v_gt)}e^{-(\alpha+i\beta t)k'^2}$$

$$f(x,t)=e^{i(k_0x-w_0t)}\left(\frac{\pi}{\alpha+i\beta}\right)^{\frac{1}{2}}e^{-i\left(\frac{(x-v_gt)^2}{4(\alpha+i\beta t)}\right)^{\frac{1}{2}}}e^{-\frac{(x-v_gt)^2}{4(\alpha+i\beta t)}}$$

Example 1: Let a wave package be described at time t = 0 by

$$\psi(x,0)=A\,exp\left(-\frac{x^2}{2a^2}+i\,k_0x\right)$$

(a) Express $\psi(x,0)$ as a superposition of plane waves.

(b) What is the approximate relation between the width of the wave packet in ` configuration (x) space and its width in k-space ?

(c) Using the dispersion relation for de Broglie waves, calculate the function $\psi(x,t)$ for any time t

(d) Discuss $|\psi(x,t)|^2$,

(e) How must the constant A be chosen. According to the probability interpretation, so that $\psi(x,t)$ describes the motion of a particle?

Sol. (a) we obtain the frequency spectrum of a wave packet $\psi(x)$ by forming the Fourier transform of the wave function :

$$\alpha(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi(x,0)\,e^{-ikx}dx$$

$$=\frac{A}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-\left(\frac{x^2}{2a^2}-ik_0x+ikx\right)}dx$$

$$=\frac{A}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-\left[\frac{1}{2a^2}\left(x^2+ix(k-k_0).2a^2+\left(ia^2(k-k_0)\right)^2-\left\{ia^2(k-k_0)\right\}^2\right)\right]}\,dx$$

$$=\frac{A}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-\frac{1}{2a^2}\left(x+ia^2(k-k_0)\right)^2}.\,e^{-\frac{a^4(k-k_0)^2}{2a^2}}\,dx$$

$$=\frac{A}{\sqrt{2\pi}}e^{-\frac{a^2(k-k_0)^2}{2}}\int dx.e^{-\frac{1}{2a^2}\left(x+i\,a^2(k-k_0)\right)^2}$$

$$=\frac{A}{\sqrt{2\pi}}e^{-\frac{(k-k_0)^2a^2}{2}}\sqrt{\pi.2a^2}=Aa\;e^{-\frac{(k-k_0)^2a^2}{2}}$$

$$\psi(x,0):=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\alpha(k)e^{ikx}dk$$

(b) $\frac{x^2}{2a^2}\sim 1 \qquad \therefore\;\; x=\pm\, a\sqrt{2}$

$$\Delta x\sim 2\sqrt{2}\,a$$

$$\frac{(\Delta k)^2a^2}{2}\sim 1 \quad \therefore\;\; \Delta k\sim 2.\frac{\sqrt{2}}{2}$$

$$\therefore\;\; \Delta x\Delta k\sim 1$$

(c) The general from of a wave function is

$$\psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\alpha(k)\;exp\;[i(kx-wt)]dk$$

The dispersion relation for de Broglie waves leads

$$w(k)=\frac{\hbar k^2}{2m}$$

Inserting $\alpha(k)$

$$\psi(x,t)=\frac{Aa}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-\frac{(k-k_0)^2a^2}{2}}e^{i(kx-wt)}dk$$

$$=\frac{Aa}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\exp\left(-\frac{a^2\left(k-k_0\right)^2}{2}+ikx-i\frac{\hbar k^2}{2m}t\right)dk$$

$$\text{Exponent}=-\frac{a^2}{2}\left(k-k_0\right)^2+i\,k\,x-\frac{i\,\hbar k^2}{2m}t$$

$$=-\frac{a^2}{2}\left[k^2+k_0^2-2k\,k_0\right]+i\,k\,x-\frac{i\,\hbar k^2}{2m}t$$

$$=-k^2\left[\frac{a^2}{2}+\frac{i\,\hbar\,t}{2m}\right]+k\left[\frac{2k_0a^2}{2}+i\,x\right]+\left(-\frac{k_0^2a^2}{2}\right)$$

$$=-\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)\left[k^2-k\,.\,\frac{\left(k_0a^2+ix\right)}{\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)}\right]-\frac{k_0^2a^2}{2}$$

$$=-\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)\left[k-\frac{1}{2}\frac{\left(k_0a^2+ix\right)}{\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)}\right]^2+\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)\left(\frac{1}{4}\left(\frac{k_0a^2+ix}{\frac{a^2}{2}+\frac{i\hbar t}{2m}}\right)^2\right)-\frac{k_0^2a^2}{2}$$

Thus $\psi(x,t)=\frac{Aa}{\sqrt{2\pi}}\sqrt{\frac{\pi}{\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)}}\,.\,e^{\left[-\frac{k_0^2a^2}{2}+\frac{1}{4}\frac{\left(k_0a^2+ix\right)^2}{\left(\frac{a^2}{2}+\frac{i\hbar t}{2m}\right)}\right]}$

$$\psi\left(x,t\right)=\frac{A}{\sqrt{\left(1+i\frac{\hbar t}{ma^2}\right)}}\exp\left(\frac{x^2-2i\,a^2k_0x+i\left(a^2\frac{\hbar k_0^2}{m}\right)t}{2a^2\left[1+i\left(\frac{\hbar t}{ma^2}\right)\right]}\right)$$

(d) $\left|\psi\left(x,t\right)\right|^2=\frac{|A|^2}{1+\left(\frac{\hbar t}{ma^2}\right)^2}\exp\left(-\frac{\left[x-\left(\frac{\hbar k_0}{m}\right)t\right]^2}{a^2\left[1+\left(\frac{\hbar t}{ma^2}\right)^2\right]}\right)$

The maximum of this ***Gaussian function*** is at the position

$$x=\frac{\hbar k_0 t}{m}$$

The maximum moves with the ***group velocity***

$$v=\frac{\hbar k_0}{m}$$

But the wave packet “flattens”: at t = 0 the width of $|\psi|^2$ is just ‘a’, and at a later time (formally speaking : at an earlier time as well) its width is given by

$$a' = a\sqrt{1+\left(\frac{\hbar t}{ma^2}\right)^2}$$

(e) Independently of time, the normalization condition for a particle has to be

$$A = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = A^2 a \times \int_{-\infty}^{\infty} e^{-\xi^2} d\xi$$

$$= |A|^2 a\sqrt{\pi}$$

$$\therefore \qquad A = \frac{1}{\left(a\sqrt{\pi}\right)^{\frac{1}{2}}}$$

As this condition is valid only for the absolute value of A, the phase of the wave remains undetermined.

1.3 The Principle of Superposition

The radical change in the physical concepts of motion in quantum mechanics as compared with Classical mechanics demands an equally radical change in mathematical formalism of the theory.

We consider first of all the way in which states are described in quantum mechanics. The state of a system can be described by a definite (in general complex) function $\psi(q)$ of the coordinates.

The square of the modulus of this function determines the probability distribution of the values of the coordinates:

$|\psi|^2 dq$ ***determines the probability that a measurement performed on the system will find the values of the coordinates to be in the element*** dq ***of configuration space***. ψ is called the wave function of the system. [E. Schrodinger1926]

- A knowledge of the wave function allows us, in principle, to calculate the probability of the various results of measurement (not necessary of the coordinates) also. The most general form of such as an expression is

$$\iint \psi(q)\ \psi^*(q')\ \phi(q,q')\ dq\ dq'$$

Where the function $\phi(q,q')$ depends on the nature of and the result of the measurement and the integration is extended over all configuration space.

For example of $\phi(q,q')=\delta(q-q_0)\delta(q'-q_0)$, then expression (1) determines the probability for a particle having $q=q_0$.

- The state of the system, and with it the wave function, in general varies with time. In this sense the wave function can be regarded as a function of time also. If we know $\psi(t)$ we also know $\psi(t+\delta t)$
- $\int|\psi|^2 dq=1$
- If $\int|\psi|^2 dq=$ diverges, then $|\psi|^2$ at two different points of configuration space determines the relative probability of the corresponding values of the coordinates.
- Note that normalized wave function is determined only to within a constant phase factor of the form $e^{i\alpha}$ (where α is any real number). This indeterminacy is in principle irremovable; it is however, unimportant since it has no effect upon any physical results.
- If $\psi_1(q) \xrightarrow{measurement}$ definite result 1

  $\psi_2(q) \xrightarrow{\qquad}$ definite result 2

  Then $C_1\psi_1+C_2\psi_2$ gives a state in which that measurement leads to either result 1 or result 2. Moreover if time dependence of ψ_1 is $\psi_1(q,t)$ and ψ_2 is $\psi_2(q,t)$

  then $C_1\psi_1(q,t)+C_2\psi_2(q,t)$ gives possible dependence of state on this.
- All equations satisfied by wave function must be ***linear*** in ψ.
- Consider a system composed of two parts, and suppose that the state of this system is given in such a way that each of its parts is completely described. Then the probability of q_1 ,the first part ,is independent of the probabilities of the coordinates q_2 of the other part:

  Thus $\psi_{12}(q_1,q_2)=\psi_1(q_1)\psi_2(q_2)$

  Also $\psi_{12}(q_1,q_2,t)=\psi_1(q_1,t)\psi_2(q_2,t)$

1.4 Operations

Let us consider some physical quantity f which characterizes the state of a quantum system. Strictly, we should speak in the following discussion not of one quantity, but of complete set of them at the same time. For brevity, we work in terms of only one physical quantity.

Eigen Values : The values which a given physical quantity can take. The set of these is referred to as the spectrum of eigen values of the given quantity.

In Classical Mechanics : quantities run through a continuous series of values.

In Quantum Mechanics also, there are physical quantities. (e.g. coordinate) whose eigenvalues occupy a continuous range. In such cases we speak of a continuous spectrum of eigenvalues.

As well as such quantities, however, there exist in Quantum Mechanics others whose eigenvalues form some discrete set; [discrete spectrum].We shall suppose that the quantity f considered here has a discrete spectrum.

The eigen values are denoted by f_n $[n = 0, 1, ...]$

The corresponding wave function of the system by ψ_n

Each of these wave function is supposed ***normalized***:

$$\boxed{\int |\psi_n|^2 \, dq = 1}$$

$$\boxed{\psi = \sum_n a_n \psi_n}$$

Conclusion : Any wave function can be, as we say, expanded in terms of the eigenfunctions of any physical quantity. A set of function in term of which such an expansion can be made is called a ***complete set***.

$|a_n|^2$ determines the ***probability*** of the corresponding value f_n of the quantity f in the state with wave function ψ.

$$\boxed{\sum_n |a_n|^2 = 1} \tag{3}$$

If the function ψ were not normalized then the relation (3) would not hold either. The sum $\sum |a_n|^2$ would then be given by some expression bilinear in ψ and ψ^*, and becoming unity when ψ was normalized. Only the integral $\int \psi \psi^* \, dq$ is such an expression.

Thus $\sum a_n a_n^* = \int \psi \psi^* \, dq$ (4)

$$= \int \psi \sum_n a_n^* \psi_n^* \, dq$$

$$\sum_n a_n a_n^* = \sum_n a_n^* \int \psi_n^* \, \psi \, dq$$

$$\therefore \qquad a_n = \int \psi \, \psi_n^* \, dq \tag{5}$$

If we substitute $\psi = \sum_n a_n \psi_n$ in (5)

$$a_n = \int \psi_n^* \sum_m a_m \psi_m \, dq$$

$$= \sum_m a_n \int \psi_n^* \psi_m \, dq \qquad \therefore \qquad \boxed{\int \psi_m \psi_n^* \, dq = \delta_{nm}}$$

Thus the set of eigenfunctions ψ_n forms a ***complete set*** of ***normalized and Orthogonal (Orthonormal)*** functions.

- We now introduce the concept of mean value $\overline{f}$ of the quantity f in the given state.

$$\overline{f} = \sum_n f_n |a_n|^2$$

We shall write $\overline{f}$ in the form of an expression which does not contain the coefficients a_n, but the function ψ itself.

We introduced a mathematical operator $\hat{f}$ defined as follows.

$$\overline{f} = \int \psi^* \left(\hat{f} \psi \right) dq$$

$$\therefore \qquad \overline{f} = \sum_n f_n \, a_n \, a_n^* = \int \psi^* \left(\sum_n a_n \, f_n \psi_n \right) dq$$

$$\hat{f}\psi = \hat{f} \sum_n a_n \psi_n = \sum_n a_n \, \hat{f} \psi_n = \sum_n a_n \, f_n \psi_n$$

Comparing

$$\hat{f}\psi = \sum_n a_n \, f_n \psi_n$$

$$= \sum_n f_n \psi_n \int \psi_n^* \psi \, dq$$

$$\hat{f}\psi = \int K(q, q') \psi(q') \, dq'$$

Where $K(q, q') = \sum_n f_n \psi_n^*(q') \psi_n(q)$

And $K(q,q')$ is called ***Kernel*** of the operator

Here $\hat{f}$ is linear operator

$$\hat{f}(\psi_1+\psi_2)=\hat{f}\psi_1+\hat{f}\psi_2$$

$$a\psi = a\hat{f}\psi$$

Here $\psi_1 \; and \; \psi_2$ are arbitrary functions and *a* is arbitrary constant.

Thus for every physical quantity in quantum mechanics there is a definite corresponding operator.

If ψ is one of the eigenfunction ψ_n i.e. all $a_n=0$, except one

$$\hat{f}\psi_n = f_n\psi_n$$

We write $\hat{f}\psi = f\ \psi$

Both the eigen values of a real physical quantity and its mean value in every state are equal. This imposes a restriction on the operators; so their average is real.

$$\therefore \qquad \int \psi^* \hat{f}\psi\, dq = \int \psi\, \hat{f}^* \psi^*\, dq$$

- Transposed operator $\tilde{\hat{f}}$

$$\int \phi\left(\hat{f}\psi\right)dq = \int \psi\left(\tilde{\hat{f}}\phi\right)dq$$

Note : complex physical quantities i.e. whose eigenvalues are complex.

$$\Rightarrow \tilde{\hat{f}} = \hat{f}^* \qquad \text{Hermitian}$$

- $\hat{f}\psi_n = f_n\psi_n, \qquad \hat{f}\psi_m = f_m\psi_n$

$$\Rightarrow (f_n - f_m)\int \psi_n\psi_m^*\, dq = 0$$

Complete set of simultaneously measurable physical quantities $f, g, \ldots$ Their operators correspond to $\hat{f}, \hat{g}, \ldots$. ψ_n corresponds to simultaneous eigenstate.

- Complex conjugate quantity $f^* \to \hat{f}^\dagger$

$$\left(\overline{f^*}\right) = \int \psi^* \hat{f}^\dagger\ \psi\, dq$$

$$= [\int \psi^* \hat{f}\psi\, dq]^*$$

$$= \int \psi\, \hat{f}^* \psi^*\, dq$$

$$= \int \psi^* \, \tilde{\hat{f}}^* \, \psi \, dq$$

$$\therefore \qquad \hat{f}^{\dagger} = \tilde{\hat{f}}^*$$

Addition and Multiplication of Operators:

$$f, g \longrightarrow \hat{f}, \hat{g}$$

Then $f + g \longrightarrow \hat{f} + \hat{g}$

- The significance of adding different physical quantities in quantum mechanics depends considerably on whether the quantities are or not simultaneously measurable.
- If f and g are simultaneous measurable, the operators $\hat{f}$ and $\hat{g}$ have common eigenfunctions, which are also eigenfunctions of $\hat{f} + \hat{g}$, and the eigenvalues of the operator $\hat{f} + \hat{g}$ are equal to the sums $f_n + g_n$.
- But if f and g cannot take simultaneously definite values, their sum $f + g$ has a more restricted significance. We can assert only that the mean value of this quantity in any state is equal to the sum of the mean values of the separate quantities:

  $$\overline{f + g} = \overline{f} + \overline{g}$$
- The eigen values and eigen functions of the operator $\hat{f} + \hat{g}$ will not, in general, now bear any relation to those of the quantities $f + g$ .It is evident that if $\hat{f}$ and $\hat{g}$ are Hermitians, the operator $\hat{f} + \hat{g}$ will be so too, so that its eigenvalues are real and are equal to those of the new quantity $f + g$ thus defined.
- The following theorem should be noted. Let f_0 and g_0 be the smallest eigenvalues of the quantities f and g and $(f + g)_0$ that of the quantity $f + g$, then

  $$(f + g)_0 \geq f_0 + g_0$$

  (the equality holds if f and g can be measured simultaneously).

Proof : Let the quantity $f + g$ in some state has the mean values $(f + g)_0$ i.e. the least value, then

$$\overline{f + g} \equiv (f + g)_0$$

$$\therefore \qquad \overline{f+g} = \overline{f} + \overline{g}$$

$$\because \overline{f} \geq f_0$$

$$\overline{g} \geq g_0$$

$$\therefore \qquad \overline{f+g} = (f+g)_0 \geq f_0 + g_0$$

Product of Two Quantities *fg* :

Case I: If f and g are simultaneously measurable

$$\hat{f}\,\hat{g}\psi_n = f\,g_n\psi_n = g_n\,\hat{f}\psi_n = g_n\,f_n\psi_n$$

$$\hat{g}\,\hat{f}\psi_n = g_n\,f_n\psi_n$$

$$\because \psi = \sum a_n\psi_n$$

$$\left[\hat{f}\,\hat{g} - \hat{g}\,\hat{f}\right]\psi = 0 \qquad \because \psi \text{ is arbitrary } \therefore \hat{f}\,\hat{g} - \hat{g}\,\hat{f} = 0$$

- The converse of the theorem is also here:

  If operators $\hat{f}$ and $\hat{g}$ commute , then all their eigenfunctions can be taken common to both.

- $\hat{f}^p$ (p is an integer) ------------ eigenvalues are f^p
- $\phi(\hat{f})$ -------------- eigenvalue are $\phi(f)$
- $\hat{f}^{-1}$ is defined as $\boxed{\hat{f}\,\hat{f}^{-1} = \hat{f}^{-1}\hat{f} = 1}$
- If f and g cannot be measured simultaneously, the concept of their product does not have the same direct meaning.
- This appears in the fact that the operator $\hat{f}\,\hat{g}$ is non Hermitian and hence can not correspond to any real physical quantity.

$$\because \int \psi\,\hat{f}\,\hat{g}\,\phi\,dq = \int \psi\,\hat{f}(\hat{g}\phi)\,dq$$

$$= \int (\hat{g}\phi)\,\widetilde{\hat{f}}\,\psi\,dq = \int\left(\widetilde{\hat{f}}\phi\right)\hat{g}\phi\,dq$$

$$= \int \phi\,\widetilde{g}\,\widetilde{\hat{f}}\,\psi\,dq$$

- Again

$$\int \psi\,\hat{f}\,\hat{g}\,\phi\,dq = \int \phi\,\tilde{\hat{f}}\,\hat{g}\,\psi\,dq$$

$$\therefore \widetilde{\left(\hat{f}\,\hat{g}\right)} = \tilde{\hat{g}}\,\tilde{\hat{f}}$$

$$\therefore \left(\widetilde{\hat{f}\,\hat{g}}\right)^{*} = \left(\tilde{\hat{g}}\right)^{*}\left(\tilde{\hat{f}}\right)^{*}$$

$$\left(\hat{f}\,\hat{g}\right)^{\dagger} = \hat{g}^{\dagger}\,\hat{f}^{\dagger} \equiv \hat{g}\,\hat{f} \qquad \text{(if } \hat{f} \text{ and } \hat{g} \text{ are Hermitian)}$$

- We note that, from the products $\hat{f}\,\hat{g}$ and $\hat{g}\,\hat{f}$ of two non commuting Hermitian operators, we can from an Hermitian operator, a symmetrical product: $\frac{1}{2}\left[\hat{f}\,\hat{g}+\hat{g}\,\hat{f}\right]$
- $\hat{f}\,\hat{g}-\hat{g}\,\hat{f}$ is an anti Hermitian operator$[\tilde{\hat{f}} = -\hat{f}^{*}]$
- $i\left[\hat{f}\,\hat{g}-\hat{g}\,\hat{f}\right]$Hermitian
- $\left\{\hat{f},\hat{g}\right\} = \hat{f}\,\hat{g}-\hat{g}\,\hat{f}$
- $\left\{\hat{f}\,\hat{g},\hat{h}\right\} = \left[\hat{f},\hat{h}\right]g+\hat{f}\left[\hat{g},\hat{h}\right]$

We notice that, if $\left[f,h\right]=0$, $\left[g,h\right]=0$ it does not in general follow that $\hat{f}$ and $\hat{g}$ commute.

The Continuous Spectrum:

- f be a physical quantity having continuous spectrum
- f also denote the eigen values
- ψ_f eigenfunction.
- $\psi(q)=\int a_f\psi_f(q)df$

where the integration is extended over the whole range of values than can be taken by the quantity f.

- We try to normalize the functions ψ_f in such a way $\left|a_f\right|^2 df$ is the probability that the physical quantity concerned, in the state described by the wave function ψ, has a value between f and $f+df$. Since the sum of the probabilities of all possible values of f must be equal to unity, we have

$$\int\left|a_f\right|^2 df = 1 \quad \text{and} \quad \left|\sum_n \left|a_n\right|^2 = 1\right|$$

- Proceeding in exactly the same way as before, we write

$$\int \psi \psi^* \, dq = \int \left| a_f \right|^2 df \tag{1}$$

and $$\int \psi \psi^* dq = \iint a_f^* \psi_f^* \psi \, df \, dq \tag{2}$$

$\therefore$ from (1) and (2)

$$\int a_f^* \, a_f \, df = \int df \, a_f^* \int \psi_f^* \psi dq$$

$$\therefore \; a_f = \int \psi_f^* \psi \, dq$$

$$a_f = \int \psi(q) \psi_f^*(q) dq$$

$$a_f = \int a'_{f'} \left(\int \psi_{f'}(q) \psi_f^*(q) dq \right) df'$$

$$\therefore \; \int \psi_{f'}(q) \psi_f^*(q) dq \equiv \delta(f' - f) \qquad \text{(A)}$$

- The function $\psi_f(q)$ satisfy still another relation similar to (A). To derive this we proceed as follows:

$$\psi(q) = \int a_f \psi_f(q) df$$

$$\because \; a_f = \int \psi(q) \psi_f^*(q) dq \qquad \text{(substituting)}$$

$$= \int \psi(q') \left(\int \psi_f^*(q') \psi_f(q) df \right) dq'$$

$$\text{Here} \therefore \; \int \psi_f^*(q') \psi_f(q) df = \delta(q' - q)$$

- There is, of course, an analogous relation for a discrete spectrum:

$$\boxed{\sum_n \psi_n^*(q') \psi_n(q) = \delta(q' - q)}$$

Compare the following formulae:

$$\psi(q) = \int a_f \psi_f(q) df$$

and

$$\int \psi_{f'} \psi_f^* \, dq = \delta(f' - f)$$

with

$$a_f = \int \psi(q) \psi_f^*(q) dq$$

$$\int \psi_f^*(q') \psi_f(q) df = \delta(q' - q)$$

$$\underset{\substack{\uparrow \\ \text{wave function} \\ \text{in the} \\ f \text{ representation}}}{a(f)} \longleftrightarrow \underset{\substack{\uparrow \\ \text{wave function} \\ \text{in the} \\ q \text{ represention}}}{\psi(q)}$$

$|\psi(q)|^2$ determines the probability for the system to have coordinates lying in a given interval dq.

$|a(f)|^2$ determines the probability for the values of the quantity f to lie in a given interval df.

$\psi_f(q)$ are eigenfunctions of the quantity f in q representation

$\psi_f^*(q)$ are eigenfunction of the coordinate q in f representation.

Let $\phi(f)$: some function of quantity f (one to one relations). Each of the functions $\psi_f(q)$ can then be regarded as an eigenfunction of the quantity ϕ.

Here, however, the normalization of these functions must be changed : The eigenfunction $\psi_f(q)$ of the quantity ϕ must be normalized by the condition:

$$\int\psi_{\phi(f')}\psi^*_{\phi(f)}\,dq=\delta[\phi(f')-\phi(f)]$$

Whereas the function ψ_f are normalized by the condition

$$\boxed{\int\psi_{f'}\psi_f^*(q)\,dq=\delta(f'-f)}$$

- The argument of the delta function becomes zero only for $f'=f$. As f' approaches f,

We have

$$\phi(f)-\phi(f)=\frac{d\phi(f)}{df}.(f'-f)$$

$$\therefore\qquad \delta\,[\phi(f')-\phi(f)]=\frac{1}{\left|\frac{d}{df}\phi(f)\right|}\delta(f'-f)$$

Comparing this

$$\int\psi_{f'}\psi_f^*\,dq=\delta(f'-f)$$

We see that the function $\psi_{\phi(f')}$ and $\psi_{\phi(f)}$ are related by

$$\int\psi_{\phi(f')}\psi^*_{\phi(f)}\,dq=\delta[\phi(f')-\phi(f)]$$

$$=\frac{1}{\left|\frac{d}{df}\phi(f)\right|}\delta(f'-f)$$

$$=\frac{1}{\left|\frac{d}{df}\phi(f)\right|}\cdot\int\psi_f\psi_f^*\,dq$$

$$\psi_{\phi(f)}=\frac{1}{\sqrt{\left|\frac{d}{df}\phi(f)\right|}}\psi_f$$

- $\psi(q)=\sum_n a_n\psi_n(q)+\int a_f\psi_f(q)df$
- $\bar{q}=\int q|\psi|^2 dq=\int\psi^* q\psi\, dq$

  $\therefore \hat{q}\equiv q$
- The eigen functions of this operator must be determined:

  $\therefore\ q\psi_{q_0}=q_0\psi_{q_0}$

Since this equation can be satisfied either by $\psi_{q_0}=0$ or by $q=q_0$, it is clear that the eigen functions which satisfy the normalization condition are

$$\psi_{q_0}=\delta\left(q=q_0\right)$$

Energy and Momentum:

The Hamiltonian Operator:

The wave function ψ completely determines the state of a physical system in quantum mechanics. This means that, if this function is given at some instant, not only are all the properties of the system at that instant described, but its behaviour at all subsequent instants is determined (only, of course, to the degree of completeness which is generally admissible in quantum mechanics).

- That is, the value of the derivative $\frac{\partial\psi}{\partial t}$ must be determined by the value of the function itself at that instant.
- By the principle of superposition, the relation between $\frac{\partial\psi}{\partial t}$ and ψ must be linear,

  $i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi$,where $\hat{H}$ is some linear operator.
- Since the integral of $\int\psi\psi^*\,dq$ is a constant independent of time, we have

$$\frac{d}{dt}\int|\psi|^2 dq=\int\frac{\partial\psi^*}{\partial t}dq+\int\psi^*\frac{\partial\psi}{\partial t}dq=0$$

or $$\frac{1}{-i\hbar}\int\left(\hat{H}^*\psi^*\right)\psi\,dq+\int\psi^*\frac{\hat{H}}{i\hbar}\psi\,dq=0$$

or $$-\frac{1}{i\hbar}\int\psi^*\,\tilde{\hat{H}}^*\psi\,dq+\frac{1}{i\hbar}\int\psi^*\hat{H}\psi\,dq=0$$

or $$\frac{1}{i\hbar}\int\Bigg[\psi^*\Bigg[\hat{H}-\tilde{\hat{H}}^*\Bigg]\psi\,dq=0$$

Since this equation must hold for an arbitrary function ψ, it follows that we must have identically $\hat{H}^{\dagger}=\hat{H}$; ***the operator*** $\hat{H}$ ***is therefore Hermitian***.

- Let us find the physical quantity to which it corresponds

  To do this, we use the limiting expression for the wave function and write

$$\psi = ae^{\frac{iS}{\hbar}}$$

$$\therefore \frac{\partial\psi}{\partial t}=\frac{i}{\hbar}\frac{\partial S}{\partial t}\psi$$

(the slowly varying amplitude need not be differentiated)

The operator $\hat{H}$ reduces to simply multiplying by $-\frac{\partial S}{\partial t}$,

$-\frac{\partial S}{\partial t}$ is the physical quantity in which the Hermitian operator $\hat{H}$ passes

$\hat{H}$: Hamiltonian of the system concerned :

$\boxed{i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi}$ is called the wave equation.

The Differentiation of Operators w.r.t. Time :

- The concept of the derivative of a physical quantity w.r.t. time cannot be defined in quantum mechanics(QM) in the same way as in Classical Mechanics(CM). For the definition of the derivative in C.M. involves the consideration of the values of the quantity at two neighboring but distinct instants of time.
- In QM however, a quantity which at some instant has a definite value does not in general have definite values at subsequent instants;

  Hence the derivative w.r.t. time must be differently defined in QM.
- It is natural to define derivative $\dot{\hat{f}}$ of a quantity $\hat{f}$ as the quantity whose mean value is equal to the derivative w.r.t. time of the mean $\hat{f}$:

$$\bar{\dot{f}}=\dot{\bar{f}}$$

$$\overline{\dot{f}} = \dot{\bar{f}} = \frac{d}{dt}\int \psi^* \hat{f}\,\psi\, dq$$

$$= \int \psi^* \frac{\partial f}{\partial t}\psi\, dq + \int \frac{\partial \psi^*}{\partial t}\hat{f}\,\psi\, dq + \int \psi^* \hat{f}\frac{\partial \psi}{\partial t} dq$$

$$= \int \psi^* \frac{\partial \hat{f}}{\partial t}\psi\, dq + \frac{1}{-i\hbar}\int H^* \psi^* \hat{f}\,\psi\, dq + \int \psi^* \hat{f}\frac{1}{i\hbar}\hat{H}\psi\, dq$$

$$= \int \psi^* \left[\frac{\partial \hat{f}}{\partial t} + \frac{1}{i\hbar}\left[\hat{f}\hat{H} - \hat{H}\hat{f}\right]\right]\psi\, dq$$

Since, on the other hand, we must have, by the definition of mean values, $\overline{\dot{f}} = \int \psi^* \hat{\dot{f}}\,\psi\, dq$, it is seen that the expression in parenthesis in the integrand is the required operator $\hat{\dot{f}}$;

$$\therefore\ \hat{\dot{f}} = \frac{\partial \hat{f}}{\partial t} + \frac{i}{\hbar}\left[\hat{H}\hat{f} - \hat{f}\hat{H}\right]$$

If $\frac{\partial \hat{f}}{\partial t} = 0, \Rightarrow \hat{\dot{f}} = \frac{i}{\hbar}\left[\hat{H}, \hat{f}\right]$

A very important class of physical quantities is formed by those whose operators do not depend explicitly on time, and also commute with $\hat{H}$, so that

$$\overline{\dot{f}} = \dot{\bar{f}} = 0$$

or $\quad \bar{f} = \text{constant}$

- In other words, the mean value of the quantity f has a definite value

We can also assert that, if in a given state the quantity f has a definite value (i.e. the wave function is an eigen function of the operator $\hat{f}$), then it will have a definitive value (the same on) at subsequent instant also.

1.5 Stationary States

The Hamiltonian of a closed system (and a system in a constant external field) can not contain the time explicitly. This follows from the fact that for such a system, all times are equivalent. Since, on the other hand, any operator commutes with itself, we reach the conclusion that ***Hamilton's function is conserved for systems which are not in a varying external field***.

As it is well known, ***a Hamilton's function which is conserved is called the energy***. The law of conservation of energy in QM signifies that, if in a given state the energy has a definite value, this value remains constant in time.

The states in which the energy has definite values are called "stationary states" of a system. They are described by wave function $\psi_n(q)$

$$\hat{H}\psi_n = E_n\psi$$

$$\therefore \psi_n = e^{-\frac{i}{\hbar}E_n t}\psi_n(q)$$

$$\hat{H}\psi(q) = E\psi$$

Smallest possible value of the energy: normal or ground state of the system

$$\boxed{\psi = \sum_n a_n e^{-\frac{i}{\hbar}E_n t}\psi_n(q)}$$

The squared modulus $|a_n|^2$ ***of the expansion coefficients, as used, determines that probabilities of various values of the energy of the system.***

- The probability distribution for the coordinates in a stationary state is determined by

  $|\overline{\psi}_n|^2 = |\psi_n|^2$; (it is independent of time)

  The same is true of the mean values

  $$\bar{f} = \int \psi_n^* \hat{f}\psi\, dq = \int \psi_n^* \dot{\hat{f}}\psi_n\, dq$$

- Among the various stationary states, there may be some which correspond to the same value of the energy (the same energy level of the system), but differ in the values of some other physical quantities. Such energy levels, to which several different stationary states correspond, are said to the ***degenerate***.

  Physically, the possibility that degenerate levels can exist is related to the fact that energy does not in general form by itself a complete set of physical quantities.

Theorem : If $\hat{f}$ and $\hat{g}$ are two conserved quantities then if $\hat{f}$ and $\hat{g}$ do not commute, then the energy levels of the system are in general degenerate:

Proof: Let ψ wave function of stationary state in which, besides the energy, the quantity $\hat{f}$ also has a definite value.

Then we can say that $\hat{g}\psi$ does not coincide with ψ; if it did, then would mean that the quantity g also had a definite value, which is impossible, since f and g cannot be measured simultaneously.

On the other hand $\hat{g}\psi$ is an eigenfunction of $\hat{H}$ corresponding to the same value E of the energy as in ψ.

$$\hat{H}\left(\hat{g}\psi\right)=\hat{g}\,\hat{H}\,\psi=E\left(g\psi\right)$$

Thus we see that the energy E corresponds to more than one eigen function i.e. energy level is degenerate.

It is clear that any linear combination of wave function corresponding to the same degenerate energy level is also an eigen function for that value of the energy.

In other words, the choice of eigen function of a degenerate level is not unique.

Arbitrary selected eigen function of a degenerate energy level are not, in general, orthogonal. By a proper unique of linear combinations of them, however, we can always obtain a set of orthogonal (and normalized) eigen functions (and this can be done in infinitely ways;

For the number of independent coefficient in a linear transformation of n functions is n^2, while the number of normalization and orthogonality condition for n function is $\frac{1}{2}n\left(n+1\right)$ i.e. less than n

1.6 Uncertainly Relation

Let $\delta x=\sqrt{\overline{\left(x-\bar{x}\right)^2}}$, $\delta p_x=\sqrt{\overline{\left(p_x-\bar{p}_x\right)^2}}$ be defined as ***Standard Deviations***.

We can specify exactly the least possible value of their product.

Let us consider the one dimensional case of a wave packet with wave function $\psi\left(x\right)$ depending on only one coordinate, and assume for simplicity that the mean values of x and p_x in this state are zero.

We consider the obvious inequality:

$$\int_{-\infty}^{\infty}\left|\alpha\,x\psi+\frac{d\psi}{dx}\right|^2dx\geq 0$$,where α is an arbitrary real constant.

On calculating this integral, noticing that

$$\int x^2 |\psi|^2 dx = (\delta x)^2$$

$$\int \left[x\psi^* \frac{d\psi}{dx} + \frac{d\psi^*}{dx} . x\psi \right] dx$$

$$= \int x \frac{d}{dx} |\psi|^2 dx = x|\psi|^2 - \int |\psi|^2 dx = 0 - 1$$

$$\left| \alpha x\psi + \frac{d\psi}{dx} \right|^2 = \left(\alpha x\psi^* + \frac{d\psi^*}{dx} \right) \left(\alpha x\psi + \frac{d\psi}{dx} \right)$$

$$= \alpha^2 x^2 |\psi|^2 + \alpha x\psi^* \frac{d\psi}{dx} + \frac{d\psi^*}{dx} \alpha x\psi + \frac{d\psi^*}{dx} \frac{d\psi}{dx}$$

$$\int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx = \frac{d\psi^*}{dx} \psi - \int \frac{d^2\psi^*}{dx^2} . \psi \, dx$$

$$0 - \frac{1}{(-i\hbar)^2} \int \psi \, p^2 \psi^* \, dx = \frac{1}{\hbar^2} (\delta p_x)^2$$

$\alpha^2 (\delta x^2) - \alpha + \frac{1}{\hbar^2} (\delta p_x)^2 \geq 0$ .If this quadratic (in α) is possible for all α, its discriminant must be negative

$$\alpha = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{4}{4} (\delta x)^2 . \frac{1}{\hbar^2} (\delta p_x)^2}$$

$$(\delta x)^2 \frac{1}{\hbar^2} (\delta p_x)^2 > \frac{1}{4}$$

$$or \; \boxed{(\delta x)(\delta p_x) > \frac{\hbar}{2}}$$

The least possible value of the product is $\frac{\hbar}{2}$, and occurs for wave packets with wave functions of the form:

$$\psi = \frac{1}{(2\pi)^{\frac{1}{4}} \sqrt{(\delta x)}} \exp \left[\frac{i}{\hbar} p_0 x - \frac{x^2}{4(\delta x)^2} \right]$$

Where p_0 and δx are constants,

The probabilities of the various values of the coordinates in such a state are:

$$|\psi|^2 = \frac{1}{\sqrt{2x}} . \frac{1}{(\delta x)} exp \left[- \frac{x^2}{2(\delta x)^2} \right]$$

- The wave function in the momentum representation

$$a(p_x) = \int \psi(x) e^{-\frac{i}{\hbar} p_x x} dx$$

$$= \text{constant.}\exp\left[-\frac{(\delta x)^2 (p_x - p_0)^2}{\hbar^2}\right]$$

$|a(p_x)|^2$ is the probability of values of momentum

1.7 The Stern-Gerlach Experiment

When we attempt to apply classical mechanics and electrodynamics to explain atomic phenomena, they lead to results which are in obvious conflict with experiments.

This is very clearly seen from the Contradiction obtained on applying ordinary electrodynamics to a model of an atom in which the electrons move round the nucleus in classical orbits.

During such motion, as in any accelerated motion of charges the electrons would have to emit electromagnetic waves continually. By this emission, the electrons would lose their energy and this would eventually cause them to fall into the nucleus. Thus according to classical electrodynamics the atom would be unstable, which does not at all agree with reality.

This marked contradiction between theory and experiment indicates that the construction of a theory applicable to atomic phenomena – that is phenomena occurring in particles of very small mass at very small distances –demands a fundamental modification of the basic physical concepts and laws.

As a starting-point for an investigation of these modifications, it is convenient to analyze the Stern-Gerlach experiment. This experiment illustrates in a dramatic manner the necessity for a radical departure from the concepts of classical mechanics.

Description of the Stern-Gerlach Experiment :

In the Stern-Gerlach (SG) experiment, silver atoms are heated in an oven. The oven has a small hole through which some of the silver atoms escape. As shown in Figure 1, the beam goes through a collimator and is then subjected to an

inhomogeneous magnetic field produced by a pair of pole pieces, one of which has a very sharp edge.

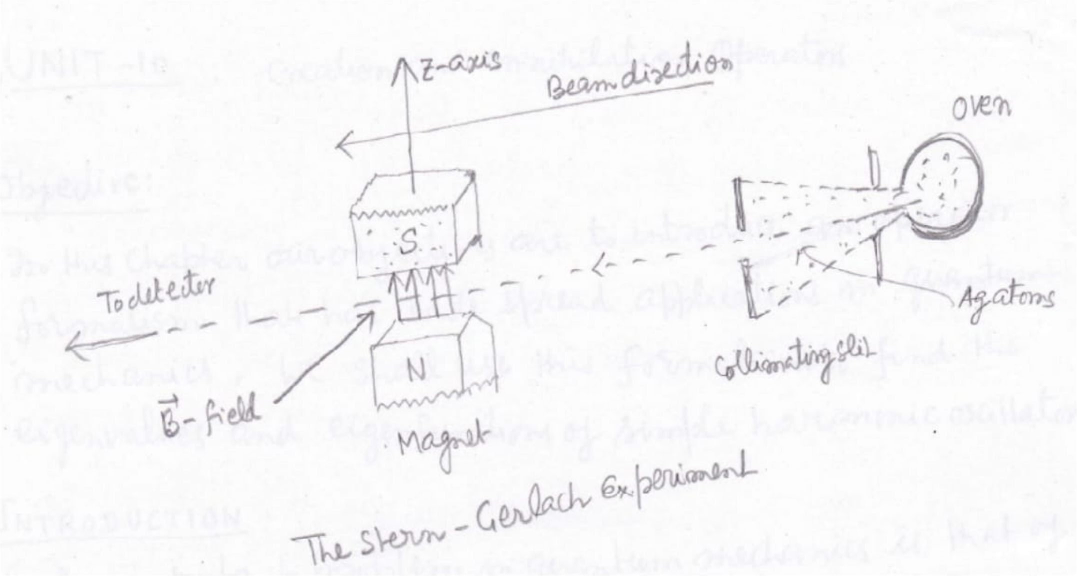


Figure1

The ***silver atom*** is made up of a nucleus and 47 electrons where 46 out of the 47 electrons can be visualized as forming a spherically symmetrical electron cloud with no net angular momentum.

If we ignore the nuclear spin, we see that the atom as a whole does have an angular momentum, which is due solely to the spin angular momentum of the 47th (5s) electron.

The 47 electrons are attached to the nucleus, which is $\sim 2 \times 10^5$ times heavier than the electron; as a result the heavy atom as a whole possess a magnetic moment equal to the spin magnetic moment of the 47th electron.

As a consequence, the magnetic moment $\vec{\mu}$ of the atom is proportional to electron spin $\vec{S}$:

$$\vec{\mu} \; \alpha \; \vec{S}$$

$$or \; \vec{\mu} = \frac{e}{m_e c} \; \vec{S} \qquad (e < 0)$$

The interaction energy of the magnetic moment with the magnetic field is :

$$U = -\vec{\mu} . \vec{B}$$

Therefore the Z-component of the force experienced by the atom is

$$F_z = -\frac{\partial U}{\partial z} = \frac{\partial}{\partial z}(\vec{\mu}\,.\vec{B})$$

$$= \frac{\partial}{\partial z}(\mu_z B_z)$$

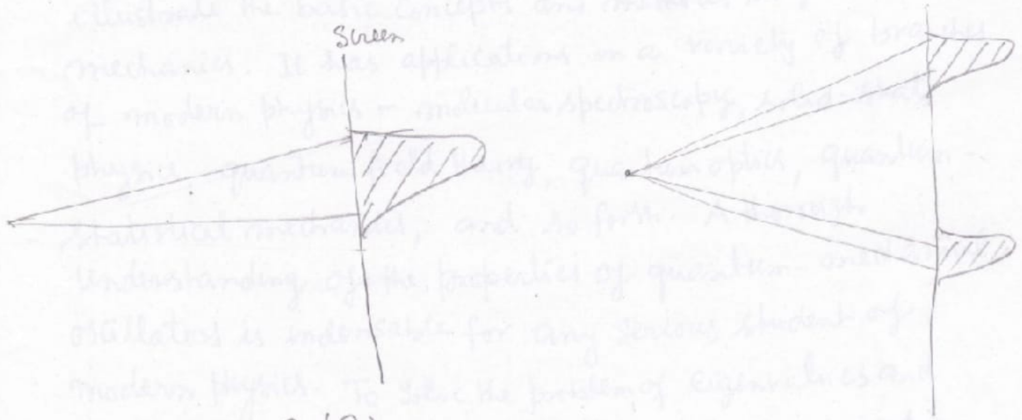
$$= \mu_z \,\frac{\partial B_z}{\partial z}$$

If $S_z < 0$, then $\mu_z > 0$ (Because $\mu_z = \frac{e}{m_e c} S_z$ and $e < 0, S_z < 0$ then atom experiences downward force, while the $\mu_z < 0\ (S_z > 0)$ atom experiences an upward force.

The ion beam is then expected to get split according to the values of μ_z. In other words, the SG (Stern-Gerlach) apparatus "measures" the Z-component of $\vec{\mu}$, or equivalently, the Z-component of $\vec{S}$.

The atoms on the oven are randomly oriented; there is no preferred direction for the orientation of $\vec{\mu}$.

If the electron were like a classical spinning object, we would expect all values of μ_z to be realized between $|\vec{\mu}|$ and $|\vec{\mu}|$. This would lead us to expect a continuous bundle out beams out of the SG apparatus (See figure 2a). Instead, What we experimentally observe is more like the situation in figure (2b).



2 (a)

2·(b)

Beams from the Stern-Gerlach apparatus; (a) is expected from classical physics, while (b) is actually observed

In other words, the S.G. apparatus splits the original silver beam into two distinct components, a phenomena referred to in the early days of quantum theory as "***space quantization***".

To the extent that $\vec{\mu}$ can be identified within a proportionality factor with the electron spin $\vec{S}$, only two possible values of the Z-component of $\vec{S}$ are observed to be possible, S_z up and S_z down, which we call $S_z +$ and $S_z -$. It turns out to be

$$S_z += \frac{1}{2}\hbar \ \ and\ S_z - = \ -\frac{1}{2}\ \hbar$$

$$\boxed{S_z + = \frac{1}{2}\hbar \ and\ S_z - = -\frac{1}{2}\hbar}$$

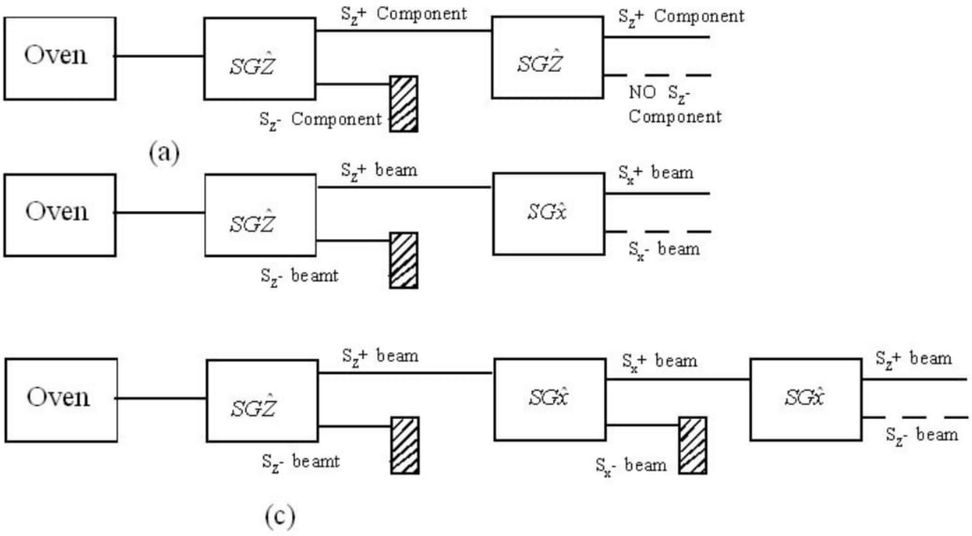
where $\hbar = 1.0546 \times 10^{-34}\ Js$

This "quantization" of the electron spin angular momentum is the first important feature we deduce from the SG experiment.

Of course we could equally choose inhomogenous field, say in the x-direction, with the beam proceeding in the y-direction. In this manner we could have separated the beam from the oven into an a $S_x +$ component and $S_x -$ component.

1.8 Sequential Stern-Gerlach Experiment

We now consider a sequential Stern-Gerlach experiment. By this we mean that the atomic beam goes through two or more SG apparatuses in sequence.



Sequential Stern-Gerlach Experiments (Fig. 2)

In the figure 2(a), we block the $S_z -$ component and let the remaining $S_z +$ component be subjected to another $SG\hat{Z}$ apparatus. This time there is only one beam component : $S_z +$ component. This result is understandable in the sense that if the atom spins are up, they are expected to remain so.

In the figure (2b), the $S_z +$ beam that enters the second apparatus ($SG\hat{x}$) is now split into two components, an S_x +component and an $S_x -$ component.

1.9 Kets, Bras and Operators

The analysis of the stern-Gerlach experiment lead us to consider a complex vector space. In the following we formulate the basic mathematics of vector spaces as used in quantum mechanics. We use the bra and ket notation developed by P.A.M. Dirac.

We consider a complex vector space whose dimensionality is specified according to the nature of a physical system under consideration.

In the Stern-Gerlach type experiments where the only quantum-mechanical degree of freedom is the spin of an atom, the dimensionality is just two, corresponding to the two possible values S_z can assume.

Later we consider the case of continuous spectra -for example the position (coordinate) or momentum of a particle - where the number of alternatives is infinite, in which case the vector space in question is known as a Hilbert space after D. Hilbert, who studied vector spaces infinite dimensions.

In quantum mechanics a physical state, for example, a silver atom with a definite spin orientation is represented by a state vector in a complex vector space.

Following Dirac, we call such a vector a ket and denote it by $|\alpha\rangle$. The state ket is postulated to contain complete information about the physical state; everything we are allowed to ask about the state is contained in the ket.

Two kets can be added :

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle \tag{1}$$

The sum $|\gamma\rangle$ is just another ket

If we multiply $|\alpha\rangle$ by a complex number C, the resulting product C$|\alpha\rangle$is another ket.

It makes no difference whether the number C stands on the left or on the right of a ket.

i.e. $C\,|\alpha\rangle = |\alpha\rangle C$ (2)

In the particular case where C is zero, the resulting ket is said to be a null ket.

One of the physical postulates is that $|\alpha\rangle$ and $C|\alpha\rangle$, with $C \neq 0$, represents the same physical state. In other words only the "direction" in the vector space is of significance.

1.10 Observable

An observable such as momentum and spin components, can be represented by an operator such as A, in the vector space in question.

Quite generally, an operator acts on a ket from the left.

$$\boxed{A|\alpha\rangle = a|\alpha\rangle} \tag{3}$$

Which is yet another ket. In general, $A|\alpha\rangle$is not a constant times $|\alpha\rangle$. However there are particular ket of importance, known as eigenkets of operator A, denoted by

$$|a'\rangle,\ |a''\rangle,\ |a'''\rangle\ ,\dots \tag{4}$$

With the property

$$\begin{aligned} A\,|a'\rangle &= a'|a'\rangle \\ A|a''\rangle &= a''\,|a''\rangle \end{aligned} \tag{5}$$

where $a', a''\dots$ are just numbers.

Notice that applying A to an eigenket just reproduces the same ket apart from a multiplicative number.

The set of numbers $\{a', a'', a''', \dots.\}$ is called the set of eigenvalues of operator A.

The physical state corresponding to an eigenket is called an eigenstate.

In the simplest case of spin $\frac{1}{2}$ systems, the eigenvalue-eigenket relation is expressed as

$$\begin{aligned} S_z\,|S_z;\,+\rangle &= \frac{\hbar}{2}\ |S_z;\,+\rangle \\ S_z\,|S_z;\,-\rangle &= \frac{\hbar}{2}\ |S_z;\,-\rangle \end{aligned} \tag{6}$$

Where are $|S_z;\,\pm\rangle$ eigenkets of S_z with eigenvalues $\pm\frac{\hbar}{2}$.

If we consider eigenkets of S_x , we can write

$$S_x\,|S_x;\,+\rangle \;=+\frac{\hbar}{2}\;|S_x;\,+\rangle$$

$$S_x\,|S_x;\,-\rangle = -\frac{\hbar}{2}\;|S_x;\,-\rangle \qquad (7)$$

It is to be noted that the dimensionality of the vector space is determined by the number of eigenkets of an observable A.

More formally, we are concerned with an N-dimensional vector space spanned by the N eigenkets of observable A. Any arbitrary ket $|\alpha\rangle$ can be written as

$$|\alpha\rangle \;=\; \sum_{a'} C_{a'}\,|a'\rangle \qquad (8)$$

With a', a'', ... upto $a^{(N)}$ where $C_{a'}$ is a complex coefficient.

Bra Space :

The vector space we have been dealing with is a ket space. We now introduce the concept of a bra space, ***a vector space "dual to" the ket space***.

We postulate that corresponding to every ket $|\alpha\rangle$ there exists a bra, denoted by $\langle\alpha|$in this dual, or bra, space.

The bra space is spanned by eigenbras $\{\langle a'|\}$ which correspond to the eigenkets $\{|a'\rangle\}$.

There is a one-to-one correspondence between a ket space and a bra space.

$$|\alpha\rangle \overset{DC}{\leftrightarrow} \langle\alpha|$$

$$|a'\rangle\,,|a''\rangle\,,\ldots.\overset{DC}{\leftrightarrow} \langle a'|,\langle a''|\;,\ldots\}$$

$$|\alpha\rangle \;+\; |\,\beta\rangle \qquad \overset{DC}{\leftrightarrow} \quad \langle\alpha| \;+\; \langle\beta| \qquad (9)$$

where DC stands for dual correspondence.

Roughly speaking, we can regard the bra space as some kind of mirror image of the ket space.

The bra dual to $C|\alpha\rangle$ is postulated to be $C^*\langle\alpha|$, not $C\langle\alpha|$,which is a very important point. More generally we have.

$$C_\alpha|\alpha\rangle + \;C_\beta|\beta\rangle \;\leftrightarrow\; {C_\alpha}^*\langle\alpha| \;+\; {C_\beta}^*\langle\beta| \qquad (10)$$

Inner Product:

We now define the ***inner product*** of a bra and a ket. The product is written as a bra standing on the left and a ket standing on the right, for example.

$$\langle\beta|\alpha\rangle = (\langle\beta|).(|\alpha\rangle) \tag{11}$$

This product is, ***in general, a complex number***.

We postulate two fundamental properties of inner products :

(i) $\boxed{\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle^*}$ (12)

(ii) $\boxed{\langle\alpha|\alpha\rangle \geq 0}$ (13)

Where the equation sign holds only is $|\alpha\rangle$ is a null ket.

Two kets $|\alpha\rangle$ and $|\beta\rangle$ are ***orthogonal*** if

$$\langle\alpha|\beta\rangle = 0 \tag{14}$$

The orthogonality relation also implies :

$$\langle\beta|\alpha\rangle = 0 \tag{15}$$

Given a ket which is not a null ket, we can form a normalized ket $|\tilde{\alpha}\rangle$ where

$$|\tilde{\alpha}\rangle = \left(\frac{1}{\sqrt{\langle\alpha|\alpha\rangle}}\right)|\alpha\rangle \tag{16}$$

With the property $\langle\tilde{\alpha}|\tilde{\alpha}\rangle = 1$ (17)

Quite generally $\sqrt{\langle\alpha|\alpha\rangle}$ is known as the norm of $|\alpha\rangle$.

Operators :

We now consider a ket vector which is a linear function of a ket vector and this will lead to the concept of a linear operator.

Suppose we have a ket $|F\rangle$ which is a function of a ket $|A\rangle$ i.e. to each ket $|F\rangle$there corresponds one ket $|F\rangle$and suppose further that the function is a linear one, which means that the $|F\rangle$ corresponding to $|A\rangle + |A'\rangle$ is the sum of the $|F\rangle's$ corresponding to $|A\rangle$ and to $|A'\rangle$, and the $|F\rangle$ corresponding to $C|A\rangle$ is C times the$|F\rangle$ corresponding to$|A\rangle$, C being any number.

Under these conditions, we may look upon the passage from $|A\rangle$ to $|F\rangle$ as the application of a linear operator to $|A\rangle$. Introducing the symbol α for the linear operator α we may write

$$|F\rangle = \alpha\,|A\rangle$$

In which the result of α operating on $|A\rangle$is written like a product of α with $|A\rangle$

We make the rule that in such products the Ket-vector must always be put on the right of the linear operator.

The above ***conditions of linearity*** may now be expressed by the equations :

$$\alpha\,\{|A\rangle + |A'\rangle\} = \alpha\,|A\rangle + \alpha\,|A'\rangle$$
$$\alpha\{C|A\rangle\} = C\,\alpha|A\rangle$$

A linear operator is considered to be completely defined when the result of its application to every ket vector is given.

Thus a linear operator is to be considered ***zero or "Null***" if the result of its application to every ket vanishes.

Two operators are said to be considered equal if they produce the same result when applied to every ket.

The sum of two linear operators is defined to be that linear operator which, operating on any ket, produces the sum of what the two linear operators separately would produce. Thus $\alpha + \beta$ isdefined by

$$(\alpha + \beta)|A\rangle = \alpha|A\rangle + \beta\,|A\rangle \quad for\ any\,|A\rangle.$$

Linear operators can also be multiplied together, the product of two linear operators being defined as that linear operators, the application of which to any ket produces the same result as the application of two linear operators successively in symbols

$$\{\alpha\beta\}|A\rangle = \alpha\,\{\beta\,|A\rangle\}$$

However this triple product is in general not the same as what we should get if we operated on $|A\rangle$first with α and then with β.

In general $\alpha\,\beta\,|A\rangle$differs from $\beta\alpha\,|A\rangle$.***The commutative axiom of multiplication does not hold for linear operators.*** It may happen as a special case that two linear operators ξ and η are such that $\xi\eta$ and $\eta\,\xi$ are equal. In this case we say that ξ commutes with η ,or ξ and η commute.

An operator α always acts on a bra from the rigid side.

$$(\langle\,A|)\ .\alpha = \langle\,A|\alpha$$

and the resulting product is another bra.

The ket $\alpha\,|A\rangle$and the bra $\langle\,A|\alpha$ are in general, not dual to each other.

We define the symbol $\alpha^{\dagger}$ as

$$\alpha\,|A\rangle \leftrightarrow \langle A|\alpha^{\dagger}.$$

The operator $\alpha^{\dagger}$ is called the ***Hermitian adjoint*** or simply the adjoint of α.

An operator α is said to be ***Hermitian*** if $\alpha = \alpha^{\dagger}$.

Outer product :

So far, we have considered the following products :

$\langle\beta|\alpha\rangle, X|\alpha\rangle, \langle\alpha|X$ and XY. Are there other products we are allowed to form? Let us multiply $|\beta\rangle$, and $\langle\alpha|$, in that order. The resulting product

$$(|\beta\rangle).(\langle\alpha|) = |\beta\rangle\langle\alpha|$$

is known as the ***outer product*** of $|\beta\rangle$ and $\langle\alpha|$.

It is easy to see that $|\beta\rangle\langle\alpha|$is an operator as it gives a new ket when applied as a ket $|P\rangle$:

$$\begin{aligned}\{|\beta\rangle\langle\alpha|\}\,|P\rangle &= |\beta\rangle\langle\alpha|P\rangle\\ &= C|\beta\rangle\\ &= a\ new\ ket\ |\beta\rangle\end{aligned}$$

Let $X = |\beta\rangle\langle\alpha|$

Then $X^{\dagger} = |\alpha\rangle\langle\beta|$

1.11 Illustrative Examples

Example 2: Consider two operators $\hat{O}_1$ and $\hat{O}_2$ and defined by the following operations :

$$\hat{O}_1\Psi(x) = \Psi(x) + x$$

$$\hat{O}_2\Psi(x) = \frac{d}{dx}\Psi(x) + 2\Psi(x)$$

Check for the linearity of $\hat{O}_1$ and $\hat{O}_2$.

Sol. Let us check for the linearity of $\hat{O}_1$ first.

$$\begin{aligned}\hat{O}_1[\Psi_1(x) + \Psi_2(x)] &= \Psi_1(x) + \Psi_2(x) + x\\ &\neq \hat{O}_1\Psi_1(x) + \hat{O}_1\Psi_2(x)\end{aligned}$$

Thus $\hat{O}_1$is not a linear operator. On the other hand.

$$\hat{O}_2[\Psi_1(x) + \Psi_2(x)] = \frac{d}{dx}\{\Psi_1(x) + \Psi_2(x)\} + 2\,[\Psi_1(x) + \Psi_2(x)]$$

$$= \left[\frac{d\ \Psi_1(x)}{dx} + 2\Psi_1(x)\right] + \left[\frac{d\ \Psi_2(x)}{dx} + 2\Psi_2(x)\right]$$

$$= \hat{O}_2 \Psi_1\ (x) + \hat{O}_2 \Psi_2\ (x)$$

It is also easy to see that

$$\hat{O}_2 C\,\Psi(x) = C\ \hat{O}_2\,\Psi(x)$$

Thus $\hat{O}_2$ is linear operator.

Example 3: Use the uncertainty relation to estimate the ground state energy and the radial coordinates of the ground state position of electron in the hydrogen atom.

Sol. If r is the radial coordinate then according to the uncertainty relation

$pr \sim \hbar$ This allows us to express the energy in terms of r :

$$E = \frac{p^2}{2m} - \frac{e^2}{r}$$

$$= \frac{\hbar^2}{2mr^2} - \frac{e^2}{r^2}$$

The minimum value of the energy is obtained from

$$\frac{\partial E}{\partial r} = -\frac{\hbar^2}{mr^3} + \frac{e^2}{r^2} = 0$$

That is , $r = \frac{\hbar^2}{me^2} = \frac{\hbar}{m\ c\ \alpha}$, $where\ \alpha = \frac{e^2}{\hbar c}$

and the corresponding value of E is $E = -\frac{1}{2}\ mc^2\alpha^2$.

As another example consider the problem of nuclear forces. These have the range of the order of one Fermi, that is am. This $10^{-13}\ cm.$ This implies $p \sim \frac{\hbar}{r} \sim 10^{-14}\ gm\ \frac{cm}{sec}$.

The kinetic energy corresponding to this momentum is :

$$\frac{p^2}{2M} \sim \frac{10^{-28}}{3.2 \times 10^{-24}} \sim 3\ \times\ 10^{-5}\ ergs$$

where M is the nucleon (proton or neutron) mass, which is $1.6\ \times\ 10^{-24}$gm. Since the potential that gives rise to the binding must more than compensate for this we require that

$$|V| \geq 3\ \times\ 10^{-5}\ ergs\ \geq 20\ MeV.$$

Again this is only a rough order of magnitude, but it does indicate that the potential energy is to be measured in MeV rather than in eV as in atoms.

1.12 Self Learning Exercise

Q.1 Test the following operators for linearity :

(a) $\hat{O}_1\Psi(x) = x^2\Psi(x)$ (b) $\hat{O}_2\Psi(x) = exp\,(\Psi(x))$

(c) $\hat{O}_3\Psi(x) = \Psi^*(x)$ (d) $\hat{O}_4\Psi(x) = x^2\,\frac{d\Psi(x)}{dx}$

Q.2 A certain system is described by the Hamiltonian operator.

$H = -\frac{d^2}{dx} + x^2$. Show that $A\,x\,\exp(\frac{-x^2}{2})$ is an eigenfunction of H and determine the eigenvalue ; also find A by normalization.

1.13 Summary

In this unit we have introduced what we might call the "quantum mechanical way of thinking" at a very early stage. We have introduced the concept of localized wave packets and their propagation. We have introduced the remarkable "principle of superposition of quantum mechanical states." This principle is the "positive" principle on which we have introduced the development of quantum mechanics. The concept of stationary states has been elaborated. The concept of an "observable" and its representation by Hermitian operator has been elaborated.

1.14 Glossary

Eigenfunction: operator $\hat{A}$ operates on function f , then in a such type of expression $\hat{A}f = af$, eigen function is f and eigenvalue is a .

Orthonormal Functions: Thus the set of eigenfunctions ψ_n forms a complete set of normalized and Orthogonal (Orthonormal) functions if $\int \psi_m \psi_n^* \, dq = \delta_{nm}$

Stationary States :The states in which the energy has definite values are called "stationary states" of a system.

1.15 Answers to Self Learning Exercise

Ans.1:

(a) $\hat{O}_1[\Psi_1(x) + \Psi_2(x)] = x^2[\Psi_1(x) + \Psi_2(x)]$

$$= x^2\Psi_1 + x^2\Psi_2$$
$$= \hat{O}_1\Psi_1 + \hat{O}_1\Psi_2$$

and

$\hat{O}_1 C\ \Psi(x) = C\ \hat{O}_1 \Psi(x)$

Thus $\hat{O}_1 is\ linear$

(b) $\hat{O}_2[\Psi_1(x) + \Psi_2(x)] = exp\ [\Psi_1(x) + \Psi_2(x)]$

$$\neq exp\ [\Psi_1(x) + exp\ \Psi_2(x)]$$

$Thus$ $\hat{O}_2$ is not a linear operator.

(c) $\hat{O}_3[\Psi_1(x) + \Psi_2(x)] = [\Psi_1(x) + \Psi_2(x)]^*$

$$= \Psi_1^*(x) + \Psi_2^*$$

$$= \hat{O}_3 \Psi_1(x) + \hat{O}_3 \Psi_2(x)$$

However $\hat{O}_3\{C\ (\Psi_1(x) + \Psi_2(x))\}$

$$= \{C\ (\Psi_1(x) + \Psi_2(x))\}^*$$

$$= C^* \Psi_1^*(x) + C^* \Psi_2^*(x)$$

$$= C^*\{\Psi_1^*(x) + \Psi_2^*(x)\}$$

$$= C^* \hat{O}_3 \{\Psi_1(x) + \Psi_2(x)\}$$

Thus $\hat{O}_3$ is not a linear operator. $\hat{O}_3$ is antilinear operator.

Note : An antilinear operator is defined as.

$$\hat{O}\{\Psi_1 \Psi_2\} = \hat{O}\Psi_1 + \hat{O}\Psi_2$$

$$and\quad \hat{O}\ C\ \Psi\{x\} = C^* \hat{O}\Psi\ (x)$$

(d) $\hat{O}_4\ \Psi\ (x) = x^2 \frac{d\ \Psi\ (x)}{dx}$. To check the linearity of $\hat{O}_4$ we proceed as

$$\hat{O}_4(\Psi_1 + \Psi_2) = x^2 \frac{d}{dx}(\Psi_1 + \Psi_2)$$

$$= x^2 \frac{d\Psi_1}{dx} + x^2 \frac{d\Psi_2}{dx}$$

$$= \hat{O}_4 \Psi_1 + \hat{O}_4 \Psi_2$$

and $\hat{O}_4(C\ \Psi\ (x)) = x^2 \frac{d}{dx} C\ \Psi\ (x)$

$$= C\ x^2 \frac{d}{dx} \Psi\ (x)$$

$= C\ \hat{O}_4\ \Psi\ (x)$Thus $\hat{O}_4$ is linear

1.16 Exercise

Q.1 The unnormalizd ground state wave f unction of a particle is given as $\Psi_0(x) = exp\left(\frac{-\alpha^4 x^4}{4}\right)$ with eigenvalue $E_0 = \frac{h^2 \alpha^2}{m}$. What is the potential in which the particle moves?

Q.2 $\Psi_1$and Ψ_2 are two linearly independent and normalized (but not orthogonal) eigenfunctions of H belonging to the same eigenvalue (i.e. they are degenerate).

(a) Show that $C_1\, \Psi_1 + C_2\, \Psi_2$ is also an eigenfunction of H belonging to the same eigenvalue as Ψ_1 or Ψ_2.

(b) Construct two linear combinations of Ψ_1 and Ψ_2 that are orthogonal to each other.

Q.3 In Yukawa meson theory of nuclear forces, Yukawa proposed that the nuclear forces arises through the emission of a new quantum, the pi-meson (also called pion), by one of the nucleons, and its absorption by the other.

If the mass of the quantum is denoted by μ , then by uncertainty principle calculate the order of the μc^2

1.17 Answers to Exercise

Ans.3 : If the mass of the quantum is denoted by μ , then its emission introduces an energy by μ and its emission introduces an energy imbalance $\Delta E \sim \mu c^2$, which can only take place for a time $\Delta t \sim \frac{\hbar}{E} \sim \frac{\hbar}{\mu c^2}$.

The range corresponding to a particle travelling for this time is of the order of $c\Delta t \sim \frac{\hbar}{\mu c}$.

If we take for the range $r_0 = 1.4 \times 10^{-13}\ cm$, then we find that :

$$\mu c^2 - \frac{\hbar c}{r_0} = \frac{10^{-27} \times 3 \times 10^{10}}{1.4 \times 10^{-13}} Ergs$$

$$= 130\ MeV$$

when the pion was finally discovered, it was found that this estimate was remarkably accurate, since for the pion $\mu\, c^2 - 140\ MeV$.

References and Suggested Readings

1. P.A.M. Dirac ,Principle of Quantum Mechanics, Fourth edition, Oxford University Press,1958
2. J. J. Sakurai, Modern Quantum Mechanics (2nd Edition), Addison-Wesley;2010

UNIT-2

Base Kets, Matrix Representations and Expectation Values

Structure of the Unit

2.0 Objectives

In this unit we will develop a powerful, abstract way of representing and working with the notion of a 'state' of a quantum mechanical system. This abstract description was invented by Paul Dirac. Dirac's motivation was to find a formalism of quantum mechanics that integrated Schrodinger's wave mechanics and Heisenberg's matrix mechanics.

In this chapter we will learn to replace the abstract quantities namely bra vectors, ket vectors, and linear operators by sets of numbers with analogous mathematical properties and to work in terms of these sets of numbers. The way in which the abstract quantities are to be replaced by numbers is not unique ,there being many possible ways corresponding to the many systems of coordinates one can have in geometry. Each of these ways is called a 'representation' and the set of numbers that replace an abstract quantity is called the 'representative' of that abstract quantity in the representation .In this unit we shall study the following:

- Eigenkets as base kets
- Completeness relation or closure
- Representative of a ket vector, a bra vector
- Matrix representation of an operator
- Matrix multiplication rule
- Measurements, observables and the uncertainty relations
- Examples

2.1 Introduction

The matrix representation of physical quantities was introduced by Heisenberg in 1925, before Schrödinger's discovery of the wave equation. In the following we shall show that an abstract ket vector will be represented by a set of numbers in a representation in which the basic vectors of representation are eigenvectors of a complete set of commuting observables. These set of numbers form a column vector of a matrix. Similarly a bra vector will be represented by a set of numbers forming a row vector. An operator will be represented by a square matrix. Matrix representation of state vectors and observables is very convenient while solving quantum problems.

2.2 Eigenkets as Base Kets

In the following we shall represent ket-vector, bra-vector and operators by the matrix. For this we need basic vectors of representation. As we know that eigenkets of an observable form a complete set, they can be used as basic kets of representation. Any arbitrary ket $|\alpha\rangle$ can be expanded in terms of the eigenkets of an observable :

$$|\alpha\rangle = \sum_{a'} C_{a'} |a'\rangle \qquad (1)$$

Multiplying $\langle \alpha'' |$ on the left and using the orthonormality property of the eigenkets of A we get

$$\langle a''|\alpha\rangle = \sum_{a'} C_{a'}\langle a''|a'\rangle$$

$$\langle a''|\alpha\rangle = C_{a''}$$

In a similar way we can write

$$\langle a'|\alpha\rangle = C_{a'} \qquad (2)$$

We can now write the equation (1) as

$$|\alpha\rangle = \sum_{a'} \langle a'|\alpha\rangle|a'\rangle$$

$$= \sum_{a'} |a'\rangle\langle a'^{|\alpha\rangle} \qquad (3)$$

Because the ket $|\alpha\rangle$is arbitrary, we must have

$$\boxed{\sum_{a'} |a'\rangle\langle a'| = 1} \qquad (4)$$

Where 1 on the right hand side of (4) is to be understood as ***the identity operator. Eq. (4) is known as the completeness relation or closure.***

If an observable ξ is having continuous eigenvalue spectrum denoted by ξ' (say) the unit operator in this case is

$$\int |\xi'\rangle d\xi'\langle \xi'| \equiv 1 \qquad (5)$$

i.e. $\sum_{a'}|a'\rangle\langle a'| = 1 \quad \xrightarrow[\text{is replaced by}]{} \quad \int|\xi'\rangle d\xi'\langle \xi'|$

The relationship (4) or (5) is very important. Given a chain of kets ,operators, or bras multiplied in legal orders, we can insert, in any place at our convenience, the identity operator written in form (4).

As an illustration $\langle\alpha|\alpha\rangle$ can be written as follows :

$$\langle\alpha|\alpha\rangle = \left\langle \alpha \middle| \left(\sum_{a'} |a'\rangle\langle a'| \right) \middle| \alpha \right\rangle$$

$$= \sum_{a'} \langle\alpha|a'\rangle\langle a'|\alpha\rangle$$

$$= \sum_{a'} |\langle a'|\alpha\rangle|^2 \qquad (6)$$

This shows that if $|\alpha\rangle$ is normalized, then the expansion coefficients must satisfy

$$\sum_{a'} |C_{a'}|^2 = \sum_{a'} |\langle a'|\alpha\rangle|^2 = 1 \qquad (7)$$

Let us now look at $|a'\rangle\langle a'|$. This is an outer product, so it is an operator. Let it operate on $|\alpha\rangle$:

$$(|a'\rangle\langle a'|)|\alpha\rangle = |a'\rangle \langle a'|\alpha\rangle = C_{a'}|a'\rangle \qquad (8)$$

We see that $|a'\rangle\langle a'|$ selects that portion of the ket $|\alpha\rangle$ parallel to $|a'\rangle$ so $|a'\rangle\langle a'|$ is known as projection-operator along the base ket $|a'\rangle$ and is denoted by

$$\Lambda_{a'} = |a'\rangle\langle a'| \qquad (9)$$

The completeness relation (4) can now be written as :

$$\sum_{a'} \Lambda_{a'} = 1 \qquad (10)$$

What are base kets?

The eigenkets of an 'observable' form a 'Complete set'. Any ket, whatsoever it may be, can always be expanded in terms of the eigenkets of the observable. These eigenkets of an observable are called 'base kets'.

2.3 Matrix Representation

We can represent an operator, say X, by a square matrix. We write the operator X as :

$$X = \sum_{a''} |a''\rangle\langle a''|X| \sum_{a'} |a'\rangle\langle a'|$$

$$= \sum_{a''}\sum_{a'} |a''\rangle\langle a''|X|a'\rangle\langle a'| \qquad (11)$$

There are all together N^2 numbers of the form $\langle a''|X|a'\rangle$, where N is the dimensionality of the ket space. We may arrange them into an $N \times N$ square matrix such that the column and row indices appear as follows :

$$\underset{\text{row}}{\langle a''|} X \underset{\text{column}}{|a'\rangle} \qquad (12)$$

Explicitly we may write the matrix as :

$$X \doteq \begin{bmatrix} \langle a^{(1)}|X|a^{(1)}\rangle & \langle a^{(1)}|X|a^{(2)}\rangle & \ldots\ldots \\ \langle a^{(2)}|X|a^{(1)}\rangle & \langle a^{(2)}|X|a^{(2)}\rangle & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots \end{bmatrix} \qquad (13)$$

Where the symbol $\doteq$ stands for “is represented by”

Using the following assumption of quantum mechanics.

$$\langle A|B\rangle = \langle B|A\rangle^* \qquad (14)$$

We can write

$$\langle a''|X|a'\rangle = \langle a'|X^\dagger|a''\rangle^* \qquad (15)$$

If an operator ,say B ,is Hermitian then

$$B^\dagger = B \qquad (16)$$

Then

$$\langle a''|B|a'\rangle = \langle a'|B|a''\rangle^* \qquad (17)$$

Matrix Multiplication of Operator :

Consider the matrix representation of the operator relation.

$$Z = X\,Y.$$

It can be written as :

$$\begin{aligned} \langle a''|Z|a'\rangle &= \langle a''|XY|a'\rangle \\ &= \textstyle\sum_{a'''}\langle a''|X|a'''\rangle\langle a'''|Y|a'\rangle \end{aligned} \qquad (18)$$

Eq. (18) is just the matrix multiplication rule.

We now consider the ket relation :

$$|\gamma\rangle \quad = X|\alpha\rangle \tag{19}$$

It can be represented as

$$\langle a'|\gamma\rangle \;=\; \langle a'|X|\alpha\rangle$$

$$= \sum_{a''} \langle a'|X|a''\rangle \langle a''|\alpha\rangle$$

But this can be seen as an application of the rule for multiplying a square matrix with a column matrix representing once the expansion coefficients of $|\alpha\rangle\ and\ |\gamma\rangle$ arrange themselves to form column matrices as follows :

$$|\alpha\rangle = \begin{bmatrix} \langle a^{(1)}|\alpha\rangle \\ \langle a^{(2)}|\alpha\rangle \\ \langle a^{(3)}|\alpha\rangle \\ .. \\ .. \end{bmatrix}, \quad |\gamma\rangle = \begin{bmatrix} \langle a^{(1)}|\gamma\rangle \\ \langle a^{(2)}|\gamma\rangle \\ \langle a^{(3)}|\gamma\rangle \\ .. \\ .. \end{bmatrix} \tag{20}$$

A bra is represented by a row matrix:

$$\langle\gamma| = \left[\langle\gamma|a^{(1)}\rangle\ ,\langle\gamma|a^{(2)}\rangle,\ \dots,\dots,\dots..\right]$$

$$= \left[\langle a^{(1)}|\gamma\rangle^{\,*}\ ,\langle a^{(2)}|\gamma\rangle^{\,*},\ \dots,\dots,\dots..\right] \tag{21}$$

The inner product $\langle\beta|\alpha\rangle$ is written as

$$\langle\beta|\alpha\rangle \;=\; \sum_{a'} \langle\beta|a'\rangle\ \langle a'|\alpha\rangle$$

$$= \left[\langle a^{(1)}|\beta\rangle^{\,*}\ ,\langle a^{(2)}|\beta\rangle^{\,*},\dots,\dots..\right] \begin{bmatrix} \langle a^{(1)}|\alpha\rangle \\ \langle a^{(2)}|\alpha\rangle \\ .. \\ .. \end{bmatrix} \tag{22}$$

Finally the outer product $|\beta\rangle\langle\alpha|$ written as

$$|\beta\rangle\langle\alpha| = \begin{bmatrix} \langle a^{(1)}|\beta\rangle\langle a^{(1)}|\alpha\rangle^{\,*} & \langle a^{(1)}|\beta\rangle\,\langle a^{(2)}|\alpha\rangle^{\,*} & \dots \\ \langle a^{(2)}|\beta\rangle\langle a^{(1)}|\alpha\rangle^{\,*} & \langle a^{(2)}|\beta\rangle\,\langle a^{(2)}|\alpha\rangle^{\,*} & \dots \\ \dots & \dots & \dots \end{bmatrix} \tag{23}$$

Also the matrix representation of an observable A becomes particularly simple if eigenkets of A themselves are used as the base kets

$$A = \sum_{a''} \sum_{a'} |a''\rangle\langle a''|A|a'\rangle\langle a'|$$

But the square matrix

$$\langle a''|A|a'\rangle = a'\langle a''|a'\rangle$$

$$= a'\delta_{a''a'} \text{ (i.e. diagonal matrix)}$$

$$\therefore A = \sum_{a'} a'|a'\rangle\langle a'|$$

$$A = \sum_{a'} a' \Lambda_{a'} \tag{24}$$

2.4 Spin Half Systems

It is here instructive to consider the special case of spin $\frac{1}{2}$ systems.

The base kets used are $|S_z;\ \pm\rangle$ which we denote for brevity as $|\pm\rangle$.

The simplest operator in the ket space spanned by $|\pm\rangle$ is the identity operator, which can be written as

$$I = \sum_{a'} |a'\rangle\langle a'|$$

$$= |+\rangle\langle+| + |-\rangle\langle-| \tag{25}$$

According to (24) we can write that any observable A can be written as

$$A = \sum_{a'} a' \Lambda_{a'}$$

Hence we can write S_z as :

$$S_z = \frac{\hbar}{2}|+\rangle\langle+| + \left(-\frac{\hbar}{2}\right)|-\rangle\langle-|$$

$$S_z = \frac{\hbar}{2}\,[|+\rangle\langle+| \;-\; |-\rangle\langle-|] \tag{26}$$

Hence it follows that

$$S_z|+\rangle = \frac{\hbar}{2}\,[|+\rangle\langle+|+\rangle \;-\; |-\rangle\langle-|+\rangle\,] = \frac{\hbar}{2}\,|+\rangle \tag{27}$$

$$(Since\ \langle+|+\rangle \;=1\ and\ \langle-|+\rangle \;=0\,)$$

$$\boxed{\langle+|+\rangle = 1\,,\ \langle+|-\rangle = 0}$$

(Because of the orthonormality properties of $|\pm\rangle$

$$\boxed{S_z|+\rangle = \frac{\hbar}{2}|+\rangle}$$

Similarly

$$\boxed{S_z|-\rangle = -\frac{\hbar}{2}|-\rangle} \tag{28}$$

It is also instructive to look at two other operators :

$$\boxed{S_+ \equiv \hbar|+\rangle\langle-| \;\;,\;\; S_- \equiv \hbar|-\rangle\langle+|} \tag{29}$$

Which are both seen to be ***non-Hermitian***

The operator S_+ acting on the spin-down ket $|-\rangle$, turns $|-\rangle$ into the spin-up ket $|+\rangle$ multiplied by $\hbar$:

$$S_+|-\rangle \equiv \hbar|+\rangle\,\langle-|-\rangle \;\;= \hbar\,|+\rangle.$$

On the other hand, the spin-up ket $|+\rangle$, when acted upon by S_+ becomes a null ket.

$$S_+|+\rangle \equiv \hbar|+\rangle\langle-|+\rangle \;\;= 0$$

So the physical interpretation of S_+ is that it raises the spin component by one unit of $\hbar$. If the spin component cannot be raised any further, we automatically get a null state.

Likewise, S_- can be interpreted as an operator that lowers the spin component by one unit of $\hbar$:

$$S_-\,|-\rangle \equiv \hbar|-\rangle\,\langle+|+\rangle \;\;= \hbar\,|-\rangle.$$

Later we will show that $S_\pm$ can be written as

$$\boxed{S_+ = S_x + iS_y \ , \ S_- = S_x - iS_y}$$

We represent the ket $|+\rangle$ of S_z in the matrix form as

$$|+\rangle = \begin{pmatrix} \langle+|+\rangle \\ \langle-|+\rangle \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\boxed{|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}}$$

and

$$|-\rangle = \begin{pmatrix} \langle+|-\rangle \\ \langle-|-\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\boxed{|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}}$$

and the S_z is represented by a 2×2 matrix.

$$S_z = \begin{pmatrix} \langle+|S_z|+\rangle & \langle+|S_z|-\rangle \\ \langle-|S_z|+\rangle & \langle-|S_z|-\rangle \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2}\hbar\langle+|+\rangle & 0 \\ 0 & -\frac{1}{2}\hbar\langle-|-\rangle \end{pmatrix}$$

$$\boxed{S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} \tag{30}$$

Similarly

$$\boxed{S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \ , S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}} \tag{31}$$

2.5 Measurements, Observables and the Uncertainty Relations

In the words of the great master P.A.M. Dirac "A measurement always causes the quantum system to jump into an eigenstate of the dynamical variable that is being measured".

We interpret Dirac's words as follows : Before a measurement of observable A is made, the system is assumed to be represented by some linear combination.

$$|\alpha\rangle \; = \; \sum_{a'} C_{a'}|a'\rangle \; = \sum_{a'} a'|a'\rangle\langle\, \alpha| \tag{32}$$

When the measurement is performed, the system is "thrown into" one of the eigenstates, say $|a'\rangle$ of observable A. In other words,

$$|\alpha\rangle \; \xrightarrow[\text{a measurement}]{} \; |a'\rangle \tag{33}$$

For example, a silver atom with an arbitrary spin orientation will change into either $|S_z;\, +\rangle$ or $|S_z;\, -\rangle$ when subjected to a Stern Gerlach(SG) apparatus of type $SG\hat{z}$.

Thus a measurement usually changes the state. The only exception is when the state is already in one of the eigenstates of the observable being measured in which case

$$|a'\rangle \; \xrightarrow[\text{a measurement}]{} \; |a'\rangle \tag{34}$$

with certainty.

When the measurement causes $|\alpha\rangle$ to change into $|a'\rangle$,it is said that A is measured to be a'.

It is in this sense that the result of a measurement yields one of the eigenvalues of the observable being measured.

Given (32), which is the state ket of a physical system before the measurement, we do not know in advance into which of the various the $|a'\rangle\,'s$ system will be thrown as the result of the measurement. We do postulate, however, that the probability for jumping into some particular $|a'\rangle$is given by :

Probability for $|a'\rangle is\ \ |\langle a'|\alpha\rangle|^2$ (35)

provided that $|\alpha\rangle$ is normalized.

The probabilistic interpretation of (35) for the squared inner product $|\langle a'|\alpha\rangle|^2$ is one of the fundamental postulates of quantum mechanics, so it cannot be proven.

We define the expectation value of A taken with respect to state$|\alpha\rangle$ as

$$< A > \equiv \langle\alpha|A|\alpha\rangle$$

$$= \sum_{a'} \sum_{a''} \langle \alpha | a'' \rangle \langle a'' | A | a' \rangle \langle a' | \alpha \rangle$$

$$= \sum_{a'} a' \, |\langle a' | \alpha \rangle|^2$$

= measured value a' , probability for obtaining a'

2.6 Illustrative Examples

Example1: If the set of eigenkets $\{|a'\rangle\}$ forms a complete orthonormal set then show that $\sum_{a'} |a'\rangle\langle a'| \equiv 1$.

Sol. We expand and arbitrary ket $|\alpha\rangle$ in terms of eigenkets $\{|a'\rangle\}$, which form a complete set :

$$|\alpha\rangle = \sum_{a'} C_{a'} |a'\rangle \qquad (1)$$

Multiplying (1) by $\langle a'|$ on both sides of (1) :

$$\langle a'|\alpha\rangle = \sum_{a'} C_{a'} \langle a'|a'\rangle$$

$$\therefore \langle a'|\alpha\rangle = C_{a'} \qquad (2)$$

($\langle a'|a'\rangle = 1$ and all other terms in the expansion are zero)

From (1), we now get

$$|\alpha\rangle = \sum_{a'} |a'\rangle\langle a'|\alpha\rangle$$

or $\boxed{\sum_{a'} |a'\rangle\langle a'| \equiv 1}$ (Identity operator)

Example 2: If $C \text{ and } D$ are two arbitrary Hermitian operators, workout which, if any of the following combinations $(i) CD$, $(ii) D^2$, $(iii) CD - DC$, $(iv)\ CDC$ and $(v) CD + DC$

(a) are Hemitian

(b) have real nonnegative expectation value.

(c) have pure imaginary expectation value.

Sol. (i) $(CD)^\dagger = D^\dagger C^\dagger = DC. Hence\ CD\ is\ not\ hermitian.$

(ii) $(D^2)^\dagger = (DD)^\dagger = D^\dagger D^\dagger = DD = D^2.$

$Hence\ D^2$ is hermitian, have real nonnegative expectation value.

(iii)$(CD - DC)^\dagger = (CD)^\dagger - (DC)^\dagger = DC - CD = -(CD - DC).\ is$ $Hence\ (CD - DC)$antihermitian, have pure imaginiary expectation value.

(iv) $(CDC)^\dagger = C^\dagger D^\dagger C^\dagger = CDC\ Hence\ (CDC)$ is Hermitian have real nonnegative expectation value.

(v) $(CD + DC)^\dagger = (CD)^\dagger + (DC)^\dagger = D^\dagger C^\dagger + C^\dagger D^\dagger = DC + CD = CD + DC\ .Hence\ CD + DC$ is hermitian, have real nonnegative expectation value.

Example 3: An electron is in a state described by the spinor given in the S_z basis as

$X = \begin{pmatrix} \frac{i}{\sqrt{5}} \\ \frac{2}{\sqrt{5}} \end{pmatrix}$. What is the probability that the electron has spin up?

Sol.

$$\begin{pmatrix} \frac{i}{\sqrt{5}} \\ \frac{2}{\sqrt{5}} \end{pmatrix} = \frac{i}{\sqrt{5}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{2}{\sqrt{5}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\equiv C_1|+\rangle + C_2|-\rangle$$

∴ Probability that the electron has spin up is

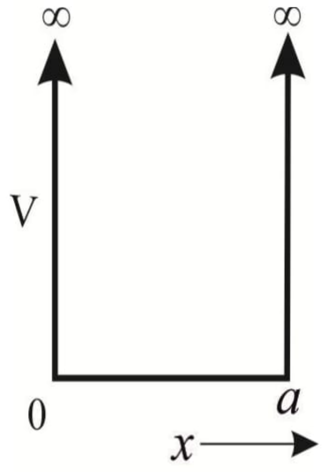
$$|C_1|^2 = \frac{1}{5}.$$

Example 4: A particle in an impenetrable potential box with walls at $x = 0$ and $x = a$ has the following wave function at some initial time :

$$\phi(x) = \frac{1}{\sqrt{5a}}\sin\frac{\pi x}{a} + \frac{3}{\sqrt{5a}}\sin\frac{3\pi x}{a} \qquad (1)$$

What are the possible results of measurement of energy on the system and with what probability would they occur? What is the form of the wave function after such a measurement? Suppose immediately after a measurement, energy is remeasured. What are now the relative probabilities of the possible outcomes?

Sol. An impenetrable potential box is shown below :



Energy eigenvalues of a particle of mass m is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \; with\, n = 1, 2, 3 \ldots\ldots$$

and energy eigenfunction are

$$\Psi_n(x) = \sqrt{\frac{2}{a}}\, \sin\frac{n\pi x}{a}$$

The given wave function (l) shows that the particle is in the superposed state of being in the state $n = 1$ and $n = 3$.The result of measurement on energy is

$$\frac{1}{5a}\left(\frac{\pi^2\hbar^2}{2ma^2}\right) + \frac{9}{5a}\left(\frac{9\pi^2\hbar^2}{2ma^2}\right) = \frac{1}{5a}\,\frac{\pi^2\hbar^2}{2ma^2}(1+8) = \frac{82}{10ma^2}\,\pi^2\hbar^2.$$

After the measurement the system will be thrown into one of the eigenstates corresponding to $n = 1 \; or \; n = 3$.

The probability of finding the system in $n = 1$ is $\frac{1}{5a}$ and in $n = 3$ is $\frac{9}{5a}$.

If the energy is remeasured (immediately after a measurement) then the result of measurement will remain unchanged as the system is now in the one of the eigenstate.

2.7 Self Learning Exercise

Q.1 Express $\langle \beta | \alpha \rangle$ in matrix form

Q.2 Show that the expectation value of an anti-Hermitian operator $(C = -C^{\dagger})$ is purely imaginary.

Q.3 Show that the operator $|a'\rangle\langle a'|$ selects that portion of ket $|\alpha\rangle$ which is parallel to $|a'\rangle$.

Note : (The operator $|a'\rangle\langle a'| \equiv \Lambda_{a'}$ is called the projection operator)

Q.4 Express the operator relationship $Z = XY$ in the matrix form. Obtain the matrix multiplication rule.

2.8 Glossary

Expectation Value: expectation value of quantity A is $\langle A \rangle = \dfrac{\int \psi^* \hat{A} \psi \, dV}{\int \psi^* \psi \, dV}$

Hermitian Operator: Self adjoint operators are called “Hermitian”

Base kets: Basekets are eigenkets of an observable.

Observable: A real dynamical variable whose eigenstates form a complete set is an observable. Thus any quantity that can be measured is an observable.

2.9 Summary

We have seen that basic vectors of representation are eigenkets of an ‘observable’ Any arbitrary ket can always be expanded in terms of the eigenkets of the observable. These eigenkets form a complete set of vectors of representation .Any operator in its own representation, i.e. in which the eigenvectors of the operator are basic vectors of representation, will be a diagonal matrix. Product of two operators will follow the matrix multiplication rule. We have illustrated these rules by the spin $\frac{1}{2}$ system.

2.10 Answers to Self Learning Exercise

Ans.1: $\langle \beta | \alpha \rangle = \sum_{a'} \langle \beta | a' \rangle \langle a' | \alpha \rangle$

$$=\left(\langle a^{(1)}|\beta\rangle^{*},\langle a^{(2)}|\beta\rangle^{*},....\right)\begin{pmatrix}\langle a^{(1)}|\beta\rangle\\ \langle a^{(2)}|\beta\rangle\\ .\\ .\\ .\\ .\end{pmatrix}$$

Ans.2: $\langle\alpha|C|\alpha\rangle=\overline{\langle\alpha|C^{\dagger}|\alpha\rangle}$

$$=\overline{\langle\alpha|-C|\alpha\rangle}$$

$$=-\overline{\langle\alpha|C|\alpha\rangle}$$

i.e. complex conjugate of $\langle\alpha|C|\alpha\rangle$ is –ve. We conclude that $\langle\alpha|C|\alpha\rangle$ is purely imaginary.

Ans.3: Applying the operator $|a'\rangle\langle a'|$ on ket $|\alpha\rangle$

We get $|a'\rangle\langle a'|\alpha\rangle=\langle a'|\alpha\rangle|a'\rangle$

$$=C_{a'}|a'\rangle$$

i.e. we get the ket $|a'\rangle$ multiplied by some constant.

Ans.4: $Z=XY$ (where Z,X,Y are some operators)

Therefore, $\langle a''|Z|a'\rangle=\langle a''|XY|a'\rangle$ (1)

Inserting the unit operator $\sum_{a'''}|a'''\rangle\langle a'''|$ in between in the relation (1), we get

$$\langle a''|Z|a'\rangle=\sum_{a'''}\langle a''|X|a'''\rangle\langle a'''|Y|a'\rangle$$

$$=\sum_{a'''}\langle a''|X|a'''\rangle\langle a'''|Y|a'\rangle$$

This is matrix multiplication rule.

2.11 Exercise

Q.1 Express $|\beta\rangle\langle\alpha|$ in matrix form

Q.2 The matrix representation of two operators A and B are given by

$$A = \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}, B = \begin{pmatrix} 3 & 2 \\ 2 & 1 \end{pmatrix}$$

Find the matrix representation of the product $C = AB$.

Q.3 Show that the expectation value of a Hermitian operator is purely real.

Q.4 Consider the base kets $|S_z;\pm\rangle$ or $(|\pm\rangle)$ of spin $\frac{1}{2}$ systems.

(a) Write identity operator :

(b) Express $\widehat{S}_z$ in terms of projection operator.

(c) Express $|+\rangle$ in the matrix form :

(d) Write S_z operator in matrix form

(e) Write S_+ and S_- operator in matrix form

Q.5 Suppose A and B are compatible observables and the eigenkets of A are nondegenerate. Show that the matrix elements $\langle a''|B|a'\rangle$ are all diagonal.

Q.6 The complete set expansion of an initial wave function $\Psi(x,0)$ of a system in terms of energy eigenfunction Ψ_n of the system has three terms; that is, $n = 1, 2$ and 3. The measurement of energy on the system represented by $\Psi(x,0)$ gives the values E_1 and E_2 with probability of $\frac{1}{4}$ and E_3 with probability $\frac{1}{2}$. Write down the most general expansion of $\Psi(x,0)$ and $\Psi(x,t)$ consistent with the data.

Q.7 Prove the completeness relation or closure.

2.12 Answers to Exercise

Ans.1: $$|\beta\rangle\langle\alpha| = \begin{bmatrix} \langle a^{(1)}|\beta\rangle\langle\alpha|a^{(1)}\rangle & \langle a^{(1)}|\beta\rangle\langle\alpha|a^{(2)}\rangle & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \langle a^{(N)}|\beta\rangle\langle\alpha|a^{(1)}\rangle & \cdots & \cdots & \cdots \end{bmatrix}$$

Ans.2:

$$\langle i|C|j\rangle = \langle i|A\sum_k |k\rangle\langle k|B|j\rangle$$

$$= \sum_k \langle i|A|k\rangle\langle k|B|j\rangle = \sum_k A_{ik}\, B_{ki}$$

$$= \begin{pmatrix} 7 & 4 \\ 8 & 5 \end{pmatrix}$$

Ans.3: $\langle \alpha | A | \alpha \rangle = \overline{\langle \alpha | A^{\dagger} | \alpha \rangle}$

$= \overline{\langle \alpha | A | \alpha \rangle}$ ($\because A^{\dagger} = A$ as A is Hermitian)

So $\langle \alpha | A | \alpha \rangle$ is real.

Ans.4 (a) $1 = \{|+\rangle\langle+|\} + \{|-\rangle\langle-|\}$

(b) $\widehat{S}_z = \left\{\frac{1}{2}\hbar|+\rangle\langle+|\right\} + \left\{\left(-\frac{1}{2}\hbar\right)|-\rangle\langle-|\right\}$

(c)

$$|+\rangle = \begin{pmatrix} \langle+|+\rangle \\ \langle-|+\rangle \end{pmatrix} \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and similarly spin down ket $|-\rangle$ will be represented as $|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

(d) $S_z \doteq \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

(e) It is instructive to look at two other operators :

$S_+ \equiv \hbar|+\rangle\langle-|$, $S_z \equiv \hbar|-\rangle\langle+|$

Thus,

$$S_+ \doteq \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad S_- \doteq \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Ans.5: $\langle a''|[A,B]|a'\rangle = \langle a''|(AB - BA)|a'\rangle = 0$

$\langle a''|[A,B]|a'\rangle - \langle a''|(BA)|a'\rangle = 0$

$a''\langle a''|B|a'\rangle - \langle a''|B|a'\rangle a' = 0$

$(a'' - a')(\langle a''|B|a'\rangle) = 0$

We get $\langle a''|B|a'\rangle = 0$ unless $a'' = a'$.

That is B is diagonal.

Ans.6 : The initial wave function is $\Psi\ (x, 0)$ given as

$$\Psi\ (x, 0) = \frac{1}{2}\ \Psi_1 + \frac{1}{2}\ e^{i\gamma}\,\Psi_2 + \frac{1}{\sqrt{2}} e^{i\delta}\,\Psi_3$$

Since the phases are not determined by the probability data.

As to $\Psi\ (x, t)$ here is the advantage of expanding in terms of energy eigenstates. These states are stationary with time dependence $\exp\left(-i\,\frac{E_n t}{\hbar}\right)$.

Therefore,

$$\Psi\,(x, t) = \frac{1}{2} \exp\left(-i\frac{E_1 t}{\hbar}\right)\ \Psi_1 + \frac{1}{2}\ e^{i\gamma}\ \exp\left(-i\frac{E_2 t}{\hbar}\right) \Psi_2 + \frac{1}{\sqrt{2}}\ e^{i\delta} \exp\left(-i\frac{E_3 t}{\hbar}\right) \Psi_3$$

Ans.7: Consider a normalized ket $|\alpha\rangle$

We express the $\langle\alpha|\alpha\rangle$ as follows :

$$1 = \langle\alpha|\alpha\rangle = \langle\alpha|\sum_{a'}|a'\rangle\langle a'|\alpha\rangle$$

$$= \sum_{a'}\langle\alpha|a'\rangle\langle a'|\alpha\rangle$$

$$= \sum_{a'}|\langle a'|\alpha\rangle|^2$$

or $\sum_{a'}|\langle a'|\alpha\rangle|^2 = 1$

The above relation is a "Closure" property.

References and Suggested Readings

1. P.A.M. Dirac , Principle of Quantum Mechanics, Fourth edition, Oxford University Press,1958
2. Amit Goswami ,Quantum Mechanics, Wm.C.Brown Publishers
3. J. J. Sakurai, Modern Quantum Mechanics (2nd Edition), Addison-Wesley;2010

UNIT-3

Commutability and Compatibility, Uncertainty Relations

Structure of the Unit

3.0 Objectives

In this unit our objectives are to discuss

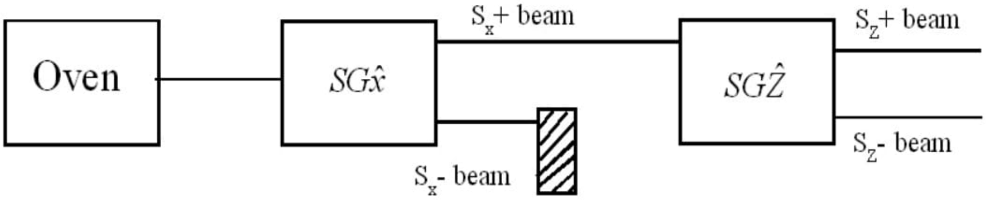
1. Commutability of two observables
2. To find the condition for the existence of a simultaneous eigenstate of two commuting observables
3. What are compatible and incompatible observables?
4. Commutability and compatibility
5. Uncertainty relations

3.1 Introduction

In this chapter we shall study that a state may be simultaneously eigenstate of two observables. The chances for the existence of a simultaneous eigenstate are most favorable if the two observables commute. We shall study the mathematical statement of commutability and compatibility of simultaneously measuring them. From this we shall derive uncertainty relations.

3.2 Spin $\frac{1}{2}$ Systems, once again

We once again consider spin $\frac{1}{2}$ systems. This time we show that the results of sequential Stern-Gerlach experiments, when combined with the postulates of quantum mechanics so far, are sufficient to determine not only the $S_{x,y}$ eigenkets, $|S_x;\ \pm\rangle$and$|S_y;\ \pm\rangle$ but also the operators S_x and S_y themselves. First, we recall that when the $S_x +$ beam is subjected to an apparatus of type $SG\hat{z}$, the beam splits into two components with equal intensities.



This means that the probability for $S_x +$ state to be thrown into$|S_z;\ \pm\rangle$,simply denoted by$|\pm\rangle$ is $\frac{1}{2}$ each ; hence,

$$|\langle +|S_x;\ \pm\rangle| = |\langle -|S_x;\ \pm\rangle| = \frac{1}{\sqrt{2}} \qquad (1)$$

We can therefore construct the $S_x +$ ket as follows :

$$|S_x;\ \pm\rangle = \frac{1}{\sqrt{2}}|\pm\rangle + \frac{1}{\sqrt{2}}\, e^{i\delta_1}|-\rangle \qquad (2)$$

With δ_1 real. The coefficient of $|+\rangle$ can be chosen to be real and positive by convention.

The $S_x -$ ket must be orthogonal to the ket $S_x +$ because the $S_x +$ alternative and $S_x -$ alternative are mutually exclusive. The orthogonality requirement leads to

$$|S_x;\ -\rangle = \frac{1}{\sqrt{2}}|+\rangle - \frac{1}{\sqrt{2}}\, e^{i\delta_1}|-\rangle \tag{3}$$

where we have, again, chosen the coefficient of $|+\rangle$to be real and positive by convention.

We can now construct the operator S_x as follows :

Using the formula :

$$A = \sum_{a'} |a'\rangle\langle a'|A \ \equiv \sum_{a'} a'|a'\rangle\langle a'|$$

We can write S_x in place of operator A and eigenkets $|S_x;\ +\rangle, |S_x;\ -\rangle$ in place of $|a'\rangle$ we get

$$\begin{aligned} S_x &= \frac{\hbar}{2}|S_x;\ +\rangle\langle S_x;\ +| + \left(-\frac{\hbar}{2}\right)|S_x;\ -\rangle\langle S_x;\ -| \\ &= \frac{\hbar}{2}\{|S_x;\ +\rangle\langle S_x;\ +| - |S_x;\ -\rangle\langle S_x;\ -|\} \end{aligned} \tag{4}$$

Substituting (2) and (3) in place of $|S_x;\ +\rangle$ and $|S_x;\ -\rangle$respectively, we get

$$S_x = \frac{\hbar}{2}\left[e^{-i\delta_1}(|+\rangle\langle +|) + e^{i\delta_1}(|-\rangle\langle +|)\right] \tag{5}$$

Notice that the S_x we have constructed is Hermitian.

Similarly we can write $\left|S_y;\ +\right\rangle$as:

$$as\ \left|S_y;\ \pm\right\rangle = \frac{1}{\sqrt{2}}|+\rangle \pm \frac{1}{\sqrt{2}}\, e^{i\delta_2}|-\rangle \tag{6}$$

$$\text{and } S_y = \frac{\hbar}{2}\left[e^{-i\delta_2}(|+\rangle\langle +|) + e^{i\delta_2}(|-\rangle\langle +|)\right] \tag{7}$$

Using the fact from sequential stern-Gerlach experiment with $SG\ \hat{x}$ followed by $SG\ \hat{y}$ we can write :

$$\left|\langle S_y;\pm|S_x;\ +\rangle\right| = \left|\langle S_y;\pm|S_x;\ -\rangle\right| = \frac{1}{\sqrt{2}} \tag{8}$$

Inserting form (2) for $|S_x;\ +\rangle$ and (6) for $|S_y;\ +\rangle$ we get

$$\left|\left(\frac{1}{\sqrt{2}}\langle +| + \frac{1}{\sqrt{2}}e^{-i\delta_2}\langle -|\right).\left(\frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}e^{i\delta_1}|-\rangle\right)\right| = \frac{1}{\sqrt{2}}$$

$$or\ \left|\frac{1}{2} + 0 + 0 + \frac{1}{2}\ e^{i(\delta_1-\delta_2)}\right| = \frac{1}{\sqrt{2}}$$

$$or \frac{1}{2}\left|1 + e^{i(\delta_1-\delta_2)}\right| = \frac{1}{\sqrt{2}} \tag{9}$$

which is satisfied only if :

$$\delta_1 - \delta_2 = \frac{\pi}{2}\ or\ \frac{-\pi}{2} \tag{10}$$

We thus see that the matrix elements of S_x and S_y cannot all be real. If the S_x matrix elements are real, the S_y matrix elements must be purely imaginary (and vice-versa).

It is convenient to take the S_x matrix elements to be real (this can always be done by adjusting arbitrary phase factors in the definition of $|+\rangle$ and $|-\rangle$ and positive and set $\delta_1 = 0$. It can be shown that $\delta_2 = \frac{\pi}{2}$. Therefore

$$|S_x;\ \pm\rangle = \frac{1}{\sqrt{2}}|+\rangle \pm \frac{1}{\sqrt{2}}\ |-\rangle \tag{11.a}$$

$$|S_y;\ \pm\rangle = \frac{1}{\sqrt{2}}|+\rangle \pm \frac{i}{\sqrt{2}}\ |-\rangle \tag{11.b}$$

and $S_x = \frac{\hbar}{2}[(|+\rangle\langle +|) + (|-\rangle\langle +|)]$ (12.a)

$$S_y = \frac{\hbar}{2}[-i(|+\rangle\langle -|) + i(|-\rangle\langle +|)] \tag{12.b}$$

The matrix representation of S_x is :

$$S_x = \begin{pmatrix} \langle +|S_x|+\rangle & \langle +|S_x|-\rangle \\ \langle -|S_x|+\rangle & \langle -|S_x|-\rangle \end{pmatrix}$$

$$\boxed{S_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}$$

Similarly

$$\boxed{S_y \doteq \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

It is easy to verify the commutation relations between the operators $S_x\ ,S_y\ ,S_z$ directly.

we write

$$S_Z = \frac{\hbar}{2}[(|+\rangle\langle+|) - (|-\rangle\langle-|)]$$

$$S_x = \frac{\hbar}{2}[(|+\rangle\langle-|) + (|-\rangle\langle+|)]$$

$$S_y = \frac{\hbar}{2}[-i(|+\rangle\langle-|) + i(|-\rangle\langle+|)]$$

Then the commutator :

$$\boxed{\left[S_x, S_y\right] \equiv S_x S_y - S_y S_x} \tag{1}$$

Above relation can be calculated as follows

We first evaluate the I term of RHS

$$S_x\, S_y = \frac{\hbar}{2}[(|+\rangle\langle-|) + (|-\rangle\langle+|)]\frac{\hbar}{2}[-i(|+\rangle\langle-|) + i(|-\rangle\langle+|)]$$

$$= \frac{\hbar^2}{4}[(|+\rangle\langle-|) + (|-\rangle\langle+|)][-i(|+\rangle\langle-|) + i(|-\rangle\langle+|)]$$

$$= \frac{\hbar^2}{4}[(-i|+\rangle\langle-|+\rangle\langle-|) - i(|-\rangle\langle+|+\rangle\langle-|) + i(|+\rangle\langle-|-\rangle\langle+|) + i(|-\rangle\langle+|-\rangle\langle+|)]$$

$$= \frac{\hbar^2}{4}[(-i|+\rangle.0.\langle-|) - i(|-\rangle.1.\langle-|) + i(|+\rangle.1.\langle+|) + i(|-\rangle.0.\langle+|)]$$

$$= \frac{\hbar^2}{4}[0 - i(|-\rangle\langle-|) + i(|+\rangle\langle+|) + 0]$$

$$\boxed{S_x S_y = i\frac{\hbar}{2} S_Z}$$

Similarly

$$S_y \; S_x = -i \; \frac{\hbar}{2} \; S_Z$$

$$Hence \quad S_x \; S_y - \; S_y \; S_x = i \, \hbar \, S_Z$$

$$\boxed{\left[S_x, S_y\right] = i\hbar S_Z} \qquad (2)$$

It can be readily shown that in general the commutation relations involving S_x , S_y , S_z can be summarized in compact form as :

$$\left[S_i \,, S_j\right] = \; i \;\; \hbar \; \epsilon_{i\,j\,k} \;\; S_k \qquad (3)$$

$$where \; i, j = 1, 2\,, 3 \; or \; x, y, z$$

where $\epsilon_{i\,j\,k} = +1\,, if \; i, j, k$ are in cyclic order and $\epsilon_{i\,j\,k} = -1 \;\,, if \; i, j, k$ can be brought in cyclic order by odd permutation of indices. If any two of the indices are same then $\epsilon_{i\,j\,k} = 0$.

The anticommutation relations

$$\left\{S_i \,, S_j\right\} = \frac{1}{2} \; \hbar^2 \; \delta_{i\,j} \qquad (4)$$

where the symbol $\{A, B\} = \; AB + BA$.

We can also define the operator $S.S \; or \; S^2$ for short, as follows :

$$\boxed{S^2 = S_x^2 + S_y^2 + S_z^2} \qquad (5)$$

Because of (4) this operator turns out to be just a constant multiple of the identity operators :

$$\boxed{S^2 = \frac{3}{4}\hbar^2} \qquad (6)$$

We obviously have $\boxed{\left[S^2, S_i\right] = 0}$

3.3 Observables,Commutability and Compatibility

A state may be simultaneously eigenstate of two observables. If the state corresponds to the ket vector $|A\rangle$ and the observables are ξ and η we should then have the equations :

$$\xi|A\rangle \;=\; \xi'|A'\rangle$$
$$\eta\,|A\rangle \;=\; \eta'\,|A'\rangle$$

Where ξ' and η' are the eigen values of ξ and η respectively. We can now deduce.

$$\xi\eta\,|A\rangle \;=\; \xi\eta'|A\rangle \;=\; \eta'\xi|A\rangle \;=\; \eta'\xi'|A\rangle$$

and $\eta\xi|A\rangle \;\geq\; \eta\xi'|A\rangle \;=\; \xi'\eta|A\rangle \;=\; \xi'\eta'|A\rangle$

or $(\xi\eta \;-\; \eta\xi)|A\rangle \;=\; 0$ (1)

This suggests that the chances for the existence of a ***simultaneous eigenstate*** are most favorable if $\xi\eta \;-\; \eta\xi \;=\; 0$ and the ***two observables commute***.

If they do not commute a simultaneous eigenstate is not impossible, but is rather an exception. On the other hand, if they do commute there exist so many simultaneous eigenstates that they form a complete set.

Observables ξ and η are defined to be compatible when the corresponding operators ***commute.***

$$\boxed{[\xi,\eta]=0} \tag{2}$$

and ***incompatible when***

$$\boxed{[\xi,\eta]\neq 0}$$

For example S^2 and S_z are compatible observables, while S_x and S_y are incompatible observables.

As an example consider the case of compatible observables A and B. As usual, we assume that the ket space is spanned by the eigenkets of A. We may also regard the same ket space as being spanned by the eigenkets of B. We now ask, How are the A eigenkets related to the B eigenkets when A and B are compatible observables?

Before answering this question we must touch upon a very important point we have bypassed earlier - the concept of degeneracy.

Suppose ***there are two (or more) linearly independent eigenkets of A having the same eigenvalue ; then the eigenvalues of the two eigenkets are said to be degenerate.***

In such a case the notation $|a'\rangle$ that labels the eigenket by eigenvalue its does not give a complete description ; furthermore, we may recall that our earlier theorem on the orthogonality of different eigenkets was proved under the assumption of no degeneracy.

Even worse, the whole concept that the ket space is spanned by $|a'\rangle$ appears to run into difficulty when the dimensionality of the ket space is larger than the number of distinct eigenvalues of A.

Fortunately, in practical applications in quantum mechanics, it is usually the case that in such a situation the eigenvalues of some other commuting observable, say B, can be used to label the degenerate eigenkets.

Now we are ready to state an important theorem :

Theorem : ***Suppose that A and B are compatible observables and the eigenvalues of A are nondegenerate. Then the matrix elements $\langle a''|B|a'\rangle$ are all diagonal.***

Proof : First recall here that the matrix elements of A are already diagonal if $\{|a'\rangle\}$ are used as the base kets:

$$\langle a'|A|a''\rangle = a'\delta_{a'a''} \tag{3}$$

Using the definition of compatible observables we note that

$$[A, B] = AB - BA = 0.$$

Hence

$$< a''|[A, B]|a' > = < a''|AB - BA|a' >= 0$$
$$or \quad < a''|AB|a' > - < a''|BA|a' >= 0$$
$$or \quad a'' < a''|B|a' > - < a''|B|a' > a' = 0$$
$$or \quad (< a''|B|a' >)\ (a'' - a') = 0$$

Hence $< a''|B|a' >$ must vanish unless $a'' = a'$.

Therefore the matrix elements $< a''|B|a' >$ are all diagonal. We can write the matrix elements of B as :

$$< a''|B|a' > = \delta_{a'a''} < a''|B|a' > \tag{4}$$

So both A and B can be represented by diagonal matrices with the same set of base kets. We can write B as :

$$B = \sum_{a''} |a'' >< a''|B| \sum_{a'''} |a''' >< a'''|$$

$$= \sum_{a''} \sum_{a'''} |a'' >< a''|B|a''' >< a'''| \quad (B\ is\ diagonal)$$

or $$B = \sum_{a''} |a'' >< a''|B|a'' >< a''| \tag{5}$$

Suppose that this operator acts on an eigenket of A :

$$B\ |a' > = \sum_{a''} |a'' >< a''|B|a'' >< a''|a' >$$

$$or \quad B\ |a' > = < a'|B|a' > \ |a' > \tag{6}$$

But this is nothing other than the eigenvalue equation for the operator B with eigenvalue :

$$b' = < a'|B|a' > \tag{7}$$

The ket $|a' >$ is therefore a simultaneous eigenket of A and B. We represent the simultaneous eigenket of A and B by $|a', b'\rangle$.

A simultaneous eigenket of A and B, denoted by $|a', b'\rangle$ has the property.

$$A\ |a', b'\rangle \ = a'|a', b'\rangle$$
$$B\ |a', b'\rangle \ = b'|a', b'\rangle$$

When there is no degeneracy, this notation is somewhat superfluous because it is clear from (7) that if we specify $'$, we necessarily know the b' that appears in

$|a', b'\rangle$. The notation $|a', b'\rangle$ is much more powerful when there are degeneracies.

For incompatible observables, for example A and B the commutator

$$AB - BA \equiv [A, B] \neq 0.$$

S^2 and S_z are compatible observables, while S_x and S_y are incompatible :

$$\boxed{\left[S^2, S_z\right] = 0} \; (Compatible\ observables)$$

and $$\boxed{\left[S_x, S_y\right] \neq 0} \quad (incompatible\ observables)$$

3.4 Uncertainty Relations

Let us derive the rules for commutation between momentum and coordinate operator. Since the result of successively differentiating with respect to one of the variables x, y, z and multiplying by another of them does not depend on the order of these operations, we have

$$\widehat{p_x} y - y\widehat{p_x} = 0\,,\ \widehat{p_x}\, z - z\widehat{p_x} = 0 \tag{1}$$

and similarly for $\widehat{p_y}$ and $\widehat{p_z}$.

To derive the commutation rule for $\widehat{P_x}$ and x, we write :

$$(\widehat{p_x} x - x\widehat{p_x})\, \phi = -i\,\hbar\, \frac{\partial}{\partial x}\,(x\,\phi) + i\,\hbar\, x\, \frac{\partial \phi}{\partial x} = -i\,\hbar\,\phi$$

We see that the result of the action of the operator $\widehat{p_x} x - x\,\widehat{p_x}$ reduces to multiplication by $-\,i\,\hbar$; the same is true, of course ,of the commutation of $\widehat{P_y}$ with y and $\widehat{P_z}$ with z. Thus we have :

$$\widehat{p_x} x - x\widehat{p_x} = -i\,\hbar\ , \tag{2a}$$

$$\widehat{p_y} y - y\widehat{p_y} = -i\,\hbar\ , \tag{2b}$$

$$\widehat{p_z} z - z\widehat{p_z} = -i\,\hbar \tag{2c}$$

All the relations (1) and (2) can be written jointly in the form :

$$\hat{p}_i x_k - x_k \hat{p}_i = -i\hbar\delta_{ik} \quad (i, k = x, y, z)$$

$$\boxed{x_k \hat{p}_i - \hat{p}_i x_k = i\hbar\delta_{ik}} \quad (i,k = x,y,z)$$

$$\widehat{p_\iota}\, x_k - x_k \widehat{p_\iota} = -i\,\hbar\,\delta_{i\,k} \qquad (i,k = x,y,z) \tag{3}$$

Before going on to examine the physical significance of these relations and their consequences, we shall set down two formulae which will be useful later.

Let $f(\vec{r})$ be some function of the coordinates.

Then $\hat{p}\, f(\vec{r}) = f(\vec{r})\hat{p} = -i\,\hbar\,\nabla f$

$$(\hat{p}\, f - f\,\hat{p})\phi = -i\,\hbar\,[\nabla(f\,\phi) - f\,\nabla\,\phi]$$

$$= -i\,\hbar\;\phi f\,\nabla$$

As ϕ is arbitrary, we find

$$\hat{p}\, f - f\,\hat{p} = -i\,\hbar\,\nabla\, f \tag{4}$$

A similar relation holds for the commutation of $\vec{r}$ with a function of the momentum operator :

$$f(\vec{p})\,\vec{r} - \vec{r}\, f\,(\vec{p}) = -i\hbar\,\frac{\partial f}{\partial \vec{p}} \tag{5}$$

It can be derived in the same way as (4) :

$$f(\vec{p})\,\vec{r}\;\phi\,(\vec{p}) \equiv f\,(\vec{p})\left(i\hbar\,\frac{\partial}{\partial \vec{p}}\right)\phi\,(\vec{p})$$

$$= i\,\hbar\, f\,(\vec{p})\,\frac{\partial}{\partial \vec{p}}\,\phi\,(\vec{p}) \tag{A}$$

$$\vec{r}\, f(\vec{p})\;\phi\,(\vec{p}) = i\,\hbar\,\frac{\partial}{\partial \vec{p}}\,(f\,(\vec{p})\,\phi\,(\vec{p}))$$

$$= i\,\hbar\,\frac{\partial f}{\partial \vec{p}}\,\phi\,(\vec{p}) + i\,\hbar\, f\,(\vec{p})\,\frac{\partial \phi}{\partial \vec{p}} \tag{B}$$

Therefore from (A) and (B) one gets

$$f(\vec{p})\,\vec{r} - \vec{r}\, f\,(\vec{p}) = -i\,\hbar\frac{\partial f}{\partial \vec{p}} \quad (which\ is\ equation\ (5))$$

The relations (1) and (2) show that the coordinate of a particle along one of the axes can have a definite value at the same time as the components of the momentum along the other two axes ; the coordinate and momentum component along the same axis, however cannot exist simultaneously.

In particular, the particle cannot be at a definite point in space and at the same time have a definite momentum $\vec{p}$.

Let us suppose that the particle is in some finite region of space, whose dimensions along the three axes are (of the order of magnitude of) $\Delta x, \Delta y, \Delta z.$

Also, let the mean value of the momentum of the particle be $\overrightarrow{p_0}$. Mathematically, this means that the wave function has the form, $\Psi = u(\vec{r})e^{-(i/\hbar)\overrightarrow{p_0}.\vec{r}}$, where $u\ (\vec{r})$ is a function which differs considerably from zero only in the region of space concerned.

We expand the function Ψ in terms of eigen functions of the momentum operator (i.e. as a Fourier integral).

$$\Psi(\vec{r}) = \int a(\vec{p})\,\Psi_p\,(\vec{r})\frac{d^3p}{(2\,\pi\,\hbar)^3} = \int a\,(\vec{p})\,e^{\frac{i}{\hbar}\vec{p}.\vec{r}}\frac{d^3p}{(2\,\pi\,\hbar)^3}$$

(Where $d^3p = dp_x\,dp_y\,dp_z$). The expansion coefficients $a\ (\vec{p})$ are, according to general formula,

$$a\ (\vec{p}) = \int \Psi\ (\vec{r})\ \Psi_p^*\ (\vec{r})\ dV$$

$$= \int u\ (\vec{r})\ e^{\left(\frac{i}{\hbar}\right)\,(\vec{p}_0 - \vec{p}).\vec{r}}\,dV$$

If this integral is to differ considerably from zero, the periods of the oscillatory factor $e^{\left(\frac{i}{\hbar}\right)\,(\vec{p}_0 - \vec{p}).\vec{r}}$ must not be small in comparison with the dimensions $\Delta x, \Delta y, \Delta z$ of the region in which the function $u\ (\vec{r})$ is different from zero.

This means that $a\ (\vec{p})$ will be considerably different from zero only for values of $\vec{p}$ such that

$$\left(\frac{1}{\hbar}\right)(p_{ox} - p_x)\Delta x \lesssim 1, etc.$$

Since $|a\,(\overrightarrow{p})|^2$ determines the probability of the various values of the momentum, the ranges of values of $p_x, p_y\,, p_z$ in which $a\,(\overrightarrow{p})$ differs from zero are just those in which the components of the momentum of the particle may be found, in the state considered. Denoting these ranges by $\Delta p_x, \Delta p_y\,, \Delta p_z$ we thus have

$$\begin{aligned} &\Delta p_x\, \Delta x \sim \hbar, \\ &\Delta p_y\, \Delta y \sim \hbar, \\ &\Delta p_z\, \Delta z \sim \hbar, \end{aligned} \qquad (6)$$

These relations, known as the uncertainty relations, were obtained by Heisenberg in 1927.

i.e. see that, the greater the accuracy with which the coordinate of particle is known (i.e. the less Δx) the greater the uncertainty Δp_x in the component of the momentum along the same axis, and vice-versa.

In particular, if the particle is at some completely definite point in space $(\Delta x = \Delta y = \Delta z = 0)$, then $\Delta p_x = \Delta p_y = \Delta p_z = \infty$. This means that all values of the momentum are equally probable.

Conversely, if the particle has a completely definite momentum $\overrightarrow{p}$ then all positions of it in space are equally probable (This is seen directly from the wave function $\Psi_{\overrightarrow{p}} = e^{\frac{i}{\hbar}\overrightarrow{p}.\overrightarrow{r}}$, whose squared modules is quite independent of the coordinates).

If the uncertainties of the coordinates and momenta are specified by the standard deviations.

$$\delta x = \sqrt{\overline{[(x-\overline{x})^2]}}\,, \quad \delta p_x = \sqrt{\overline{[(p_x-\overline{p_x})^2]}}$$

We can specify exactly the least possible value of their product.

Let us consider the one dimensional case of a wave packet with wave function $\Psi\,(x)$ depending on only one coordinate, and assume for simplicity that the mean values of x and p_x in this state are zero.

We consider the obvious inequality

$$\int_{-\infty}^{\infty} \left| \alpha\, x\, \Psi + \frac{d\Psi}{dx} \right|^2 \, dx \geq 0$$

Where α is an arbitrary real constant.

On calculating this integral, noticing that

$$\int x^2 |\Psi|^2 dx = (\delta x)^2$$

Note : $\delta x = \ x - \overline{x}$

$$\therefore\ (\delta x)^2 = x^2 - (\overline{x})^2 - 2x\,.\overline{x}$$

$$\overline{(\delta x)^2} = \overline{x^2} - (\overline{x})^2$$

$$= \overline{x^2}\ (\because\ (\overline{x})^2 = 0)$$

$$= \int x^2 |\Psi|^2\, dx$$

And

$$\int \left(x \frac{d\Psi^*}{dx} \Psi + x\ \Psi^* \frac{d\Psi}{dx} \right) dx = \int x \frac{d|\Psi|^2}{dx}\, dx = -\int |\Psi|^2\, dx = -1$$

Also $\int \frac{d\Psi^*}{dx} \frac{d\Psi}{dx}\, dx = -\int \Psi^* \frac{d^2\Psi}{dx^2}\, dx$

$$= \frac{1}{\hbar^2} \int \Psi^*\, p_x^2\ \Psi dx = \frac{1}{\hbar^2}\ (\delta p_x)^2$$

Using these values, we obtain

$$\alpha^2 (\delta x)^2 - \alpha + \frac{1}{\hbar^2} (\delta p_x)^2 \geq 0$$

If this quadratic (in α) trinomial is positive for all α, its discriminant must be negative which gives the inequality.

$$\boxed{\delta x \delta p_x \geq \frac{1}{2}\hbar} \qquad (7)$$

The least possible value of the product is $\frac{1}{2}\hbar$ and occurs for wave packets with wave functions of the form

$$\Psi = \frac{1}{(2\pi)^{\frac{1}{4}}\sqrt{\delta x}} \exp\left(\frac{i}{\hbar}\, p_0 x - \frac{x^2}{4\,(\delta x)^2}\right) \tag{8}$$

where p_0 and δx are constants.

The probabilities of the various values of the coordinates in such a state are :

$$|\Psi|^2 = \frac{1}{\sqrt{(2\pi)}\,\delta x} \exp\left(-\frac{x^2}{2\,(\delta x)^2}\right)$$

and thus have a Gaussian distribution about the origin (the mean value $\overline{x} = 0$) with standard deviation δx.

The wave function in the momentum representation is

$$a\,(p_x) = \int_{-\infty}^{\infty} \Psi(x) e^{-\frac{i}{\hbar} p_x x}\, dx$$

Calculation of the integral gives

$$a\,(p_x) = cosntant \times \exp\left[-\frac{(\delta x)^2 (p_x - p_0)^2}{\hbar^2}\right]$$

The distribution of probabilities of values of the momentum, $|a\,(p_x)|^2$, is also Gaussian about the mean value $\overline{p}_x = p_0$ with standard deviation $\delta p_x = \frac{\hbar}{2\delta x}$, so that the product $\delta p_x\,.\;\delta x$ is indeed $\frac{1}{2}\hbar$.

Finally we shall derive another useful relation. Let f and g be two physical quantities whose operators obey the commutation rule

$$\hat{f}\,\hat{g} - \hat{g}\,\hat{f} = -i\,\hbar\,\hat{c} \tag{9}$$

Where $\hat{c}$ is the operator of some physical quantity c. On the right-hand side of the equation the factor $\hbar$ is introduced in accordance with the fact that in the classical limit (i.e. as $\hbar \to 0$) all operators of physical quantities reduce to multiplication by these quantities and commute with one another.

Thus, in the quasi-classical case, we can, to a first approximation, regard the right-hand side of equation (9) as being zero.

In the next approximation, the operator $\hat{c}$ can be replaced by the operator of simple multiplication by the quantity *c*.

We then have

$$\hat{f}\ \hat{g} - \hat{g}\ \hat{f} = -i\,\hbar\, c$$

This equation is exactly analogous to the relation

$\hat{p}_x\, x - x\, \hat{p}_x = -i\,\hbar$, the only difference being that, instead of the constant $\hbar$, we have the quantity to $\hbar c$.

We can therefore conclude, by analogy with the relation $\Delta x\ \Delta p_x \sim \hbar$, that in the quasi-classical case there is an uncertainty relation

$$\Delta f . \Delta g \sim \hbar c \tag{10}$$

For the quantities f and g.

In particular, if one of these quantities is the energy $(\hat{f}\ \equiv \hat{H}\,)$ and the operator $(\hat{g}\,)$ of the other does not depend explicitly on time, then

$$c = \dot{g}\ (\because \frac{i}{\hbar}\left(\hat{H}\,\hat{g} - \hat{g}\,\hat{H}\,\right) = \dot{g} \quad \therefore c = \dot{g})$$

and the uncertainty relation in the quasi-classical case is :

$$\Delta E\ \Delta g \sim \hbar\ \dot{g}$$

Example : Consider the function defined by

$$f(x) = \int_{-\infty}^{\infty} dk\ g\ (k) e^{i\,k\,x} \tag{1}$$

The real part of $f(x)$ is given by $\int_{-\infty}^{\infty} dk\ g\ \ (k) \cos kx,$ and this is a linear superposition of waves of wavelength $\lambda = \frac{2\pi}{k}$, since for a given k each wave reproduces itself when x changes to $x + \frac{2\pi}{k}$.

To illustrate such a wave packet, let us choose

$$g\ (k) = e^{-\alpha(k-k_0)^2} \tag{2}$$

The integral can be done: with $k' = k - k_0$ we have

$$f(x) = \int_{-\infty}^{\infty} dk\, g\,(k) e^{i\,(k-k_0)\,x} \,.\, e^{i\,k_o\,x}$$

$$= e^{i\,k_o\,x} \int_{-\infty}^{\infty} dk'\, e^{i\,k\prime\,x}\ .e^{-\alpha\,k'^2}$$

$$= e^{i\,k_o\,x} \int_{-\infty}^{\infty} dk'\, e^{-\alpha\,\left[k' - \left(\frac{ix}{2\,\alpha}\right)\right]^2} .\,e^{-x^2/4\alpha} \qquad (\because dk = dk'),$$

where in the last step we have completed squares.

It is justified to let $k' - (ix/2\alpha) = q$ and still keep the integral along the real axis.

Making use of

$$\int_{-\infty}^{\infty} dk\, e^{-\alpha\,k^2} = \sqrt{\frac{\pi}{\alpha}} \tag{3}$$

we obtain

$$f(x) = \sqrt{\frac{\pi}{\alpha}}\,.\,e^{i\,k_0\,x}\,.\,e^{-(x^2/4\alpha)} \tag{2}$$

The factor $e^{i\,k_0\,x}$ is known as a "Phase factor", since $\left|e^{i\,k_0\,x}\right|^2 = 1.$ Thus the absolute square of $f(x)$ is

$$|f(x)|^2 = \frac{\pi}{\alpha}\, e^{-x^2/2\alpha} \tag{5}$$

This function peaks at $x = 0$ and depending on the magnitude of α, it represents a broad (α large) or very narrow (α small) wave packet. As it stands, one might be willing to consider $|f(x)|^2$ as a representation of a particle.

The width of the packet may be taken to be $2\sqrt{2\alpha}$, since the function falls off to $\frac{1}{e}$ of its peak value.

The width of $|f(x)|^2$ and $|g(k)|^2$ are correlated.

The function $|g(k)|^2$ is peaked about k_0 with width $\frac{2}{\sqrt{2\alpha}}$. There is a reciprocity here : a function strongly localized in x is broad in k and vice-versa.

The product of two "widths" is

$$\Delta k \; \Delta x \sim \frac{2}{\sqrt{2\alpha}} .2\sqrt{2\alpha} = 4 \qquad (6)$$

The exact value of the numerical constant is not important ; What matters is that it is independent of α and of order unity.

This is a general property of functions that are Fourier transforms of each other. We represent it by the formula

$$\Delta x \; \Delta k \; \gtrsim \; 0 \qquad (7)$$

There, we imply by 0(1) that this number is not significantly different from 1.

3.5 Illustrative Examples

Example 1: Consider a particle whose normalized wave function is :

$$\Psi(x) = \; 2\,\alpha\,\sqrt{\alpha}\;x\;e^{-\alpha\,x} \qquad\qquad x > 0$$

$$= 0 \qquad\qquad x < 0$$

(a) For what value of x does $P(x) = \; |\Psi(x)|^2$ peak?

(b) Calculate $< x >$ and $< x^2 >$.

(c) What is the probability that the particle is found between $x = 0$ and $x = \frac{1}{\alpha}$?

Sol.

(a) The peak is $P(x)$ occurs when $\frac{d}{dx}\,P(x) = \; 0$ that is $\frac{d}{dx}\,(x^2 e^{-2\,\alpha\,x}) = \; 2\,x\,(-1\,\alpha\,x) e^{-2\,\alpha\,x} = 0$

that is $x = \frac{1}{\alpha}$

(b) $< x > = \; \int_0^\infty dx\;x\;(4\alpha^3\;x^2\;e^{-2\,\alpha\,x})$

$$= \frac{1}{4\alpha}\int_0^\infty dy\;\,y^3\;e^{-y} = \frac{3!}{4\alpha} = \frac{3}{2\alpha}$$

$$< x^2 > = \int_0^\infty dx\;x^2\;(4\alpha^3\;x^2\;e^{-2\,\alpha\,x}) = \frac{4!}{8\,\alpha^2} = \frac{3}{\alpha^2}$$

(c) The desired probability is :

$$P = \int_0^{(1/\alpha)} dx\,(4\alpha^3)x^2\,e^{-2\,\alpha\,x} = \frac{1}{2}\int_0^{2} dy\,y^2 e^{-y} = 0.32$$

Example 2: The expectation value of an anti-Hermitian operator is purely imaginary.

Sol. An anti-Hermitian operator C is defined as $C = -C^{\dagger}$.

Therefore $< a'|C|a'' > = < a''|C^{+}|a' >^{*}$

$$= < a''|C|a' >^{*} \qquad (\because C^{\dagger} = -C)$$

Hence, for expectation value we get

$$< a'|C|a' > = - < a'|C|a' >^{*}$$

That is $< a'|C|a' >$ is purely imaginary.

3.6 Self Learning Exercise

Q.1 Given that $g(k) = \frac{N}{k^2+\alpha^2}$, Calculate the form of $f(x)$. Plot the two functions and show that $\Delta k\ \Delta x > 1$. Independent of your choice of α.

Q.2 Show that the expectation value of a Hermitian operator is purely real.

3.7 Summary

By using Stern- Gerlach experiments we have expanded $|S_x;+\rangle$ ket in terms of basic eigenkets of $\hat{S}_{z'}$ we have considered $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, in a representation in which $\hat{S}_z$ is diagonal. For spin $\frac{1}{2}$ systems these are famous Pauli matrices. We have established the relationship between wave functions in coordinate space and wave functions in momentum space. They are Fourier transform of each other.

3.8 Glossary

Degeneracy: there are two (or more) linearly independent eigenkets of A having the same eigenvalue ; then the eigenvalues of the two eigenkets are said to be degenerate.

3.9 Answers to Self Learning Exercise

Ans.2: Let B be a Hermitian operator.

therefore

$$< a''|B|a' > = < a'|B|a'' >^*$$

For expectation value, we write

$$< a'|B|a' > = < a'|B|a' >^*$$

That is

$$< a'|B|a' > \quad is\, real.$$

3.10 Exercise

Q.1 Suppose $|i\rangle$ and $|j\rangle$ are eigenkets of some Hermitian operator A. Under what conditions can we conclude that $|i\rangle \ + |j\rangle$ is also an eigenket of A? Justify your answer.

Q.2: Consider a wave packet defined by

$$f(x) = \int_{-\infty}^{\infty} dk\, g\,(k)\, e^{i\,k\,x}$$

With $g(k)$ given by

$$\begin{aligned} g\,(k) = \ 0 \quad &; \ k < -\frac{K}{2} \\ = N \quad &; \ -\frac{K}{2} < k < \frac{K}{2} \\ = 0 \quad &; \ \frac{K}{2} < k \end{aligned}$$

(a) Find the for of $f\,(x)$

(b) Find the value of N for which $\int_{-\infty}^{\infty} dx\, |f\,(x)|^2 = 1$

(c) How is this related to the choice of N for which $\int_{-\infty}^{\infty} dk\, |g(k)|^2 = \frac{1}{2\pi}$

(d) Show that a reasonable definition of Δx for your answer to (a) yields

$\Delta k\ \Delta x > 1$ independent of the value of K.

3.11 Answers to Exercise

Ans. 1: $|i\rangle$ and $|j\rangle$ are degenerate eigenkets. These are different eigenkets belonging to the same eigenvalue of A.

References and Suggested Readings

1. L.D.Landau and E.M.Lifshitz ,Quantum Mechanics(Non relativistic theory) Vol-3 ,third edition, Butterworth Heinmann
2. J.J Sakurai, Modern Quantum Mechanics ,Addition Wesley Publishing Company,2008
3. P.A.M. Dirac ,Principle of Quantum Mechanics, Fourth edition, Oxford University Press,1958
4. Amit Goswami **,**Quantum Mechanics ,Wm.C. Brwon Publishers

UNIT-4

Change of Basis:Similarity Transformation, Unitary Transformation, Trace of a Matrix

Structure of the Unit

4.0 Objectives

In this unit we shall discuss the following

- Change of basis and transformation
- Unitary operator; infinitesimal unitary transformation
- Trace of an operator ;Trace theorems

- Diagonalization of matrix

4.1 Introduction

In the preceding units we developed a powerful abstract way of representing the abstract quantities namely bra vectors, ket vectors and linear operations by sets of numbers. There exists the similarity between the geometry of the abstract complex vector space (Hilbert space)and geometrically in ordinary Euclidean space.

A “representation” in the quantum -vector space corresponds to the introduction of a coordinate system in the Euclidian space. Just as we study rotations of coordinate system in analytic geometry, we must now consider the transformation from one representation to another in the general space. Along with the old unprimed basis we consider a new primed basis. The new basis vectors may be expressed in terms of the old ones. We will find the matrix of transformation coefficients. We shall study “similarity transformation” and “Unitary transformation”.

4.2 Transformation Operator

- Suppose we have two incompatible observables A and B. The ket space in question can be viewed as being spanned either by the set $\left\{ |a'\rangle \right\}$ or by the set $\left\{ |b'\rangle \right\}$.
- For example, for spin $\frac{1}{2}$ systems $|S_z \pm\rangle$ may be used as our base kets; alternatively, $|S_x \pm\rangle$ may be used as our base kets.
- The two different sets of base kets, of course, span the same ket space.
- Our aim is in finding out how the two descriptions are related.
- Changing the set of base kets is referred to as a ***change of basis*** or a ***change of representation.***
- The basis in which the base Eigenkets are given by $\left\{ |a'\rangle \right\}$ is called the A representation or, sometimes, the A diagonal representation because the square matrix corresponding to A is diagonal in this basis.
- Our basic task is to construct a transformation operator that connects the old orthonormal set $\left\{ |a'\rangle \right\}$ and the new orthonormal set $\left\{ |b'\rangle \right\}$.

4.3 Unitary Operator

Theorem: Given two sets of base kets, both satisfying orthonormality and completeness, there exists a unitary operator U such that

$$\left|b^{(1)}\right\rangle = U\left|a^{(1)}\right\rangle, \left|b^{(2)}\right\rangle = U\left|a^{(2)}\right\rangle, \;\ldots.\left|b^{(n)}\right\rangle = U\left|a^{(n)}\right\rangle \tag{1}$$

By a **unitary operator** we mean an operator fulfilling the conditions

$$\boxed{U^\dagger U = 1} \tag{2}$$

as well as $UU^\dagger = 1$ (3)

Proof: We prove this theorem by explicit construction. We assert that the operator

$$U = \sum_k \left|b^{(k)}\right\rangle\left\langle a^{(k)}\right| \tag{4}$$

will do the job. To verify this we apply this U to $\left|a^{(\ell)}\right\rangle$,clearly

$$\begin{aligned} U\left|a^{(\ell)}\right\rangle &\equiv \sum_k \left|b^{(k)}\right\rangle\left\langle a^{(k)}\middle|a^{(\ell)}\right\rangle \\ &= \sum_k \left|b^{(k)}\right\rangle \delta_{k\ell} \qquad \left(\because \left\langle a^{(k)}\middle|a^{\ell}\right\rangle = \delta_{k\ell}\right) \\ &= \left|b^{(\ell)}\right\rangle \end{aligned} \tag{5}$$

Furthermore U is unitary:

$$U^\dagger U = \sum_k \sum_\ell \left|a^{(\ell)}\right\rangle\left\langle b^{(\ell)}\middle|b^{(k)}\right\rangle\left\langle a^{(k)}\right| = \sum_k \left|a^{(k)}\right\rangle\left\langle a^{(k)}\right| = 1 \tag{6}$$

Similarly, we prove $UU^\dagger = 1$,hence proved. Following theorems concerning unitary operators may be noted:

Theorem-1: ***The eigenvalues of a unitary operator are complex numbers of unit modulus.***

Theorem-2: ***The eigenvectors of a unitary operator are mutually orthogonal (We assume there is no degeneracy.)***

4.4 Transformation Matrix

- It is instructive to study the matrix representation of the U operator in the old $\left\{\left|a'\right\rangle\right\}$ basis. We have

$$\langle a^{(k)} | U | a^{(\ell)} \rangle = \langle a^{(k)} | b^{(\ell)} \rangle \tag{7}$$

which is obvious from (5).

- In other words, the matrix elements of the U operator are built up of the inner products of old base bras and new base kets.
- The square matrix made up of $\langle a^{(k)} | U | a^{(\ell)} \rangle$ is referred to as transformation matrix from the $\{|a'\rangle\}$ basis to the $\{|b'\rangle\}$ basis.
- We can expand an arbitrary ket $|\alpha\rangle$ in old basis whose expansion coefficients $\langle a' | \alpha \rangle$ are known in the old basis:

$$|\alpha\rangle = \sum_{\ell} |a^{(\ell)}\rangle \langle a^{(\ell)} | \alpha \rangle \tag{8}$$

How can we obtain $\langle b^{(k)} | \alpha \rangle$,the expansion coefficients in the new basis? To find the expansion coefficients $\langle b^{(k)} | \alpha \rangle$, we multiply (8) by $\langle b^{(k)} |$

$$\langle b^{(k)} | \alpha \rangle = \sum_{\ell} \langle b^{(k)} | a^{(\ell)} \rangle \langle a^{(\ell)} | \alpha \rangle$$

or
$$\langle b^{(k)} | \alpha \rangle = \sum_{\ell} \langle a^{(k)} | U^{\dagger} | a^{(\ell)} \rangle \langle a^{(\ell)} | \alpha \rangle \tag{9}$$

In matrix notation, eq.(9) states that the column matrix for $|\alpha\rangle$ in the new basis can be obtained just by applying the square matrix $U^{\dagger}$ to the column matrix in the old basis:

$$(\text{New}) = (U^{\dagger})\,(\text{old}) \tag{10}$$

The relationships between the old matrix elements and the new matrix elements are also easy to obtain:

$$\begin{aligned}\langle b^{(k)} | X | b^{(\ell)} \rangle &= \sum_{m} \sum_{n} \langle b^{(k)} | a^{(m)} \rangle \langle a^{(m)} | X | a^{(n)} \rangle \langle a^{(n)} | b^{(\ell)} \rangle \\ &= \sum_{m} \sum_{n} \langle a^{(k)} | U^{\dagger} | a^{(m)} \rangle \langle a^{(m)} | X | a^{(n)} \rangle \langle a^{(n)} | U \; | a^{(\ell)} \rangle\end{aligned}$$

This is simply the well-known formula for a similarity transformation in matrix algebra:

$$\boxed{X' = U^{\dagger} X U} \tag{12}$$

4.5 Trace of an operator

The trace of an operator X is defined as the sum of diagonal elements:

$$Tr(X) = \sum_{a'} \langle a' | X | a' \rangle \tag{13}$$

Theorem : $Tr\,XY = Tr\,YX$

Proof: $Tr\,XY = \sum_{\iota} \langle i | X | i \rangle$

$$= \sum_{i\,j} \left[\langle i | X | j \rangle \langle j | Y | i \rangle \right]$$

$$TrXY = \sum_{i\,j} \left[\langle j | Y | i \rangle \langle i | X | j \rangle \right]$$

$$= \sum_{j} \langle j | YX | j \rangle$$

Trace XY= Trace (YX)

This is the ***cyclic property of trace of matrix.***

4.6 Diagonalization

We are interested in obtaining the eigenvalue b' and the eigenket $|b'\rangle$ with the property.

$$\boxed{B|b'\rangle = b'|b'\rangle} \tag{14}$$

First, we rewrite this as

$$\left\langle a'' | B | \sum_{a'} |a'\rangle \langle a' | b' \right\rangle = b' \langle a'' | b' \rangle,$$

or $$\sum_{a'} \langle a'' | B | a' \rangle \langle a' | b' \rangle = b' \langle a'' | b' \rangle \tag{15}$$

We can write this in matrix notation as

$$\begin{pmatrix} B_{11} & B_{12} & B_{13} & \cdots & \cdots \\ B_{21} & B_{22} & B_{23} & \cdots & \cdots \\ B_{31} & B_{32} & B_{33} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} C_1^{(l)} \\ C_2^{(l)} \\ C_3^{(l)} \\ .. \\ .. \end{pmatrix} = b^l \begin{pmatrix} C_1^{(l)} \\ C_2^{(l)} \\ C_3^{(l)} \\ .. \\ .. \end{pmatrix} \tag{16}$$

With $B_{ij} = \left\langle a^{(i)} \middle| B \middle| a^{(j)} \right\rangle$ (17)

and $C_k^\ell = \left\langle a^{(k)} \middle| b^\ell \right\rangle$ (18)

As we know from linear algebra, that for ***nontrivial solutions for*** $C_k^{(l)}$ ***are possible only if the characteristic equation.***

$\det(B - \lambda I) = 0$ ***is satisfied***

- This is an n$^{\text{th}}$ order algebraic equation for λ, and the N-roots obtained are to be identified with the various $b^{(\ell)}$'s we are trying to determine.
- Knowing $b^{(\ell)}$ we can solve for the corresponding $C_k^{(\ell)}$'s up to an overall constant to be determined from the normalization condition.
- Comparing (18) with (7), we see that they $C_k^{(\ell)}$'s are just the elements of the unitary matrix involved in the change of basis $\{|a'\rangle\} \to \{|b'\rangle\}$.
- For this procedure the Hermiticity of B is important. For example the matrix $S_+ \equiv S_x + iS_y$ which reads in S_z basis as $S_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$ ***is non Hermitian***. It cannot be diagonalized by any unitary matrix.

4.7 Illustrative Examples

Example 1:

Using the rules of bra-ket algebra, prove or evaluate the following:

(a) $Tr(XY) = Tr(YX)$, where X and Y are operators and Tr is the abbreviation for Trace.

(b) $(XY)^\dagger = Y^\dagger X^\dagger$, where X and Y are operators.

Sol.

(a) By definition

Trace $XY =$ Sum of the diagonal elements of the matrix XY

$$TraceXY = \sum_i \langle i|XY|i\rangle \tag{1}$$

Inserting the unit operator $\sum_j |j\rangle\langle j|$ in the right-hand-side of (1), we get :

$$Trace(XY) = \sum_i \langle i|X|\sum_j |j\rangle\langle j|Y|i\rangle$$
$$= \sum_J \sum_i \langle j|Y|i\rangle\langle i|X|j\rangle$$
$$= \sum_j \langle j|YX|j\rangle$$
$$= Trace YX$$

(b) Consider the operator XY acting on ket$|\alpha\rangle$. It can be written as $XY|\alpha\rangle$ By definition its corresponding bra is$\langle\alpha|(XY)^\dagger$ (1)

We can write dual corresponding bra of the ket $XY|\alpha\rangle$ as follows :

$$XY|\alpha\rangle \leftrightarrow (\langle\alpha|Y^\dagger)X^\dagger$$
$$= \langle\alpha|Y^\dagger X^\dagger \quad (2)$$

From equations (1) and (2), we find :

$$\boxed{(XY)^\dagger = Y^\dagger X^\dagger}$$

Example 2: Show that the trace of an operator is independent of the representation.

Sol. $TrX = \sum_{a'}\langle a'|X|a'\rangle$

$$= \sum_{a'}\sum_{b'}\sum_{b''}\langle a'|b'\rangle\langle b'|X|b''\rangle\langle b''|a'\rangle$$

Now rearranging, we get

$$TrX = \sum_{a'}\sum_{b'}\sum_{b''}\langle b''|a'\rangle\langle a'|b'\rangle\langle b'|X|b''\rangle$$

Using $\sum_a |a'\rangle\langle a'| \equiv 1$

We get

$$TrX = \sum_{b'}\sum_{b''}\langle b''|b'\rangle\langle b'|X|b''\rangle$$
$$= \sum_{b'}\langle b'|X|b'\rangle \text{ , using} \left(\langle b''|b'\rangle = \delta_{b''b'}\right)$$

Hence $Tr\,X$ in *a*- representation =Trace X in *b*-representation

Example 3 : Prove that if A is Hermitian operator, then e^{iA} is unitary operator.

Sol. We have $A = A^{\dagger}$

$$(e^{iA}) = 1 + (iA) + \frac{[(iA)^2]}{2!} + \frac{[(iA)^3]}{3!} +$$

Now $$(e^{iA})^{\dagger} = 1 + (iA)^{\dagger} + \frac{[(iA^{\dagger})^2]}{2!} + \frac{[(iA^{\dagger})^3]}{3!} + \ldots$$

$$= 1 + (-iA^{\dagger}) + \frac{(-iA^{\dagger})^2}{2!} + \frac{(-iA^{\dagger})^3}{3!} + \ldots$$

$$= 1 - iA^{\dagger} + \frac{(iA^{\dagger})^2}{2!} - \frac{(iA^{\dagger})^3}{3!} + \ldots.$$

Since A is Hermitian, therefore

$$(e^{iA})^{\dagger} = 1 - iA + \frac{(iA)^2}{2!} - \frac{(iA)^3}{3!} + \ldots$$

$$= e^{-iA}$$

So $e^{iA}.(e^{iA})^{\dagger} = e^{iA}.e^{-iA} = I$

Therefore e^{iA} is unitary operator.

Hence proved

Example 4: Prove that, under a unitary transformation, Hermitian operator remains its Hermitian character.

Sol. We have Hermitian $H = H^{\dagger}$ (Hermitian)

By unitary transformation

$$H \rightarrow H' = UHU^{\dagger}$$

Now we must prove

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

$$(H')^{\dagger} = (UHU^{\dagger})^{\dagger} = UH^{\dagger}U^{\dagger}$$

$$= UHU^{\dagger}, \text{ because } H = H^{\dagger}$$

$$= H'$$

Hence proved

Example 5: Prove that the fundamental commutation relation $[x, p_x] = i\hbar$ remains unchanged under unitary transformation.

Sol. We consider unitary operator U that effects the transformation. Then ,We have

$$x' = UxU^\dagger \text{ and } p'_x = Up_xU^\dagger$$

$$[x', p'_x] = x'p'_x - p'_xx'$$

$$= (UxU^\dagger)(Up_xU^\dagger) - (Up_xU^\dagger)(UxU^\dagger)$$

$$= Uxp_xU^\dagger - Up_xxU^\dagger$$

$$= U(xp_x - p_xx)U^\dagger$$

$$= Ui\hbar U^\dagger$$

$$= i\hbar$$

Hence proved

4.8 Self Learning Exercise

Q.1 An operator corresponding to infinitesimal transformation can be expressed as $U \approx 1 + i\varepsilon F$, where ε is infinitesimal. Show that U is unitary if the operator F is Hermitian.

Q.2 Prove that $\Pi_{a'}(A - a')$ is the null Operator.

Q.3 Verify that the following matrices are unitary :

$$\frac{1}{2^{1/2}}\begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}, \frac{1}{2}\begin{bmatrix} 1+i & 1-i \\ 1-i & 1+i \end{bmatrix}$$

Verify that the determinant is of the form $e^{i\theta}$ in each case. Are any of the above matrices Hermitian?

Q.4 Express the expectation value of an operator $\hat{Q}$ in terms of its matrix elements.

4.9 Illustrative Examples

Example 6: Find out the condition when a Hermitian matrix H will also be unitary.

Sol. ***A matrix H is called Hermitian if H is equal to its Hermitian conjugate*** $H^\dagger$.

i.e. $\boxed{H = H^\dagger}$.

When H is ***Unitary***, then $H^\dagger$ is equal to H^{-1}

i.e. $\boxed{H^\dagger = H^{-1}}$

From above two conditions

$$H = H^{\dagger} = H^{-1}$$

Hence, H must be equal to its inverse.

Because $HH^{-1} = I \simeq$ unit matrix :

So H.H = I or $H^2 = I$.

In this case the product of matrix with itself must be a unit matrix.

Example 7: Show that

"Any two eigenvectors corresponding to two distinct eigenvalues of a unitary matrix are orthogonal".

Sol. Let us consider unitary matrix A,

then property of unitary matrix we have

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

Let $\phi_1(x)$ and $\phi_2(x)$ be the two eigenvectors corresponding to two distinct eigenvalues λ_1 and λ_2 of unitary matrix A.

$$A\phi_1(x) = \lambda_1 \phi_1(x) \qquad (1)$$

$$A\phi_2(x) = \lambda_2 \phi_2(x) \qquad (2)$$

We take the transpose conjugate of eq. (1) we get

$$(A\phi_1(x))^{\dagger} = (\lambda_1 \phi_1(x))^{\dagger}$$

or $\phi_1(x)^{\dagger} A^{\dagger} = \lambda_1^{*} \phi_1(x)^{\dagger}$ (3)

Post multiplying eq. (3) by eq. (2),we get

$$(\phi_1(x)^{\dagger} A^{\dagger})(A\phi_2(x)) = (\lambda_1^{*} \phi_1(x)^{\dagger})(\lambda_2 \phi_2(x))$$

or $\phi_1(x)^{\dagger}(A^{\dagger} A)\phi_2(x) = \lambda_1^{*} \lambda_2 \phi_1(x)^{\dagger} \phi_2(x)$

or $\phi_1(x)^{\dagger} \phi_2(x) = \lambda_1^{*} \lambda_2 \phi_1(x)^{\dagger} \phi_2(x)$

or $(1 - \lambda_1^{*} \lambda_2)\phi_1(x)^{\dagger} \phi_2(x) = 0$

We know the eigenvalues of a unitary matrix are of unit modulus i.e, $\lambda_1^{*} \lambda_1 = 1$, so

$$\left(\lambda_1^{*} \lambda_1 - \lambda_1^{*} \lambda_2\right) = \lambda_1^{*}(\lambda_1 - \lambda_2) \neq 0 \qquad \because \qquad \lambda_1 \neq \lambda_2$$

$$\therefore \quad \phi_1(x)^{\dagger} \phi_2(x) = 0 .$$

Therefore $\phi_1(x)$ and $\phi_2(x)$ are orthogonal.

Example 8: The base vectors of a representation are

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Construct a transformation matrix U for transformation to another representation having base vectors

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \text{ and } \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

Sol.

The transformation matrix U must be such that

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

After solving, we obtain

$$U_{11} = \frac{1}{\sqrt{2}},\ U_{21} = \frac{1}{\sqrt{2}},$$

$$U_{12} = -\frac{1}{\sqrt{2}},\ U_{22} = \frac{1}{\sqrt{2}}$$

Then

$$\mathrm{U} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix},$$

And $$U^{\dagger} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

Here $$UU^{\dagger}=\begin{pmatrix}\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\end{pmatrix}\begin{pmatrix}\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\end{pmatrix}$$

$$UU^{\dagger}=\begin{pmatrix}\left(\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right) & \left(-\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right)\\ \left(-\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right) & \left(\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right)\end{pmatrix}$$

$$UU^{\dagger}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}=\mathrm{I}$$

It follows that $UU^{\dagger}=I$.

Hence U is unitary operator.

4.10 Summary

In this unit our intention has been to provide a working knowledge of the mathematical structure which underlies quantum mechanics .We have defined Unitary operator which transforms from one set of base kets to another set of base kets. With the help of illustrative examples these ideas have been explained**.**

4.11 Glossary

Eigenfunction: operator $\hat{A}$ operates on function f , then in a such type of expression $\hat{A}f=af$, eigenfunction is *f* and eigenvalue is a .

Orthonormal Functions: Thus the set of eigenfunctions ψ_n forms a complete set of normalized and Orthogonal (Orthonormal) functions if $\int\psi_m\psi_n^*\,dq=\delta_{nm}$

4.12 Answers to Self Learning Exercise

Ans.4: Let us consider a ket $|\psi_i>$ which represents the complete set of basis vectors.

The arbitrary key vectors $|\psi>$ can be expanded in terms of the $|\psi_i>$ is :

$$|\psi\rangle=\sum_i c_i|\psi_i> \qquad (1)$$

In the state $|\psi>$,

the expectation value of $\hat{Q}$ can be written as

$$<\hat{Q}>=\langle\psi|\hat{Q}|\psi\rangle \qquad (2)$$

From eq.(1) & (2) we get

$$<\hat{Q}>=\sum_i c_i^* <\psi_i|\hat{Q}\sum_j c_j|\psi_i>$$

$$=\sum_{i,j} c_i^* c_j <\psi_i|\hat{Q}|\psi_j>$$

$$=\Sigma c_i^* c_j Q_{ij}$$

$$=\sum_{i,j} c_i^* Q_{ij} c_j$$

Hence Proved

4.13 Exercise

Q.1 Consider two kets $|\alpha\rangle$ and $|\beta\rangle$. Suppose $\langle a'|\alpha\rangle$, $\langle a''|\alpha\rangle$ ……. and $\langle a'|\beta\rangle$, $\langle a''|\beta\rangle$ ….. are all known, where $|a'\rangle$, $|a''\rangle$ form a complete set of base kets . Find the matrix representation of the operator $|\alpha\rangle\langle\beta|$ in that basis.

Q.2 Suppose $|i\rangle$ and $|j\rangle$ are Eigen kets of some Hermitian operator A. Under what condition we can conclude that $|i\rangle+|j\rangle$ is also an Eigenket of A? Justify your answer.

Q.3 A certain observable in quantum mechanics has 3×3 matrix representation as follows:

$$\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

(a) Find the normalized Eigenvectors of this observable and corresponding Eigenvalues. Is there any degeneracy?

(b) Give physical example where all this is relevant.

Q.4 Evaluate the commutators

(a) $\left[x^2, p^2\right]$,

(b) $\left[x_i, G(p)\right]$

(c) $[p_i, F(X)]$

Q.5 What is a unitary operator? Show that any algebraic relationship between operators and kets remains invariant under unitary transformation.

Q.6 Prove that

$$\overline{|P><Q|} = |Q><P|$$

Q.7 Prove that

$$<n|m> = \sum_i <n|i><i|m>$$

here $|n\rangle$ and $|m\rangle$ are two arbitrary ket vectors and the vectors $|i\rangle$ are the complete set of basis vectors.

Q.8 Consider a coordinate system be transformed by a transformation matrix T. Prove that if T commutes with the Hamiltonian H, then the Hamiltonian is invariant with respect to this transformation.

Q.9 Show that a unitary operator remains unitary under a unitary transformation.

4.14 Answers to Exercise

Ans.6: Let us consider

$\alpha = |P><Q|$ and

Let $|B> = \alpha|A> = [<Q|A>]|P>$

Therefore

$$<B| = \overline{<Q|A>}<P|$$
$$= \langle A|Q\rangle\langle P|$$

But $<B| = <A|\bar{\alpha}$, so

$$\bar{\alpha} = |Q><P|$$

Ans.7 : The arbitrary ket vectors $|n\rangle$ and $|m\rangle$ can be expanded in terms of the basis $|i\rangle$'s.

$$|n\rangle = \sum_i c_i |i\rangle, \text{ where } c_i = \langle i|n\rangle$$

$$|m\rangle = \sum_i c'_i |i\rangle, \text{ where } c'_i = \langle i|m\rangle$$

$$\therefore \qquad \langle n|m\rangle = \sum_i <i|n>^*|i>^*\sum_j <j|m>|j>$$

$$= \sum_{i,j} <n|i><j|m><i|j>$$

$$= \sum_{i,j} <n|i> <j|m> \delta_{ij}$$

$$= \sum_i <n|i> <i|m>$$

Ans.8: We know that

$x' = Tx$ and $\psi(x') = T\psi(x)$.

x' represents the new coordinate system and x old one

Let us operate T on $H\psi$

Then we have

$T\,H(x)\,\psi(x) = H(x)\,T\psi(x)$

($\because$ T commutes with H)

$$T\,H(x)\,\psi(x) = H(x)\,\psi(x') \tag{1}$$

$$T\,[H(x)\,\psi(x)] = H(x')\,\psi(x') \tag{2}$$

From eq.(1) and (2),we get

$H(x) = H(x')$

Thus Hamiltonian is invariant with respect to coordinate transformation by matrix *T*.

Ans.9 : Let us consider be operator A,

$AA^\dagger = I = A^\dagger A$.

By the unitary transformation, $A \to A'$,

$A' = UAU^\dagger$

we have to prove the following

$A'A'^\dagger = A'^\dagger A' = I$.

Since U is unitary matrix, we have

$UU^\dagger = U^\dagger U = I$

We have,

$(A')^\dagger A' = (UAU^\dagger)^\dagger UAU^\dagger$

$$= (UA^{\dagger}U^{\dagger})UAU^{\dagger}$$

$$= UA^{\dagger}(U^{\dagger}U)AU^{\dagger}$$

$$= U(A^{\dagger}A)U^{\dagger}$$

$$= UU^{\dagger} = I$$

Similarly, we can prove

$$A'(A')^{\dagger} = U^{\dagger}U = I$$

References and Suggested Readings

1. J. J. Sakurai, Modern Quantum Mechanics (2nd Edition), Addison-Wesley;2010
2. P.A.M. Dirac ,Principle of Quantum Mechanics(The International Series of Monographs on Physics)
3. Eugen Merzbacher ,Quantum Mechanics ,third Edition ,John Wiley & Sons (Asia) Pte Ltd.1999
5. Ajoy Ghatak & S. Lokanathan ,Quantum Mechanics "Theory and Applications" Fourth Edition ,Macmillan India Ltd,1999
6. Gupta Kumar Sharma ,Quantum Mechanics ,Jai Prakash Nath &Co.Meerut,2000
7. Leonard I.Schiff, Quantum Mechanics (Third Edition), McGraw Hill International Editions ,1968

UNIT-5

Position, Momentum and Translation Operators, Wave functions in Position and Momentum Space

Structure of the Unit

5.0 Objectives

- What are basic vectors of representation? Properties of basic vectors.
- Coordinate representation:position eigenkets and position measurements
- Translation operator
- Quantum Poisson Bracket
- Wavefunctions in position and momentum space
- Momentum operator in the position basis
- Momentum space wavefunction
- Connection between coordinate and momentum representations
- Gaussian wave Packet

5.1 Introduction

In the preceding units we introduced an algebraic scheme involving certain abstract quantities of three kinds. namely bra vectors, ket vectors, and linear operators and we expressed some of the fundamental laws of quantum mechanics in terms of them. It would be possible to continue to develop the theory in terms of these abstract quantities and to use them for applications to particular problems.

However, for some purposes it is more convenient to replace the abstract quantities by sets of numbers with analogus mathematical properties and to work in terms of these sets of numbers. The procedure is similar to using coordinates in geometry and has the advantage of giving one greater mathematical power for the solving of particular problems.

The way in which the abstract quantities are to be replaced by numbers is not unique, there being many possible ways corresponding to the many systems of coordinates one can have in geometry. Each of these ways is called a representation and the set of numbers that replace an abstract quantity is called the 'representative' of that abstract quantity in the representation. We shall use coordinate representation in which basic vectors of representation are position eigenkets of the position operator. We can equally use the momentum basis of representation in which basic vectors of representation are momentum eigenkets .

5.2 Properties of the Basic Vectors

Using the notation the δ-function, we can proceed with the theory of representations. Let us suppose first that we have a single observable ξ forming by itself a complete commuting set, the condition for this being that there is only one eigenstate of ξ belonging to any eigenvalue ξ' and let us set up an orthogonal representation in which the basic vectors are Eigenvectors of ξ and are written $\langle \xi' | , | \xi' \rangle$.

In the case when the eigenvalues of ξ are discrete, we can normalize the basic vectors, and we then have

$$\boxed{\langle \xi' | \xi'' \rangle = 0 \qquad (\xi' \neq \xi'')}$$

$$\boxed{\langle \xi' | \xi' \rangle = 1}$$

These equations can be combined into the single equation

$$\boxed{\langle \xi' | \xi'' \rangle = \delta_{\xi'\xi''}} \tag{1}$$

where the symbol δ with two suffixes has the meaning

$$\left.\begin{aligned} \delta_{rs} &= 0 \text{ when } r \neq s \\ &= 1 \text{ when } r = s \end{aligned}\right\} \tag{2}$$

In the case when the Eigenvalues of ξ are continuous we cannot normalize the basic vectors.

If we now consider the quantity $\langle \xi' | \xi'' \rangle$, with ξ' fixed and ξ'' varying, then this quantity vanishes for $\xi' \neq \xi''$ and that it's integral over the range of ξ'' extending through the value ξ' is finite and assume it to be equal to 1.

We express this by Dirac δ-function:

$$\langle \xi' | \xi'' \rangle = \delta(\xi' - \xi'') \tag{3}$$

where $\delta(\xi' - \xi'')$ is the improper function defined as

$$\left.\begin{aligned} &\delta(\xi' - \xi'') = 0 \;\; for \; \xi' \neq \xi'' \\ &and \int_{-\infty}^{\infty} \delta(\xi' - \xi'')\, d\xi'' = 1 \end{aligned}\right\} \tag{4}$$

For the discrete case

$$\sum_{\xi'} |\xi'\rangle\langle\xi'|\xi''\rangle = \sum_{\xi'} \xi'\delta_{\xi'\xi''} = |\xi''\rangle$$

This equation holds for any basic ket $|\xi''\rangle$ and hence, since the basic kets form a complete set,

$$\boxed{\sum_{\xi'} |\xi'\rangle\langle\xi'| = 1} \tag{5}$$

Similarly, for the continuous case, we have

$$\int |\xi'\rangle d\xi' \langle\xi'|\xi''\rangle = \int |\xi'\rangle d\xi' \delta(\xi' - \xi'') = |\xi''\rangle \tag{6}$$

This holds for any basic ket $|\xi''\rangle$ and hence

$$\int |\xi'\rangle d\xi' \langle\xi'| = 1 \tag{7}$$

5.3 Coordinate Representation: Position Eigen kets and Position Measurements

The position Eigenkets $|x'\rangle$ of the position operator x satisfying

$$\boxed{x|x'\rangle = x'|x'\rangle} \tag{8}$$

are postulated to form a complete set. Here x' is just a number with dimension of length, for example, while x is an operator.

The state ket for an arbitrary physical state can be expanded in terms of $\{|x'\rangle\}$:

$$|\alpha\rangle = \int_{\infty}^{\infty} dx' |x'\rangle\langle x'|\alpha\rangle \qquad (\text{Since} \int_{-\infty}^{\infty} dx' |x'\rangle\langle x'| \equiv 1)$$

5.4 Translation Operator

We now introduce the very important concept of translation, or spatial displacement.

Suppose we start with a state that is well localized around $\vec{x}'$. Let us consider an operation that changes this state into another well- localized state, this time around $\vec{x}' + d\,\vec{x}'$ with everything else unchanged. Such an operation is defined to be an infinitesimal translation by $d\,\vec{x}'$ and the operator that does the job is denoted by

$$T\left(d\,\vec{x}'\right)$$

So $$\boxed{T\left(d\vec{x'}\right)\left|\vec{x'}\right\rangle = \left|\vec{x'}+d\vec{x'}\right\rangle} \tag{9}$$

where a possible arbitrary phase factor is set to unity by conversion.

Notice that the right-hand side of eq.(9) is again a position Eigen ket, but this time with Eigenvalue $\vec{x'}+d\vec{x'}$ obviously $\left|\vec{x'}\right\rangle$ is not an Eigenket of the ***infinitesimal translation operator.***

We can examine the effect of infinitesimal translation on $\left|\alpha\right\rangle$ as follows:

$$\begin{aligned}\left|\alpha\right\rangle \to T\left(d\vec{x'}\right)\left|\alpha\right\rangle &= T\left(d\vec{x'}\right)\int d^3x' \left|\vec{x'}\right\rangle\left\langle\vec{x'}\right|\alpha\right\rangle \\ &= \int d^3x' \left|\vec{x'}+d\vec{x'}\right\rangle\left\langle\vec{x'}\right|\alpha\right\rangle\end{aligned} \tag{10}$$

We also write the right-hand side of (10) as

$$\int d^3x' \left|\vec{x'}+d\vec{x'}\right\rangle\left\langle\vec{x'}\right|\alpha\right\rangle = \int d^3x' \left|\vec{x'}\right\rangle\left\langle\vec{x'}-d\vec{x'}\right|\alpha\right\rangle \tag{11}$$

because the integration is over all space and $\left|\vec{x'}\right\rangle$ is just an integration variable. This shows that the Wave function of the translated State $T\left(d\vec{x'}\right)\left|\alpha\right\rangle$ is obtained by substituting $\vec{x'}-d\vec{x'}$ for $\vec{x'}$ in $\left\langle\vec{x'}\right|\alpha\right\rangle$.

We now list the properties of the infinitesimal translation operator $T(d\vec{x'})$. It is reasonable to require that if the ket $\left|\alpha\right\rangle$ is normalized to unity, the translated ket $T(d\vec{x'})\left|\alpha\right\rangle$ also be normalized to unity, so

$$\left\langle\alpha\middle|\alpha\right\rangle = \left\langle\alpha\right|T^+(d\vec{x'})T(d\vec{x'})\left|\alpha\right\rangle \tag{12}$$

This condition is guaranteed by demanding that the infinitesimal translation be unitary

First Property: $T^+(d\vec{x'})T(d\vec{x'}) = 1$ (13)

For the second property, suppose we consider two successive infinitesimal translations first by $d\vec{x}'$ and subsequently by $d\vec{x}''$,we expect the net result to be just a single translation operation by the vector sum $d\vec{x}' + d\vec{x}''$,so we demand that

Second Property: $T(d\vec{x}'')T(d\vec{x}') = T(d\vec{x}' + d\vec{x}'')$ (14)

Third Property: $T(-d\vec{x}') = T^{-1}(d\vec{x}')$ (15)

Fourth Property: $\lim_{d\vec{x}' \to 0} T(d\vec{x}') = 1$ (16)

and that the difference between $T(d\vec{x}')$ and the identity operator be of first order in $d\vec{x}'$.

It is now easy to demonstrate that if we take the infinitesimal translation operator to be

$$T(d\vec{x}') = 1 - i\vec{K}.d\vec{x}' \tag{17}$$

where the components of $\vec{K}$, K_x, K_y, and K_z are ***Hermitian Operators***, then all the properties listed are satisfied.

5.5 Commutation Relation, Quantum Poisson Bracket

Accepting (17) to be the correct form for $T(d\vec{x}')$,we are in a position to derive an extremely fundamental relation between the $\vec{K}$ operator and the $\vec{x}$ operator. First, note that

$$\begin{aligned} \vec{x}T(d\vec{x}')\left|\vec{x}'\right\rangle &= \vec{x}\left|\vec{x}' + d\vec{x}'\right\rangle \\ &= \left(\vec{x}' + d\vec{x}'\right)\left|\vec{x}' + d\vec{x}'\right\rangle \end{aligned} \tag{18a}$$

and

$$T(d\vec{x}')\vec{x}\left|\vec{x}'\right\rangle = \vec{x}'T(d\vec{x}')\left|\vec{x}'\right\rangle$$

$$= \vec{x}' \left| \vec{x}' + d\vec{x}' \right\rangle \tag{18b}$$

Hence from (18a) and (18b)

$$\left\{ \vec{x}\, T\left(d\vec{x}' \right) - T\left(d\vec{x}' \right) \vec{x} \right\} \left| \vec{x}' \right\rangle = d\vec{x}' \left| \vec{x}' + d\vec{x}' \right\rangle$$

Or $$\left[\vec{x}, T\left(d\vec{x}' \right) \right] \left| \vec{x}' \right\rangle \approx d\vec{x}' \left| \vec{x}' \right\rangle$$

We therefore have an operator identity

$$\left[\vec{x}, T\left(d\vec{x}' \right) \right] = d\vec{x}' \tag{19}$$

or $\vec{x}\left(1 - i\vec{K}.d\vec{x}' \right) - \left(1 - i\vec{K}.d\vec{x}' \right)\vec{x} = d\vec{x}'$

or $-i\vec{x}\vec{K}.d\vec{x}' + i\vec{K}.d\vec{x}'\vec{x} = d\vec{x}'$

By choosing $d\vec{x}'$ in the direction of $\vec{x}_j$, we obtain

$$x_i K_j - K_j x_i = i\delta_{ij} \tag{20}$$

or $\left[x_i, K_j \right] = i\delta_{ij}$

where δ_{ij} is understood to be multiplied by the identity operator.

Equation (20) is the fundamental ***commutation relation*** between the position operators x, y, z and the K operator K_x, K_y, K_Z.

We should remember that so far the K operator is defined in terms of the infinitesimal translation operator. What is the physical significance of $\vec{K}$ .If we put $\vec{K} = \dfrac{\vec{p}}{\hbar}$ in(20), we find

$$x_i \frac{p_j}{\hbar} - \frac{p_j}{\hbar} x_i = i\delta_{ij}$$

or $$x_i p_j - p_j x_i = i\hbar\delta_{ij} \tag{21}$$

where $i = 1,2,3$ stands for $x_1 = x, x_2 = y, x_3 = z$, and similarly $p_j = p_x$ for $j = 1$ etc.

The relations (21) can be written explicitly as

$$xp_x - p_x x = i\hbar$$

$$xp_y - p_y x = 0 \text{ etc.}$$

All these commutation relations can be summarized in the following form:

$$\boxed{\left[x_i, p_j\right] = i\hbar\delta_{ij}} \qquad \{\text{Quantum Poisson Bracket}\} \qquad (22)$$

Thus the operator of infinitely small translation can be written as

$$T\left(d\vec{x}'\right) = 1 - i\vec{K}.d\vec{x}'$$

$$= 1 - i\frac{\vec{p}}{\hbar}.d\vec{x}' \qquad (23)$$

where $\vec{p}$ is the momentum operator.

5.6 Position-Momentum Uncertainty Relation

The commutation relation (22) imply, for example, that x and p_x (but not x and p_y) are compatible observables. ***It is therefore impossible to find simultaneous Eigen kets of*** x ***and*** p_x:

If $\Delta X = X - \overline{X}$

$$\overline{(\Delta X)^2} = \overline{\left(X - \overline{X}\right)^2}$$

$$= \overline{X^2} - \left(\overline{X}\right)^2$$

,then the position-momentum uncertainty relation becomes

$$\overline{(\Delta X)^2}.\overline{(\Delta p_x)^2} \geq \frac{\hbar^2}{4} \qquad (24)$$

By compounding N infinitesimal translation, each of which is characterized by a spatial displacement $\frac{\Delta x'}{N}$ in the x-direction, and letting $N \to \infty$ we obtain

$$T\left(\Delta x' \hat{x}\right) = \lim_{N\to\infty}\left(1 - \frac{ip_x \Delta x'}{N\hbar}\right)^N$$

$$= \exp\left(\frac{-ip_x \Delta x'}{\hbar}\right) \tag{25}$$

Here $\exp\left(\frac{-ip_x \Delta x'}{\hbar}\right)$ is understood to be a function of the operator p_x; generally, for any operator x we have $\exp x \equiv 1 + x + \frac{x^2}{2!} + ...$

It is instructive to work out the effect of $T\left(d\vec{x}'\right)$ on momentum Eigen ket $|\vec{p}'\rangle$

$$T\left(d\vec{x}'\right)\left|\vec{p}'\right\rangle = \left(1 - \frac{i\vec{p}'.d\vec{x}'}{\hbar}\right)\left|\vec{p}'\right\rangle$$

$$= \left(1 - \frac{i\vec{p}'.d\vec{x}'}{\hbar}\right)\left|\vec{p}'\right\rangle \tag{26}$$

We see that the momentum Eigen ket remains the same even through it suffers a slight phase change, so unlike $\left|\vec{x}'\right\rangle$, $\left|\vec{p}'\right\rangle$ is an Eigen ket of $T\left(d\vec{x}'\right)$, which we anticipated because

$$\left[\vec{p}, T\left(d\vec{x}'\right)\right] = 0$$

5.7 Illustrative Examples

Example 1: Show that in the case of a stationary state with a discrete spectrum the mean value of the momentum is $\bar{\hat{p}} = 0$.

Sol. From Heisenberg form of equation of motion, we know that

$$\dot{\hat{r}} = \frac{i}{\hbar}\left[\hat{H}\hat{r} - \hat{r}\hat{H}\right] \qquad \text{where } \hat{H} \text{ is the Hamiltonian}$$

$$\therefore m\dot{\hat{r}} = \frac{im}{\hbar}\left[\hat{H}\hat{r} - \hat{r}\hat{H}\right] \qquad \text{where m is the mass of the particle}$$

or $\hat{\vec{p}} = \frac{im}{\hbar}\left[\hat{H}\hat{r} - \hat{r}\hat{H}\right]$

The mean value of $\hat{\vec{p}}$ in the state ψ in the case of discrete spectrum is

$$\overline{\hat{p}} = \frac{im}{\hbar}\left[\{\psi^*(\hat{H}\hat{r} - \hat{r}\hat{H})\psi\}\right]d\tau$$

In the stationary state ,we have

$$\hat{H}\psi = E\psi \,, \hat{H}^*\psi^* = E\psi^*$$

and we thus have

$$\overline{\hat{\mathrm{p}}} = \frac{im}{\hbar}\int\left[\psi^*\hat{H}\hat{\vec{r}}\psi - \psi^*\hat{\vec{r}}\hat{H}\psi\right]d\tau$$

$$= \frac{im}{\hbar}\left[\int\psi^*\hat{H}\hat{\vec{r}}\psi d\tau - \int\psi^*\hat{\vec{r}}\hat{H}\psi d\tau\right]$$

$$= \frac{im}{\hbar}\left[E\int\psi^*\hat{\vec{r}}\psi d\tau - E\int\psi^*\hat{\vec{r}}\psi d\tau\right]$$

$$= 0$$

$$\therefore \overline{\hat{p}} = 0$$

Example 2: Express in terms of $\hat{\vec{p}}$ the operator of a parallel displacement over any finite (not only infinitesimal distance $\vec{a}$.

Sol. We define the operator of displacement $\hat{T}_{\vec{a}}$ as

$$\hat{T}_{\vec{a}}\psi(\vec{r}) = \psi(\vec{r} + \vec{a})$$

Expanding the function $\psi(\vec{r} + \vec{a})$ in a Taylor series,

We have

$$\psi(\vec{r} + \vec{a}) = \psi(\vec{r}) + \vec{a}.\frac{\partial\psi(\vec{r})}{\partial\vec{r}} + ...,$$

Or, introducing the operator $\hat{p} = -i\hbar\vec{\nabla}$,

$$\psi(\vec{r} + \vec{a}) = \left[1 + \frac{i}{\hbar}\vec{a}.\vec{p} + \frac{1}{2}\left(\frac{i}{\hbar}\vec{a}.\vec{p}\right)^2 + ...\right]\psi(\vec{r})$$

The expression in brackets is the operator

$$\hat{T}_{\vec{a}} = e^{\frac{i}{\hbar}\vec{a}.\vec{p}}$$

This is the required “Operator of the finite displacement”.

Example 3: Show that the equation of motion is $\dot{x} = \hat{p}/m$, where $\hat{p}$ is the operator associated with momentum.

Sol. We have

$$i\hbar\,\dot{x} = \left[\hat{x}, \hat{H}\right]$$

$$= \hat{x}\hat{H} - \hat{H}\hat{x}$$

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

$$= -\frac{\hbar^2}{2m}x\frac{\partial^2}{\partial x^2} + xV(x) + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}x - V(x)x$$

$$= -\frac{\hbar^2}{2m}\left(x\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2}x\right) = -\frac{\hbar^2}{2m}\left[x, \frac{\partial^2}{\partial x^2}\right]^{\dagger}$$

$$= +\frac{\hbar^2}{2m}.2\frac{\partial}{\partial x}$$

$$\therefore \dot{x} = \frac{\hbar}{i}\frac{1}{m}\frac{\partial}{\partial x} = \frac{\hat{p}}{m}, \text{ since } \hat{p} \rightarrow -\frac{\hbar}{i}\frac{\partial}{\partial x}$$

5.8 Wave functions in Position and Momentum Space

For simplicity we consider one dimensional case. The base kets are position eigen kets satisfying.

$$|x|x'\rangle = |x|x'\rangle \tag{27}$$

These position Eigen kets are normalized in such a way that the orthogonally Condition reads

$$\boxed{\langle x''|x'\rangle = \delta\left(x' - x''\right)} \tag{28}$$

Any ket representing a physical state can be expanded in terms of $|x'\rangle$,

$$|\alpha\rangle = \int dx'|x'\rangle\langle x'|\alpha\rangle \tag{29}$$

and that the expansion coefficient $\langle x'|\alpha\rangle$ is interpreted in such a way that

$$\left|\langle x'|\alpha\rangle\right|^2 dx' \tag{30}$$

is the probability for the particle to be found in a narrow interval dx' around x'.

In our formalism the inner produce $\langle x'|\alpha\rangle$ is what is usually referred to as the wave function $\underset{\alpha}{\psi}(x')$ for state $|\alpha\rangle$:

$$\langle x'|\alpha\rangle = \underset{\alpha}{\psi}(x') \tag{31}$$

We now consider the inner product $\langle\beta|\alpha\rangle$. In the position basis we can express this inner product as: $\langle\beta|\alpha\rangle = \int dx' \langle\beta|x'\rangle\langle x'|\alpha\rangle \qquad \left(\because \int dx'|x'\rangle\langle x'| \equiv 1\right)$

$$= \int dx' \underset{\beta}{\psi}^*(x') \underset{\alpha}{\psi}(x') \tag{32}$$

So $\langle\beta|\alpha\rangle$ characterizes the overlap between the two wave functions.

The more general interpretation of $\langle\beta|\alpha\rangle$, independent of representation, is that it represents the probability amplitude for state $|\alpha\rangle$ to be found in state $|\beta\rangle$.

We now interpret the expression

$$|\alpha\rangle = \sum_{a'} |a'\rangle\langle a'|\alpha\rangle \tag{33}$$

using the language of wave functions. In the position basis we can write (33) as

$$\langle x'|\alpha\rangle = \sum_{a'} \langle x'|a'\rangle\langle a'|\alpha\rangle \tag{34}$$

or $\underset{\alpha}{\psi}(x') = \sum_{a'} C_{a'} U_{a'}(x')$

where $U_{a'}(x') = \langle x'|a'\rangle$ (35)

and $C_{a'} = \langle a'|\alpha\rangle$

Let us now examine how $\langle\beta|A|\alpha\rangle$ can be written using the wave functions for $|\alpha\rangle$ and $|\beta\rangle$ clearly, we have

$$\langle\beta|A|\alpha\rangle = \int dx' \int dx'' \langle\beta|x'\rangle\langle x'|A|x''\rangle\langle x''|\alpha\rangle$$

$$= \int dx' \int dx'' \underset{\beta}{\psi}^*(x')\langle x'|A|x''\rangle \underset{\alpha}{\psi}(x'') \tag{36}$$

So to be able to evaluate $\langle\beta|A|\alpha\rangle$, we must know the matrix element $\langle x'|A|x''\rangle$, which is, in general, a function of two variables x' and x''.

5.9 Momentum Operator in the Position Basis

We now examine how the momentum operator may look in the x-basis-that is, in the representation where the position Eigenkets are used as basekets.

Our starting point is the definition of momentum as the generator of infinitesimal translations:

$$\left(1-\frac{ip\Delta x'}{\hbar}\right)|\alpha\rangle = T(\Delta x')|\alpha\rangle$$

$$= \int dx' T(\Delta x')|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx' |x'+\Delta x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx' |x'\rangle\langle x'-\Delta x'|\alpha\rangle$$

$$= \int dx' |x'\rangle\left(\langle x'|\alpha\rangle - \Delta x' \frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right) \tag{37}$$

A comparison of both sides yields

$$p|\alpha\rangle = \int dx' |x'\rangle\left(-i\hbar\frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right) \tag{38}$$

$$\langle x'|p|\alpha\rangle = -i\hbar\frac{\partial}{\partial x'}\langle x'|\alpha\rangle \tag{39}$$

where we have used the orthogonality property (28).

For the matrix element p in the x-representation, we obtain

$$\langle x'|p|x''\rangle = -i\hbar\frac{\partial}{\partial x'}\delta(x'-x'') \tag{40}$$

We can now evaluate $\langle\beta|p|\alpha\rangle$ in the x-representation:

$$\langle\beta|p|\alpha\rangle = \int dx'' \int dx' \langle\beta|x'\rangle\langle x'|p|x''\rangle\langle x''|\alpha\rangle$$

$$= \int dx'' \int dx' \langle\beta|x'\rangle\left(-i\hbar\frac{\partial}{\partial x'}\right)\delta(x'-x'')\langle x''|\alpha\rangle$$

Integrating over x'', we get

$$\langle\beta|p|\alpha\rangle = \int dx'\langle\beta|x'\rangle\left(-i\hbar\frac{\partial}{\partial x'}\right)\langle x'|\alpha\rangle$$

$$= \int dx'\,\psi_\beta^*(x')\left(-i\hbar\frac{\partial}{\partial x'}\right)\psi_\alpha(x') \tag{41}$$

where we have made use of the formula

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a) \tag{42}$$

Also we can obtain the following involving p^n

$$\langle x'|p^n|\alpha\rangle = (-i\hbar)^n\frac{\partial^n}{\partial x'^n}\langle x'|\alpha\rangle \tag{43}$$

5.10 Momentum Space Wave Functions

The basic Eigen kets in the p-basis specify

$$\boxed{p|p'\rangle = p'|p'\rangle} \tag{44}$$

and $\boxed{\langle p'|p''\rangle = \delta(p'-p'')}$ (45)

An arbitrary state ket $|\alpha\rangle$ can therefore be expanded as follows:

$$|\alpha\rangle = \int dp'|p'\rangle\langle p'|\alpha\rangle \tag{46}$$

We define momentum space wave function $\langle p'|\alpha\rangle$ as

$$\langle p'|\alpha\rangle = \phi_\alpha(p') \tag{47}$$

If $|\alpha\rangle$ is normalized i.e.

$\langle\alpha|\alpha\rangle = 1$, then we obtain

$$\int dp'\langle\alpha|p'\rangle\langle p'|\alpha\rangle = 1$$

$$or \int dp'\varphi_\alpha^*(p')\varphi_\alpha(p') = 1$$

$$or \boxed{\int|\varphi_\alpha(p')|^2\,dp' = 1} \tag{47a}$$

5.11 Connection between Coordinate and Momentum Representations

Let us take a system with one degree of freedom, describable in terms of x and p with Eigen values of x running from $-\infty$ to ∞ and let us an Eigen ket $|p'\rangle$ of p. Its representative in the coordinate representation is $\langle x'|p'\rangle$ satisfies

$$p'\langle x'|p'\rangle = \langle x'|p|p'\rangle = -i\hbar\frac{d}{dx'}\langle x'|p'\rangle$$

or $$\frac{d\langle x'|p'\rangle}{\langle x'|p'\rangle} = \frac{ip'}{\hbar}dx'$$

The solution to this differential equation for $\langle x'|p'\rangle$ is

$$\langle x'|p'\rangle = N\exp\left(\frac{ip'x'}{\hbar}\right) \tag{48}$$

where N is the normalization constant to be determined.

To get the normalizations constant N let us first consider

$$\langle x'|x''\rangle = \int dp'\langle x'|p'\rangle\langle p'|x''\rangle$$

or $$\delta(x'-x'') = \int dp' N\exp\left(\frac{ip'x'}{\hbar}\right)N^*e\frac{-ip'x''}{\hbar}$$

$$= |N|^2\int dp'\exp\left[\frac{ip'(x'-x'')}{\hbar}\right]$$

$$= 2\pi\hbar|N|^2\delta(x'-x'') \tag{49}$$

Choosing N to be purely real and positive by convention, we finally have

$$\boxed{\langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{ip'x'}{\hbar}\right)} \tag{50}$$

We can now demonstrate the relationship between the position-space wave function and momentum-space wave function.

For this we rewrite

$$\langle x'|\alpha\rangle = \int dp'\langle x'|p'\rangle\langle p'|\alpha\rangle \tag{51a}$$

and $$\langle p'|\alpha\rangle = \int dx'\langle p'|x'\rangle\langle x'|\alpha\rangle \tag{52a}$$

or $$\boxed{\underset{\alpha}{\psi}(x') = \left(\frac{1}{\sqrt{2\pi\hbar}}\right)\int dp'\exp\left(\frac{ip'x'}{\hbar}\right)\underset{\alpha}{\varphi}(p')} \tag{51b}$$

and $$\boxed{\psi_\alpha(p') = \left(\frac{1}{\sqrt{2\pi\hbar}}\right)\int dx \exp\left(-\frac{ip'x'}{\hbar}\right)\psi_\alpha(x')} \tag{52b}$$

This pair of equations is just what one expects from Fourier's inversion theorem.

5.12 Self Learning Exercise

Q.1 Show that the operator $\hat{x} = i\hbar\frac{d}{dp}$ is Hermitian.

Q.2 If x and p_x are the coordinate and momentum operators, prove that

$[x, p_x^n] = ni\hbar\, p_x^n$

5.13 Gaussian Wave Packet

Consider a Gaussian wave packet, whose x-space wave function is given by

$$\langle x'|\alpha\rangle = \left(\frac{1}{\pi^{1/4}\sqrt{d}}\right)\exp\left[ikx' - \frac{x'^2}{2d^2}\right] \tag{53}$$

This is a plane wave with wave number k modulated by a Gaussian Profile centered on the origin.

The probability of observing the particle vanishes very rapidly for $|x'| > d$;

The probability density $|\langle x'|\alpha\rangle|^2$ has Gaussian shape with width d.

Now, we have to evaluate the expectation values of x, x^2 p, p^2

The expectations value of x is clearly zero by symmetry:

$$\langle x\rangle = \int_{-\infty}^{\infty} dx'\langle\alpha|x'\rangle x'\langle x'|\alpha\rangle = \int_{-\infty}^{\infty} dx'|\langle x'|\alpha\rangle|^2 x' = 0$$

For x^2 we obtain

$$\begin{aligned}\langle x^2\rangle &= \langle\alpha|x^2|\alpha\rangle = \int\langle\alpha|x^2|x'\rangle dx'\langle x'|\alpha\rangle \\ &= \int dx'x'^2\langle\alpha|x'\rangle\langle x'|\alpha\rangle \\ &= \int dx'x'^2|\langle x'|\alpha\rangle|^2 \\ &= \frac{1}{\pi^{1/2}d}\int_{-\infty}^{\infty} dx'x'^2\exp\left(\frac{-x'^2}{d^2}\right) = \frac{d^2}{2}\end{aligned} \tag{54}$$

This leads to

$$\left\langle (\Delta x)^2 \right\rangle = \left\langle x^2 \right\rangle - \left\langle x \right\rangle^2$$

$$\left\langle (\Delta x)^2 \right\rangle = \frac{d^2}{2} \tag{55}$$

For the dispersion of the position operator.

The expectation values of p and p^2 can also be computed as follows.

$$\begin{aligned}
\langle p \rangle &= \langle \alpha | p | \alpha \rangle \\
&= \int \langle \alpha | x' \rangle dx' \langle x' | p | \alpha \rangle \\
&= \int \langle \alpha | x' \rangle dx' \left(-i\hbar \frac{d}{dx'} \right) \langle x' | \alpha \rangle \\
&= \int dx' \langle \alpha | x' \rangle (-i\hbar) \frac{d}{dx'} \langle x' | \alpha \rangle \\
&= \hbar k
\end{aligned} \tag{56}$$

(After substituting for $\langle \alpha | x' \rangle$ and $\langle x' | \alpha \rangle$ etc.) and integrating.

Similarly

$$\left\langle p^2 \right\rangle = \frac{\hbar^2}{2d^2} + \hbar^2 k^2 \tag{58}$$

and $\left\langle \left(\Delta p^2 \right) \right\rangle = \left\langle p^2 \right\rangle - \left\langle p \right\rangle^2$

$$\left\langle \left(\Delta p^2 \right) \right\rangle = \frac{\hbar^2}{2d^2} \tag{59}$$

We can check the Heisenberg uncertainty relation

$$\left\langle (\Delta x)^2 \right\rangle \left\langle (\Delta p)^2 \right\rangle = \frac{\hbar^2}{4} \tag{60}$$

In this case the uncertainty product is independent of d. So far a Gaussian wave packet we actually have an equality relation rather than the more general inequality relation. For this reason a ***Gaussian wave packet is often called a minimum uncertainly wave packet.***

We can also obtain

$$\langle p'|\alpha\rangle = \left(\frac{1}{\sqrt{2\pi\hbar}}\right)\left(\frac{1}{\pi^{1/4}\sqrt{d}}\right)\int_{-\infty}^{\infty} dx' \exp\left(\frac{-ip'x'}{\hbar} + ikx' - \frac{x'^2}{2d^2}\right)$$

$$= \sqrt{\frac{d}{\hbar\sqrt{\pi}}}\exp\left[\frac{-(p'-\hbar k)^2 d^2}{2\hbar^2}\right] \tag{61}$$

5.14 Illustrative Examples

Example 4 : Prove that, if the wave function in coordinate space is normalized, the momentum wave function is also normalized.

Sol. We have

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = 1 \tag{62}$$

The momentum wave function is given by Fourier transform of $\psi(\mathrm{x})$:

$$\phi(\mathrm{k}) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \psi(\mathrm{x}) \mathrm{e}^{-\mathrm{ikx}} \mathrm{dx} \tag{63}$$

where $\psi(\mathrm{x}) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi(\mathrm{k})\mathrm{e}^{\mathrm{ikx}}\mathrm{dk}$ (64)

Now we have

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = \int_{-\infty}^{\infty} \psi^*(\mathrm{x})\psi(\mathrm{x})\mathrm{dx}$$

$$= \int_{-\infty}^{\infty} \mathrm{dx}. \left\{\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi^*(\mathrm{k})\mathrm{e}^{-\mathrm{ikx}}\mathrm{dk}\right\}\left\{\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi(\mathrm{k}')\mathrm{e}^{\mathrm{ik'x}}\mathrm{dk}'\right\}$$

Here, from eq. (63) we substitute for $\psi^*(\mathrm{x})$ and $\psi(\mathrm{x})$. By integration,

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = \int_{-\infty}^{\infty} \mathrm{dk}\, \phi^*(\mathrm{k}) \int_{-\infty}^{\infty} \mathrm{dk}'\phi(\mathrm{k}') \times \left\{\frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i(k'-k)x}}\mathrm{dk}\right\}$$

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi^*(\mathrm{k})\phi(\mathrm{k}')\delta(\mathrm{k}'-\mathrm{k})\mathrm{dk}'\mathrm{dk},$$

By the expression of delta function

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = \int_{-\infty}^{\infty} \phi^*(\mathrm{k})\phi(\mathrm{k})\,\mathrm{dk}$$

$$\int_{-\infty}^{\infty} |\psi(\mathrm{x})|^2 \, \mathrm{dx} = \int_{-\infty}^{\infty} |\phi(\mathrm{k})|^2 \, \mathrm{dk}$$

On using (1), we have

$$\int_{-\infty}^{\infty} |\phi(\mathrm{k})|^2 \, \mathrm{dk} = 1$$

i.e. the momentum wavefunction is also normalized.

Example 5: Express $\hat{x}$ in the momentum representation.

Sol. The position representation $|x\rangle$ is defined by the eigenstates of the position operator $\hat{x}$ by

$$\hat{x}|x\rangle = x|x\rangle$$

In its own space, operating by x is the same thing as multiplying by x.

The expectation value of x in the state $|\psi\rangle$ is given by

$$\langle \hat{x} \rangle = \langle \psi | \hat{x} | \psi \rangle$$

$$= \langle \psi | \int |x\rangle dx \langle x | |x| \int dx' |x'\rangle dx' \langle x' | |\psi\rangle$$

where we have introduced unit operator $\int |x\rangle dx \langle x|$ and $\int |x'\rangle dx' \langle x'|$. Thus

$$\langle \hat{x} \rangle = \int dx \langle \psi | x \rangle \int dx' \langle x | x | x' \rangle \langle x' | \psi \rangle$$

$$= \int dx \langle \psi | x \rangle \int dx' x \delta(x - x') \langle x' | \psi \rangle$$

$$= \int dx \int dx' \langle \psi | x \rangle x \delta(x - x') \langle x' | \psi \rangle$$

$$= \int dx \langle \psi | x \rangle \langle x | \psi \rangle x \text{ (using the property of } \delta\text{-function)}$$

$$= \int dx \psi^*(x) x \psi(x) \tag{65}$$

What is the form of $\hat{x}$ in the momentum representation? For this we consider the expectation value of $\hat{x}$ in the state $|\psi\rangle$ again, but this time we expand $|\psi\rangle$ in the momentum representation. This gives

$$\langle \hat{x} \rangle = \langle \psi | \hat{x} | \psi \rangle = \langle \psi | \int | p \rangle dp \langle p | \hat{x} | \psi \rangle$$

$$= \int dp \langle \psi | p \rangle \langle p | \hat{x} | \psi \rangle$$

Denoting $\langle p | \hat{x} | \psi \rangle$ by $\langle p | \beta \rangle$ where

$$|\beta\rangle = \hat{x}|\psi\rangle$$, we find

$$\langle\hat{x}\rangle = \langle\psi|\hat{x}|\psi\rangle$$

$$= \int dp\langle\psi|p\rangle\langle p|\beta\rangle$$, and our job is to evaluate it in the representation.

For this we consider $\langle x|\beta\rangle$. We expand it using the ket bra sum rule for the *p*-basis.

$\langle x|\beta\rangle = \langle x|\int|p\rangle dp\langle p|\beta\rangle$, where we have introduced unit operator in the p-basis viz $\int|dp\rangle dp\langle dp| \equiv 1$.

We find

$$\langle x|\beta\rangle = \int dp\langle x|p\rangle\langle p|\beta\rangle$$

$$= \int dp.e^{\frac{ipx}{\hbar}}\langle p|\beta\rangle \text{ where } \langle x|p\rangle \equiv e^{\frac{ipx}{\hbar}} \tag{66}$$

But we can also expand $\langle x|\beta\rangle$ as

$$\langle x|\beta\rangle = \langle x|x|\psi\rangle = x\langle x|\psi\rangle$$

$$= x\int dp\langle x|p\rangle\langle p|\psi\rangle$$

$$= x\int dpe^{\frac{ipx}{\hbar}}a(p)$$

where $\langle p|\psi\rangle \equiv a(p)$, we write

$$\langle x|\beta\rangle = \int dp\left(-i\hbar\frac{d}{dp}e^{\frac{ipx}{\hbar}}\right)a(p)$$

Now integrating by parts, we get

$$\langle x|\beta\rangle = \frac{\hbar}{i}\left[e^{\frac{ipx}{\hbar}}.a(p)\right]_{-\infty}^{\infty} - \frac{\hbar}{i}\int dpe^{\frac{ipx}{\hbar}}\frac{da(p)}{dp}$$

So long as we consider bound states, $a(p) \to 0$ as $p \to \pm\infty$ and the first term goes to zero. We are left with

$$\langle x|\beta\rangle = i\hbar\int dpe^{\frac{ipx}{\hbar}}\frac{da(p)}{d\beta}$$

Comparing with equation (i), given above we find

$$\langle p|\beta\rangle = 2\hbar\frac{d}{dp}a(p)$$

Hence we get for

$$\langle x\rangle = \langle\psi|\hat{x}|\psi\rangle = \int dp\langle\psi|p\rangle\langle p|\beta\rangle$$

$$= \int dpa^*(p)\left(i\hbar\frac{d}{dp}\right)a(p)$$

Thus $\hat{x} = i\hbar\frac{d}{dp}$ in the momentum representation.

Example 6: Find the eigenfunctions and eigenvalues of the momentum operators.

Sol. They are determined by the vector equation

$$-i\hbar\nabla\psi = \hat{p}\psi \tag{67}$$

The solutions are of the form

$$\psi = Ce^{\frac{i}{\hbar}\vec{p}.\vec{r}} \tag{68}$$

Where C is a constant. If all three components of the momentum are given simultaneously, we see that this completely determines the wave function of the particle. In other words, the quantities p_x, p_y, p_z form one of the possible complete sets of physical quantities for a particle.

Their eigenvalues form a continuous spectrum extending from $-\infty$ to $+\infty$.

According to the rule for normalizing the eigenfunctions of a continuous spectrum, the integral $\int\psi^*_{p'}\psi_p dV$ taken over all space $(dV = dxdydz)$ must be equal to the delta function $\delta(\vec{p'} - \vec{p})$.

However, it is more natural to normalize the eigen functions of the particle momentum by the delta function of the momentum difference divided by $2\pi\hbar$:

$$\int\psi^*_{p'}\psi_p dV = \delta\left(\frac{\vec{p'} - \vec{p}}{2\pi\hbar}\right)$$

or equivalently

$$\int\psi^*_{p'}\psi_p dV = (2\pi\hbar)^3\,\delta(\vec{p'} - \vec{p})$$

(since $\delta\left(\frac{\overrightarrow{p'}-\overrightarrow{p}}{2\pi\hbar}\right) \equiv \delta\left(\frac{p'_x-p_x}{2\pi\hbar}\right).\delta\left(\frac{p'_y-p_y}{2\pi\hbar}\right).\delta\left(\frac{p'_z-p_z}{2\pi\hbar}\right)$

$$= \left(2\pi\hbar\right)^3 \delta(p'_x-p_x).\delta(p'_y-p_y).\delta(p'_z-p_z)$$

Now substituting for $\psi_{p'}\psi^*_{p'}$, etc., we get

$$|C|^2 \int e^{\frac{i}{\hbar}(\overrightarrow{p'}-\overrightarrow{p}).\vec{r}} dV = \left(2\pi\hbar\right)^3 \delta(\overrightarrow{p'}-\overrightarrow{p})$$

We now use the well known formula

$$\int_{-\infty}^{\infty} e^{i\alpha\varepsilon} d\varepsilon = 2\pi\delta(\alpha)\text{, we get}$$

$$|C|^2 . \left(2\pi\right)^3 \delta\left(\frac{\overrightarrow{p'}-\overrightarrow{p}}{\hbar}\right) = \left(2\pi\hbar\right)^3 \delta(\overrightarrow{p'}-\overrightarrow{p})$$

Or $|C|^2 . \left(2\pi\right)^3 .\hbar^3 \delta(\overrightarrow{p'}-\overrightarrow{p}) = \left(2\pi\hbar\right)^3 \delta(\overrightarrow{p'}-\overrightarrow{p})$

(Here we have used the well known formula $\delta(\mathrm{ax}) = \frac{1}{|a|}\delta(x)$)

Finally, we find

$$|C|^2 = 1$$

Thus $\boxed{\psi_{\vec{p}} = e^{\frac{i}{\hbar}\vec{p}.\vec{r}}}$

5.15 Summary

In this chapter we have studied two important basis of representing abstract quantities like bras ,kets, operators namely position basis and momentum basis. These two modes of representation are connected with each other. We can study the development of quantum mechanics in either representation.

5.16 Glossary

Momentum basis : p-basis

Coordinate basis : q -basis or x -basis

Quantum Poision Bracket: [u,v]=uv-vu

5.17 Answers to Self Learning Exercise

Ans.1: Consider arbitrary functions $\psi(p), \phi(p)$ which vanish at infinity. We have

$$\int \phi \hat{x} \psi \, dp$$

$$= \int \phi \left(i\hbar \frac{d}{dp} \right) \psi \, dp$$

$$= \int \phi i\hbar \frac{d\psi}{dp} dp$$

Integrating by parts, we get

$$= i\hbar \left\{ \phi\psi - \int \frac{d\phi}{dp} \psi \, dp \right\}$$

$$= -i\hbar \int \frac{d\phi}{dp} \psi \, dp \equiv \psi(p) \left(i\hbar \frac{d\phi}{dp} \right)^{*} dp \equiv \int \psi x^{*} \phi dp$$

and this is the condition that the operator $\hat{x} = i\hbar \frac{d}{dp}$ should be Hermitian.

Ans.2: $[x, p_x^n] = [x, p_x^{n-1} p_x]$

$= [x, p_x] p_x^{n-1} + p_x [x, p_x^{n-1}]$

$= i\hbar\, p_x^{n-1} + p_x \left([x, p_x] p_x^{n-2} + p_x [x, p_x^{n-2}] \right.$

$= 2i\hbar\, p_x^{n-1} + p_x^2 \left([x, p_x] p_x^{n-3} + p_x [x, p_x^{n-3}] \right.$

$= 3i\hbar\, p_x^{n-1} + p_x^3 [x, p_x^{n-3}]$

Continuing, we get

$[x, p_x^n] = ni\hbar\, p_x^{n-1}$

5.18 Exercise

Q.1 Prove the following

$$\langle p' | x | \alpha \rangle = i\hbar \frac{\partial}{\partial p'} \langle p' | \alpha \rangle$$

$$\langle \beta | x | \alpha \rangle = \int dp' \phi_{\beta}^{*}(p') i\hbar \frac{\partial}{\partial p'} \phi_{\alpha}(p')$$

where $\phi_\alpha(p') = \langle p'|\alpha\rangle$ and $\phi_\beta(p') = \langle p'|\beta\rangle$ are momentum-space wave functions.

Q.2 Establish a connection between momentum and coordinate representation of a ket vector.

Q.3 Deduce an expression for the momentum operator in position basis.

Q.4 Show that the operator of infinitely small translation in space can be expressed as

$$T\left(d\vec{x}\right) = 1 - i\frac{\vec{p}}{\hbar}.d\vec{x}$$

Q.5 A particle is constrained in a potential V (x) = 0 for $0 \le x \le a$ and $V(x) = \infty$ otherwise. In the x-representation, the wave function of the particle is given by

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

Find the momentum function $\Phi(p)$.

5.19 Answers to Exercise

Ans.5: $\Phi(p) = \dfrac{1}{\sqrt{2p\hbar}}\displaystyle\int_{-\infty}^{\infty}\psi(x)e^{-\frac{ipx}{\hbar}}dx$

$$\Phi(p) = \frac{1}{\sqrt{\pi\hbar a}}I$$

Where $I = \displaystyle\int_0^a \sin\frac{2\pi x}{a}e^{-\frac{ipx}{\hbar}}dx$

Integrating by parts,

$$I = \left[-\frac{\hbar}{ip}\sin\frac{2\pi x}{a}e^{-\frac{ipx}{\hbar}}\right]_0^a - \int_0^a\left(-\frac{\hbar}{ip}\right)e^{-\frac{ipx}{\hbar}}\frac{2\pi}{a}\cos\frac{2\pi x}{a}dx$$

$$I = \frac{2\pi\hbar}{ipa}\left[\cos\frac{2\pi x}{a}\left(-\frac{\hbar}{ip}\right)e^{-\frac{ipx}{\hbar}}\right]_0^a - \frac{2\pi\hbar}{ipa}\int_0^a\left(-\frac{\hbar}{ip}\right)e^{-\frac{ipx}{\hbar}}\left(-\frac{2\pi}{a}\right)\sin\frac{2\pi x}{a}dx$$

$$I = \frac{2\pi\hbar}{ipa}\left(-\frac{\hbar}{ip}\right)\left(e^{-ipa/\hbar} - 1\right) + \frac{4\pi^2\hbar^2}{a^2p^2}I$$

$$I\left(1-\frac{4\pi^2\hbar^2}{a^2p^2}\right)=\frac{2\pi\hbar^2}{ap^2}\left(e^{-ipa/\hbar}-1\right)$$

$$I=\frac{2\pi a\hbar^2}{a^2p^2-4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}}-1\right)$$

Thus,

$$\Phi(p)=\frac{1}{\sqrt{\pi\hbar a}}\frac{2\pi a\hbar^2}{a^2p^2-4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}}-1\right)$$

$$=\frac{2\pi^{1/2}a^{1/2}\hbar^{3/2}}{a^2p^2-4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}}-1\right)$$

References and Suggested Readings

1. J.J Sakurai,Modern Quantum Mechanics,Addition Wesley Publishing Company,2008
2. Gupta Kumar Sharma ,Quantum Mechanics ,Jai Prakash Nath &Co.Meerut,2000
3. G.Aruldas, Quantum Mechanics ,Second Edition ,PHI learning Private Limited, Delhi ,2013
4. E.Merzbacher,Quantum Mechanics,Second Edition,John Wiley &Sons,New York,2000

UNIT -6

Quantum Dynamics , Schrodinger versus Heisenberg Picture

Structure of the Unit

6.0 Objectives

In this unit we shall study the following

- Dynamical development of the state kets or observables

- Hamiltonian operator
- Energy eigenkets ,stationary state
- Time dependence of expectation values.
- Schrodinger versus Heisenberg picture
- Heisenberg equation of motion
- Ehrenfest's theorem

6.1 Introduction

This chapter is devoted to the time development of state kets or observables. We shall develop equation representing the time development of stateket vector in the form of Schrodinger equation (the dynamical variables remaining fixed).In another picture state vectors remain fixed in time and dynamical variables develop in time in the form of Heisenberg's equation of motion. We shall discuss Heisenberg picture versus Schrodinger picture.

6.2 Quantum Dynamics

This chapter is devoted exclusively to the dynamic development of state kets and or observables. In other words, we are concerned here with the quantum-mechanical analogue of Newton's (or Lagrange's or Hamilton's) equations of motion.

6.3 Time Evolution Operator and Schrodinger equation

Our basic concern here is, how does a state ket change with time? Suppose we have a physical system whose state ket at t_0 be represented by $\left|\alpha\right\rangle$.At later times, we do not, in general, expect the system to remain in the same state $\left|\alpha\right\rangle$. Let us denote the ket corresponding to the state at some later time by

$$\left|\alpha,t_0;t\right\rangle,\ \left(t>t_0\right) \tag{1}$$

where we have written α,t_0 to remind ourselves that the system used to be in state $\left|\alpha\right\rangle$ at some earlier reference time t_0.Because time is assumed to be continuous parameter we expect

$$\underset{t\to t_0}{Lim}\left|\alpha,t_0;t\right\rangle=\left|\alpha\right\rangle \tag{2}$$

and we may as well as use a shorthand notation,

$$\left|\alpha,t_0;t\right\rangle=\left|\alpha\right\rangle=\left|\alpha,t_0\right\rangle \tag{3}$$

- Our basic task is to study the time evolution of a state ket:

$$\left|\alpha,t_0\right\rangle=\left|\alpha\right\rangle \xrightarrow{\textit{time evolution}} \left|\alpha,t_0;t\right\rangle \tag{4}$$

Put in another way, we are interested in asking how the state ket changes under a time displacement $t_0 \to t$ .The two kets are related by an operator which we call the time-evolution operator $U\left(t_0,t\right)$:

$$\left|\alpha,t_0;t\right\rangle=U\left(t,t_0\right)\left|\alpha,t_0\right\rangle \tag{5}$$

- We assume that if the state ket is initially normalized to unity, it must remain normalized to unity at all later times:

$$\left|\alpha,t_0\right|\alpha,t_0\rangle=1\Rightarrow\langle\alpha,t_0;t\left|\alpha,t_0;t\right\rangle=1 \tag{6}$$

$$=\left\langle\alpha,t_0\right|U^{+}\left(t,t_0\right)U\left(t,t_0\right)\left|\alpha,t_0\right\rangle$$

i.e. $U^{+}\left(t,t_0\right)U\left(t,t_0\right)=1$ (7)

or in other words, unitarity is one of the fundamental property of the time evolution operator U. Another feature we require of the U operator is the composition property:

$$U\ \left(t_2,t_0\right)=U\left(t_2,t_1\right)U\left(t_1,t_0\right),\left(t_2>t_1>t_0\right) \tag{8}$$

- It also turns out to be advantageous to consider an infinitesimal time-evolution operator $U\left(t_0+dt,t_0\right)$

$$\left|\alpha,t_0;t_0+dt\right\rangle=U\left(t_0+dt,t_0\right)\left|\alpha,t_0\right\rangle \tag{9}$$

Because of continuity, the infinitesimal time-evolution operator must reduce to identity operator as *dt* goes to zero:

$$\underset{dt\to 0}{Lim}\,U\left(t_0+dt,t_0\right)=1 \tag{10}$$

We expect

$$U\left[t_0+dt,t_0\right]=1-i\Omega dt \tag{11}$$

where Ω is a Hermitian Operator.

The ***operator*** Ω ***has the dimension of frequency or inverse time. We relate*** Ω ***to the Hamiltonian operator H:***

$$\Omega = \frac{H}{\hbar} \tag{12}$$

To sum up, the infinitesimal time-evolution operator is written as

$$U(t_0 + dt, t_0) = 1 - \frac{iHdt}{\hbar} \tag{13}$$

where H, the Hamiltonian operator, is assumed to be Hermitian.

The Schrödinger Equation:

We are now in a position to derive the fundamental differential equation for the time evolution operator $U(t,t_0)$. We export the composition property of the time-evolution operator as follows:

$$\begin{aligned} U(t+dt,t_0) &= U(t+dt,t)U(t,t_0) \\ &= \left(1 - \frac{iHdt}{\hbar}\right)U(t,t_0) \end{aligned} \tag{14}$$

where the time difference $(t - t_0)$ need not be infinitesimal, we have

$$U(t+dt,t_0) - U(t,t_0) = -\frac{iH}{\hbar}dtU(t,t_0) \tag{15}$$

which can be written in differential equation form:

$$\boxed{i\hbar\frac{\partial}{\partial t}U(t,t_0) = HU(t,t_0)} \tag{16}$$

This is the Schrodinger equation for the time evolution operator. Everything that has to do with time-development follows from this fundamental equation.

Equation (16) immediately leads to the Schrodinger equation for a state ket. Multiplying both sides of (16) by $|\alpha,t_0\rangle$ on the right, we obtain

$$i\hbar\frac{\partial}{\partial t}U(t,t_0)|\alpha,t_0\rangle = HU(t,t_0)|\alpha,t_0\rangle \tag{17}$$

But $|\alpha,t_0\rangle$ does not depend on t, so this is the same as

$$i\hbar\frac{\partial}{\partial t}|\alpha,t_0;t\rangle = H|\alpha,t_0;t\rangle \tag{18}$$

6.4 Energy Eigenkets

To be able to evaluate the effect of the time-evolution operator on a general initial ket $|\alpha\rangle$, we must know how it acts on the base kets used in expanding $|\alpha\rangle$.

This is particularly straight forward if the base kets used are Eigenkets of A such that

$$[A,H]=0 \tag{19}$$

Then the Eigenkets of A are also Eigenkets of H, called energy eigenkets, whose eigenvalues are denoted by $E_{a'}$:

$$H|a'\rangle = E_{a'}|a'\rangle \tag{20}$$

We can now expand the time-evolution operator in terms of $|a'\rangle\langle a'|$. Taking $t_0=0$ for simplicity we obtain

$$\exp\left(\frac{-iHt}{\hbar}\right) = \sum_{a'}\sum_{a''}|a''\rangle\langle a''|\exp\left(\frac{-iHt}{\tau}\right)|a'\rangle\langle a'|$$

$$= \sum_{a'}|a'\rangle\exp\left(\frac{-iE_{a'}t}{\tau}\right)\langle a'| \tag{21}$$

The time-evolution operator written in this form enables us to solve any initial-value problem. Once the expansion of the initial ket in terms of $\{|a'\rangle\}$ is known.

As an example, suppose the initial ket expansion reads.

$$|\alpha,t_0=0\rangle = \sum_{a'}|a'\rangle\langle a'|\alpha\rangle = \sum_{a'}c_{a'}|a'\rangle \tag{22}$$

We then have

$$|\alpha,t_0=0;t\rangle = \exp\left(\frac{-iHt}{\hbar}\right)|\alpha,t_0=0\rangle$$

$$= \sum_{a'}|a'\rangle\langle a'|\alpha\rangle\exp\left(\frac{-iE_{a'}t}{\hbar}\right) \tag{23}$$

In other words, the expansion coefficient changes with time as

$$C_{a'}(t=0)\to C_{a'}(t) = C_{a'}(t=0)\ \exp\left(\frac{-iE_{a'}t}{\hbar}\right) \tag{24}$$

with its modulus unchanged.

A special case of interest is where the initial state happens to be one of $\{|a'\rangle\}$ itself. We have

$$|\alpha, t_0 = 0\rangle = |a'\rangle \tag{25}$$

and at a later time

$$|\alpha, t_0 = 0; t\rangle = |a'\rangle \exp\left(\frac{-iE_{a'}t}{\hbar}\right) \tag{26}$$

So if the system is initially a simultaneous eigenstate of A and H, it remains so at all times. The most that can happen is the phase modulation, $\exp\left(\frac{-iE_{a'}t}{\hbar}\right)$. It is in this sense that an observable compatible with H is a constant of motion.

6.5 Time Dependence of Expectation Values

It is instructive to study how the expectation value of an observable changes as a function of time. Suppose that at t=0 the initial state is one of the Eigenstates of an observable *A* that commutes with *H*.

We now look at the expectation value of some other observable B, which need not commute with A nor with H. Because at a later time we have.

$$|a', t_0 = 0; t\rangle = U(t,0)|a'\rangle \quad \text{for the state/ket,} \tag{27}$$

$\langle B\rangle$ is given by

$$\begin{aligned}\langle B\rangle &= \langle a'|U^{+}(t,0)BU(t,0)|a'\rangle \\ &= \left\langle a'\left|\exp\left(\frac{iE_{a'}t}{\tau}\right)B\exp\left(\frac{-iE_{a'}t}{\hbar}\right)\right|a'\right\rangle \\ &= \langle a'|B|a'\rangle\end{aligned} \tag{28}$$

which is independent of t. So the expectation value of an observable taken with respect to an energy Eigenstate does not change with time. For this reason an energy ***Eigenstate is often referred to as a Stationary State.***

The Situation is more interesting when the expectation value is taken with respect to a “superposition “of energy Eigen states, or a non-stationary state.

Suppose that initially we have

$$\left|\alpha, t_0 = 0\right\rangle = \sum_{a'} c_{a'} \left|a'\right\rangle \tag{29}$$

We easily compute the expectation value of B to be $\langle B\rangle$

$$\langle B\rangle = \left[\sum_{a'} C^*_{a'} \langle a'| \exp\left(\frac{iE_{a'}t}{\hbar}\right)\right] .B. \left[\sum_{a''} C_{a''} \exp\left(\frac{-iE_{a''}t}{\hbar}\right) |a'\rangle\right]$$

$$= \sum_{a'} \sum_{a''} C^*_{a'} C_{a''} \langle a'|B|a''\rangle \exp\left[\frac{-i(E_{a''} - E_{a'})t}{\hbar}\right] \tag{30}$$

So this time the expectation value consists of oscillating terms whose angular frequencies are determined by Bohr's frequency condition.

$$\omega_{a''a'} = \frac{E_{a''} - E_{a'}}{\hbar} \tag{31}$$

Spin Precession:

We consider an extremely simple system which, however, illustrates the basic formalism we have developed .We start with a Hamiltonian of a spin $\frac{1}{2}$ system with magnetic moment $\frac{e\hbar}{2m_e c}$ subjected to an external magnetic field $\vec{B}$:

$$H = -\left(\frac{e}{m_e c}\right) \vec{S}.\vec{B} \text{ (e<0 for the election)} \tag{32}$$

We take $\vec{B}$ to be a static, uniform magnetic field in the Z-direction. We can then write H as

$$H = -\left(\frac{eB}{m_e c}\right) S_z \tag{33}$$

Because S_z and H differ just by a multipliable constant, they obviously commute. The S_z Eigen state are also energy Eigenstates, and the corresponding energy Eigenvalues are

$$E_{\pm} = \pm \frac{e\hbar B}{2m_e c} \text{ ,for } S_z \pm \tag{34}$$

It is convenient to define w in such a way that the difference in the two energy Eigen values is $\hbar w$

$$\omega \equiv \frac{|e|B}{m_e c} \tag{35}$$

All the information on time development is contained in the time evolution operator

$$U(t,0) = \exp\frac{-i\omega S_z t}{\hbar} \tag{36}$$

We apply this to the initial state. The base kets we must use in expanding the initial kets are obviously the S_z Eigen kets, $|+\rangle$ and $|-\rangle$,which are also energy eigenkets. Suppose that at t=0, the system is characterization by:

$$|\alpha\rangle = C_+|+\rangle + C_-|-\rangle \tag{37}$$

We see that the state ket at some later time is

$$|\alpha, t_0 = 0; t\rangle = C_+ \exp\left(\frac{-i\omega t}{2}\right)|+\rangle + C\_\exp\left(\frac{-i\omega t}{2}\right)|-\rangle \tag{38}$$

Let us suppose that the initial ket $|\alpha\rangle$ represents the spin up (or, more precisely, $S_Z +$) state, $|+\rangle$ which means that $C_+ = 1,\ C_- = 1$ (39)

At a later time, it becomes

$$|\alpha, t_0 = 0; t\rangle = c_+ \exp\left(\frac{-i\omega t}{2}\right)|+\rangle \tag{40}$$

that is it is still in the spin-upstate, which is no surprise because this is a stationary state.

Next, let us suppose that initially the system is in the $S_x +$ state:

$$|S_x +\rangle = C_+|+\rangle + C_-|-\rangle \tag{41}$$

Evidently $C_+ = C_- = \dfrac{1}{\sqrt{2}}$ (42)

- It is straight forward to workout the probabilities for the system to be found in the $|S_x \pm\rangle$ state at some later time t:

$$\left|\langle S_x \pm | \alpha, t_0 = 0; t\rangle\right|^2$$

$$= \left| \left[\frac{1}{\sqrt{2}} \langle + | \pm \frac{1}{\sqrt{2}} \langle - | \right] \cdot \left[\frac{1}{\sqrt{2}} \exp\left(\frac{-i\omega t}{2}\right) |+\rangle + \frac{1}{\sqrt{2}} \exp\left(\frac{+i\omega t}{2}\right) |-\rangle \right] \right|^2$$

$$= \left| \frac{1}{2} \exp\left(\frac{-i\omega t}{2}\right) \pm \frac{1}{2} \exp\left(\frac{+i\omega t}{2}\right) \right|^2$$

$$= \begin{cases} \cos^2 \frac{\omega t}{2} \ for\ S_x + & (43a) \\ \sin^2 \frac{\omega t}{2} \ for\ S_x - & (43b) \end{cases}$$

Even through the spin is initially in the positive x-direction, the magnetic field in the Z-direction causes it to rotate; as a result we obtain a finite probability for finding s_x at some later time. The sum of the two probabilities is seen to be unity at all times.

We can write for expectation value of as S_x

$$\langle S_x \rangle = \frac{\hbar}{2} \cos^2\left(\frac{\omega t}{2}\right) + \left(\frac{-\hbar}{2}\right) \sin^2\left(\frac{\omega t}{2}\right)$$

$$= \frac{\hbar}{2} \cos \omega t \tag{44}$$

So this quantity oscillates with an angular frequency corresponding to the difference of the two energy Eigen values divided by $\hbar$.

In a similar way

$$\langle S_y \rangle = \frac{\hbar}{2} \sin \omega t \tag{45}$$

and $\langle S_z \rangle = 0$ (46)

Physically this means that the spin precesses in the xy plane

6.6 Illustrative Examples

Example 1: Define differentiation of operators with respect to time and deduce that the time differentiation of an operator $\widehat{f}$ with respect to time is given by

$$\hat{\dot{f}} = \frac{\partial \hat{f}}{\partial t} + \frac{i}{\hbar} \left[\hat{H} \hat{f} - \hat{f} \hat{H} \right]$$

Sol. The derivative $\dot{f}$ of a quantity f is defined as the quantity whose mean value is equal to the derivative , with respect to time ,of the mean value $\overline{f}$. Thus we have the definition

$$\overline{\dot{f}} = \dot{\overline{f}}$$

Starting from this definition, it is easy to obtain an expression for the quantum-mechanical operator $\hat{\dot{f}}$ corresponding to the quantity $\dot{f}$:

$$\overline{\dot{f}} = \dot{\overline{f}} = \frac{d}{dt}\int \psi^* \hat{f} \psi \, dq$$

$$= \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi \, dq + \int \frac{\partial \psi^*}{\partial t} \hat{f} \psi \, dq + \int \psi^* \hat{f} \frac{\partial \psi}{\partial t} dq$$

Substituting for $\frac{\partial \psi}{\partial t}, \frac{\partial \psi^*}{\partial t}$ their expressions according to Schrodinger's equation:

$$\overline{\dot{f}} = \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi \, dq + \frac{i}{\hbar} \int \left(\hat{H}^* \psi^* \right) \hat{f} \psi \, dq - \frac{i}{\hbar} \int \psi^* \hat{f} \left(\hat{H} \psi \right) dq$$

Since the operator $\hat{H}$ is Hermitian, we have

$$\int \left(H^* \psi^* \right) \left(\hat{f} \psi \right) dq = \int \psi^* \hat{H} \hat{f} \psi \, dq$$

Thus $\overline{\dot{f}} = \int \psi^* \left(\frac{\partial \hat{f}}{\partial t} + \frac{i}{\hbar} \hat{H} \hat{f} - \frac{i}{\hbar} \hat{f} \hat{H} \right) \psi \, dq$

Since, by the definition of mean values $\overline{\dot{f}} = \int \psi^* \hat{\dot{f}} \psi \, dq$, therefore

$$\hat{\dot{f}} = \frac{\partial \hat{f}}{\partial t} + \frac{i}{\hbar} \left(\hat{H} \hat{f} - \hat{f} \hat{H} \right)$$

Example 2: Prove the relation $\left(\frac{\partial \hat{H}}{\partial \lambda} \right)_{nn} = \frac{\partial E_n}{\partial \lambda}$, where λ is a parameter on which the Hamiltonian $\hat{H}$ (and therefore the energy eigenvalues E_n) depends.

Sol. It is proved as follows :

Differentiating the equation $\left(\hat{H} - E_n \right) \psi_n = 0$ with respect to λ and then multiplying on the left by ψ_n^*, we obtain

$$\psi_n^*\left(\hat{H}-E_n\right)\frac{\partial\psi_n}{\partial\lambda}=\psi_n^*\left(\frac{\partial E_n}{\partial\lambda}-\frac{\partial\widehat{H}}{\partial\lambda}\right)\psi_n$$

On integration with respect to q , the left hand side gives zero, since

$$\int\psi_n^*\left(\hat{H}-E_n\right)\frac{\partial\psi_n}{\partial\lambda}dq$$

$$=\int\frac{\partial\psi_n}{\partial\lambda}\left(\hat{H}-E_n\right)^*\psi_n^*dq$$ the operator $\hat{H}$ being Hermitian.

The right hand side gives the required equation :

$$\frac{\partial E_n}{\partial\lambda}\int\psi_n^*\psi_n dq=\int\psi_n^*\frac{\partial\widehat{H}}{\partial\lambda}\psi_n dq$$

or $$\frac{\partial E_n}{\partial\lambda}=\left(\frac{\partial\hat{H}}{\partial\lambda}\right)_{nn}$$

6.7 The Schrodinger versus the Heisenberg Picture

The approach to quantum dynamics in which the time development is considered by ***the time evolution operator that affects state kets ; this approach to quantum dynamics is known as the Schrodinger picture.***

There is another formulation of quantum dynamics where ***observables, rather than state kets, vary with time; this second approach is known as the Heisenberg Picture.***

In the Schrodinger picture the operators corresponding to observables like x , p_x S_z and are fixed in time, while state kets vary with time.

In contrast ,in the Heisenberg picture the operators corresponding to observables vary with time; the state kets are fixed, frozen so to speak, at what they were at t_0. It is convenient to set to in $U(t,t_0)$ to zero for simplicity and work with U(t), which is defined by

$$U(t,t_0=0)=U(t)=\exp\left(\frac{-iHt}{\hbar}\right) \tag{47}$$

We define the Heisenberg Picture observable by

$$A^{(H)}(t)\equiv U^+(t)A^{(S)}U(t)$$

where the superscripts H and S stand for Heisenberg and Schrodinger respectively

At t=0, the Heisenberg Picture observables and the corresponding Schrodinger respectively observables coincide.

$$A^{(H)}(0) = A^{(S)} \tag{48}$$

The state kets also consider between the two pictures at t=0; at later t the Heisenberg picture state ket is frozen to what it was at t=0:

$$\left|\alpha, t_0 = 0; t\right\rangle_H = \left|\alpha, t_0 = 0\right\rangle$$

Independent of t. This is in contrast with the Schrodinger- picture state ket

$$\left|\alpha, t_0 = 0; t\right\rangle_S = u(t)\left|\alpha, t_0 = 0\right\rangle \tag{49}$$

6.8 The Heisenberg Equation of Motion

We now derive the fundamental equation of motion in the Heisenberg picture.

We assume that $A^{(S)}$ does not depend explicitly on time

Using $A^{(H)}(t) \equiv U^{+}(t) A^{S} U(t)$ (50)

We obtain by differentiating (50) with respect to t:

$$\frac{d}{dt}A^{(H)} = \frac{\partial U^{+}}{\partial t}A^{(S)}U + U^{+}A^{(S)}\frac{\partial U}{\partial t}$$

$$= -\frac{1}{i\hbar}U^{(+)}HUU^{+}A^{(S)}U + \frac{1}{i\hbar}U^{+}A^{(S)}UU^{+}Hu$$

$$= \frac{1}{i\hbar}\left[A^{(H)}, U^{+}HU\right]$$

Where we have used

$$\frac{\partial U}{\partial t} = \frac{1}{i\hbar}HU \text{ ,}$$

and $\frac{\partial U^{+}}{\partial t} = \frac{1}{i\hbar}U^{+}H$

We define $H^{(H)} = U^{+}HU$,

but U and H commute; as a result $U^{+}HU = H$

So, we can write $\boxed{\frac{d}{dt}A^{(H)}=\frac{1}{i\hbar}\left[A^{(H)},H\right]}$

This equation is known as the ***Heisenberg equation of motion.***

6.9 Self Learning Exercise

Q.1 Deduce the equation of continuity using Schrödinger's equation :

$$\frac{\partial\rho}{\partial t}+div\vec{j}=0$$

Q.2 Consider a one-dimensional simple Harmonic oscillator.

Using $\left.\begin{matrix}a\\a^{+}\end{matrix}\right\}=\sqrt{\frac{mw}{2\hbar}}\left(x\pm\frac{ip}{mw}\right)$

and $a|n\rangle=\sqrt{n}|n-1\rangle$

$a^{+}|n\rangle=\sqrt{n+1}|n+1\rangle$

Evaluate $\langle m|x|n\rangle,\langle m|p|n\rangle$, $\langle m|\{x,p\}|n\rangle$, $\langle m|x^{2}|n\rangle$ and $\langle m|p^{2}|n\rangle$.

6.10 Applications of the Heisenberg equation of motion: Ehrenfest theorem

Apply the Heisenberg equation of motion to a free particle of mass m. The Hamiltonian is

$$H=\frac{p^{2}}{2m}=\frac{1}{2m}\left(p_{x^{2}}+p_{y^{2}}+p_{z^{2}}\right)$$

$$\therefore\frac{dp_{i}}{dt}=\frac{1}{2\hbar}[p_{i},H]=0$$

Thus for a free particle, the momentum operator is a constant of motion.

We now add potential $V(\vec{x})$ to our earlier free particle Hamiltonian

$$H=\frac{p^{2}}{2m}+V(\vec{x})$$

Heisenberg equation of motion gives

$$\frac{dp_{i}}{dt}=\frac{1}{i\hbar}\left[p_{i},V\left(\vec{x}\right)\right]$$

$$= \frac{1}{i\hbar}(-i\hbar)\frac{\partial V\left(\vec{x}\right)}{\partial x_i}$$

$$= -\frac{\partial}{\partial x_i}V\left(\vec{x}\right) \tag{51}$$

On the other hand, we see that

$$\frac{dx_i}{dt} = \frac{1}{i\hbar}[x_i, H]$$

$$= \frac{1}{i\hbar}\left[x_i, \frac{p_i^2}{2m}\right] = \frac{1}{2mi\hbar}\left[x_i, p_i^2\right]$$

$$= \frac{2\hbar}{2mi\hbar}\frac{\partial}{\partial p_i}\left(p_i^{\,2}\right)$$

$$\frac{dx_i}{dt} = \frac{1}{2m}2p_i = \frac{p_i}{m}$$

Substituting (51), we find

$$m\frac{d^2\vec{x}}{dt^2} = -\nabla V(\vec{x})$$

This is known as ***Ehrenfest theorem***

6.11 Illustrative Examples

Example 3: Show that in quantum mechanics, the time dependence of the expectation value of a dynamical variable q can be expressed as

$$\frac{\mathrm{d}}{\mathrm{dt}} < q >= \left\langle \frac{i}{\hbar}[\hat{H}, \hat{Q}] + \frac{\partial \hat{Q}}{\partial t} \right\rangle$$

where $\hat{Q}$ is the operator corresponding to q and, $[\hat{H}, \hat{Q}]$ is the commutator bracket of Hamiltonian operator with $\hat{Q}$.

Sol. Expectation Value of q

$$< q >= \int \Psi^* \hat{Q} \Psi \, d\tau, \tag{52}$$

where $\hat{Q}$ is operator of dynamical variable q. Because Ψ is a function of time, the expectation value q is also in general, a function of time.

$$\frac{d}{dt}<q>=\int\left(\frac{\partial\Psi^{*}}{\partial t}\hat{Q}\Psi+\Psi^{*}\frac{\partial\hat{Q}}{\partial t}\Psi+\Psi^{*}\hat{Q}\frac{\partial\Psi}{\partial t}\right)d\tau$$

The middle term is zero except when $\hat{Q}$ involves time explicitly. Using the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t}=H\Psi$$

and its complex conjugate is given by,

$$-i\hbar\frac{\partial\Psi^{*}}{\partial t}=H\Psi^{*}$$

we have

$$\frac{d}{dt}<q>=\frac{i}{\hbar}[(\hat{H}\Psi^{*})\hat{Q}\Psi-\Psi^{*}\hat{Q}(\hat{H}\Psi)]d\tau+\int\Psi^{*}\frac{\partial\hat{Q}}{\partial t}\Psi d\tau$$

Since H is a Hermitian operator*, eq. (2) becomes

$$\frac{d}{dt}<q>=\left\langle\frac{i}{\hbar}\int\Psi^{*}(\hat{H}\hat{Q}-\hat{Q}\hat{H})\Psi\,d\tau+\frac{\partial\hat{Q}}{\partial t}\right\rangle$$

We define $(\hat{H}\hat{Q}-\hat{Q}\hat{H})$ by the name commutator bracket of $\hat{H}$, $\hat{Q}$ and it is given the notation. $[\hat{H},\hat{Q}]$.

Thus finally

$$\frac{d}{dt}<q>=\left\langle\frac{i}{\hbar}[(\hat{H},\hat{Q}]+\frac{\partial\hat{Q}}{\partial t}\right\rangle$$

Example 4: Find the acceleration operator $\hat{\dot{v}}$ and deduce the Newton's equation in quantum mechanics

$$m\dot{\vec{v}}=-\nabla U$$

Sol. $$\hat{\dot{\vec{v}}}=\frac{i}{\hbar}\left(\hat{H}\hat{\vec{v}}-\hat{\vec{v}}\hat{H}\right)=\frac{i}{m\hbar}\left(\hat{H}\hat{\vec{p}}-\hat{\vec{p}}\hat{H}\right)$$

Using $\hat{H}=\frac{\hat{p}^{2}}{2m}+U(\vec{r})$, we obtain

$$\hat{\dot{\vec{v}}}=\frac{i}{m\hbar}\left[U\left(\vec{r}\right)\hat{\vec{p}}-\hat{\vec{p}}U\left(\vec{r}\right)\right]$$

$$=\frac{i}{m\hbar}(i\hbar)\nabla U\qquad\left(U\left(\vec{r}\right)\hat{\vec{p}}-\hat{\vec{p}}U\left(\vec{r}\right)=i\hbar\nabla U\right)$$

$$m\dot{\vec{v}} = -\nabla U$$

6.12 Summary

We have studied time evolution operator and found the time development of wave function in the form of Schrodinger's wave equation. In Heisenberg's picture the state vectors remain fixed and dynamical variables vary with time. This picture is convenient when we compare a quantum analogue with that of classical physical system.

6.13 Glossary

Expectation Value: expectation value of quantity A is $\langle A\rangle = \dfrac{\int \psi^* \hat{A}\psi\, dV}{\int \psi^* \psi\, dV}$

Commutator Bracket: $\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$

6.14 Answers to Self Learning Exercise

Ans.1: We know that the integral $\int |\psi|^2 dV$, taken over some finite volume V is the probability of finding the particle in this volume.

We calculate the derivative of this probability with respect to time."

$$\frac{d}{dt}\int |\psi|^2 dV = \int \left(\psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t}\right) dV$$

$$= \frac{i}{\hbar}\int \left(\psi \hat{H}^* \psi^* - \psi^* \hat{H}\psi\right) dV$$

Substituting here

$$\hat{H} = \hat{H}^* = -\frac{\hbar^2}{2m}\Delta + U(x,y,z)$$

and using the identity

$$\psi\Delta\psi^* - \psi^*\Delta\psi = \mathrm{div}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right)$$

We obtain

$$\frac{d}{dt}\int |\psi|^2 dV = -\int div\,\vec{j}\, dV$$

where $\vec{j}$ denotes the vector

$$\vec{j} = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right)$$

$$= \frac{1}{2m}\left(\psi\hat{p}^*\psi^* + \psi^*\hat{p}\psi\right)$$

The integral of div $\vec{j}$ can be transformed by Gauss's theorem into an integral over the closed surface which bounds the volume V:

$$\frac{d}{dt}\int|\psi|^2 dV = -\oint \vec{j}.d\vec{S}$$

$$= -\int div\,\vec{j}dV$$

The vector $\vec{j}$ and the probability density $|\psi|^2$ satisfy the equation

$$\frac{\partial}{\partial t}\int|\psi|^2 + div\,\vec{j} = 0$$

which is equation of continuity

6.15 Exercise

Q.1 Prove the relation involving velocity operator and momentum operator of a particle of mass m

$$\hat{v} = \hat{\vec{v}} = \frac{i}{\hbar}\left[\hat{H}\vec{r} - \vec{r}\hat{H}\right]$$

Q.2 Write the time dependent Schrödinger equation for a free particle in the momentum space and obtain the form of the wave function.

Q.3 Consider a particle of mass m subjected to a one-dimensional potential of the following form

$$V = \begin{cases} \frac{1}{2}kx^2 & for\; x > 0 \\ \infty & for\; x < 0 \end{cases}$$

(i) What is the ground state energy

(ii) What is the expectation value $\langle x^2 \rangle$ for the ground state?

Q.4 An electron is subjected to a uniform, time-independent magnetic field of strength B is the positive Z-direction. At t=0 the electron is known to be in an eigenstate of $S.\hat{n}$ with eigen value $\frac{\hbar}{2}$, where $\hat{n}$ is a unit vector, lying in the xz-plane, that makes an angle β with the Z-axis.

(i)Obtain the probability for finding the electron in the $S_x = \frac{\hbar}{2}$ state as a function of time.

(ii)Find the expectation value of S_x as a function of time.

Q.5 Deduce Heisenberg form of equation of motion.

Q.6 Distinguish between Heisenberg picture and Schrodinger picture.

Q.7 Show that the matrix elements of a Heisenberg operator $\hat{F}_H$ in the energy representation are given by :

$$\exp\left[\frac{i}{h}(E_n - E_m)t\right](\hat{F}_S)_{nm}$$

where $\hat{F}_S$ is the same operator in the Schrödinger picture.

6.16 Answers to Exercise

Ans.1: Using $\hat{H} = \frac{\hat{p}^2}{2m} + U(x,y,z)$

We get $\vec{v} = \frac{i}{2m\hbar}\left[p^2\vec{r} - \vec{r}p^2\right]$

$$= \frac{i}{2m\hbar}\left[(-i\hbar)\frac{\partial}{\partial \vec{p}}\left(p^2\right)\right]$$

$$= \frac{\hbar}{2m\hbar}2\vec{p} = \frac{\vec{p}}{m}$$

Ans.2: The Schrödinger equation in the momentum space is :

$$i\hbar\frac{\partial\Phi(p,t)}{\partial t} = \frac{p^2}{2m}\Phi(p,t)$$

$$\frac{\partial\Phi}{\partial t} = \frac{-ip^2}{2\hbar m}\Phi(p,t)$$

$$\frac{d\Phi}{\Phi} = \frac{-ip^2}{2\hbar m} dt$$

Integrating, $\ln \Phi = \frac{-ip^2 t}{2\hbar m} + \text{Const an t}$

$$\Phi (p, t) = A \exp \left(\frac{-ip^2 t}{2\hbar m} \right) \text{ where A is constant.}$$

When $t = 0$, $\Phi (p, 0) = A$. Thus

$$\Phi (p, t) = \Phi (p, 0) \exp \left(\frac{-ip^2 t}{2\hbar m} \right)$$

which is the form of wave function in momentum space.

Ans.7: Let $|\psi_i\rangle$, $i = 1, 2.....$ be the eigenvectors of Hamiltonian $\hat{H}$, therefore

$$H|\psi_m\rangle = E_m |\psi_m\rangle . \tag{1}$$

Hence $e^{-i\hat{H}t/h} |\psi_m\rangle = \left[1 - \frac{i}{\hbar} \hat{H}t + \left(\frac{i}{\hbar} \hat{H} \right)^2 \frac{t^2}{2!} + ... \right] |\psi_m\rangle$

$$= \left[1 - \frac{i}{\hbar} E_m t + \left(\frac{i}{\hbar} E_m \right)^2 \frac{t^2}{2!} + ... \right] |\psi_m\rangle$$

$$= e^{-(i/\hbar)E_m t} |\psi_m\rangle ,$$

Using eq. (1). Similarly we have

$$\langle \psi_n | e^{(i/\hbar)\hat{H}t} = e^{(i/\hbar)E_n t} \langle \psi_n |,$$

Because an operator operates on a bra vector on the left. So the matrix elements of Heisenberg operator $\hat{F}_H$ are

$$\left(\hat{F}_H \right)_{nm} = \langle \psi_n | \hat{F}_H | \psi_m \rangle$$

$$= \langle \psi_n | e^{(i/\hbar)\hat{H}t} \hat{F}_S e^{-(i/\hbar)\hat{H}t} | \psi_m \rangle$$

$$= e^{(i/\hbar)(E_n - E_m)t} \langle \psi_n | \hat{F}_S | \psi_m \rangle$$

$$= e^{(i/\hbar)(E_n - E_m)t} (\hat{F}_S)_{nm}$$

In the $\hat{H}$-representation or energy representation.

References and Suggested Readings

1. P.A.M. Dirac ,Principle of Quantum Mechanics, Fourth edition, Oxford University Press,1958
2. J. J. Sakurai, Modern Quantum Mechanics (2nd Edition), Addison-Wesley;2010
3. Eugen Merzbacher ,Quantum Mechanics ,third Edition ,John Wiley & Sons (Asia) Pte Ltd.1999
4. L.D.Landau and E.M.Lifshitz ,Quantum Mechanics(Non relativistic theory) Vol-3 ,third edition, Butterworth Heinmann
5. Ajoy Ghatak & S.Lokanathan ,Quantum Mechanics "Theory and Applications" Fourth Edition ,Macmillan India Ltd,1999
6. Gupta Kumar Sharma ,Quantum Mechanics ,Jai Prakash Nath &Co.Meerut,2000
7. G.Aruldas, Quantum Mechanics ,Second Edition ,PHI learning Private Limited, Delhi ,2013

UNIT -7

Simple Harmonic Oscillator , Creation and Annihilation Operators

Structure of the Unit

7.0 Objectives

In this unit our objectives are to introduce an operator formalism that has wide spread applications in quantum mechanics .We shall use this formalism to find the eigenvalues and eigen functions of simple harmonic oscillator.

7.1 Introduction

An important problem in quantum mechanics is that of simple harmonic oscillator. This problem can be used to illustrate the basic concepts and methods in quantum mechanics. It has applications in a variety of branches of modern physics-molecular spectroscopy, solid state physics, quantum field theory, quantum optics, quantum statistical mechanics and so forth. Although understanding of the properties of quantum mechanical oscillators is insensible for any serious student of modern physics. To solve the problem of eigenvalues and eigenfunctions of harmonic oscillator it is convenient to define two non Hermitian operators known as the annihilation operator and the creation operator, respectively. We shall solve the problem of Simple harmonic oscillator using the formalism of annihilation and creation operator.

7.2 Creation and Annihilation Operators

In the following we describe an operator formalism that has widespread applications in quantum mechanics, notably in dealing with harmonic oscillators and in describing many particle systems.

We begin by formulating and solving the following simple problem: Suppose an operator *a* satisfies. $[a, a^{+}] = 1$ (1)

The problem is to find the Eigenvalues of the Hermitian operators $a^{+}a$, and to relate the Eigen vectors.

(Note: a^{+} denotes the Hermitian conjugate of *a*, and $[A, B]$is, of course, the commutator AB-BA.

- We first note that, if $|\alpha\rangle$ is a normalized Eigenvector with

$$a^{+}a|\alpha\rangle = \alpha|\alpha\rangle \tag{2}$$

Then $\alpha = \langle\alpha|a^{+}a|\alpha\rangle = \| a|\alpha\rangle \|^{2} \geq 0$ (3)

That is, the Eigenvalues are all real and non-negative.

- Using the identity $[AB,C]=A[B,C]+[A,C]B$ we note

$$[a^+a,a]=[a,a]a=-a \tag{4}$$

and $$[a^+a,a^+]=a^+[a,a^+]=a^+ \tag{5}$$

or, equivalent by

$$(a^+a)a=a(a^+a-1) \tag{4'}$$
$$(a^+a)a^+=a^+(a^+a+1) \tag{5'}$$

- From eq. (4) we have, for an Eigenvector $|\alpha\rangle$

$$(a^+a)a|\alpha\rangle=a\ (a^+a-1)|\alpha\rangle=a\ (\alpha-1)|\alpha\rangle=(\alpha-1)a|\alpha\rangle \tag{6}$$

Therefore $a|\alpha\rangle$ is an Eigen vector with Eigen value $\alpha-1$, unless $a|\alpha\rangle=0$.

Similarly $a^+|\alpha\rangle$ is an Eigen vector with Eigen value $(\alpha+1)$, unless $a^+|\alpha\rangle=0$

- The norm of $a|\alpha\rangle$ is found form

$$\|a|\alpha\|^2=\langle\alpha|a^+a|\alpha\rangle=\alpha\langle\alpha|\alpha\rangle=\alpha$$

or $$\|a|\alpha\|=\sqrt{\alpha} \tag{7}$$

Similarly,

$$\|a^+|\alpha\|=\sqrt{\alpha+1} \tag{8}$$

- Now, suppose that $a^n|\alpha\rangle\neq 0$ for all n, they by repeated application of (6), $a^n|\alpha\rangle$ is an eigen vector of a^+a with Eigen value $\alpha-n$.

This contradicts eq. (3), because $\alpha-n<0$ for sufficiently large n. therefore we must have $a^n|\alpha\rangle\neq 0$ but $a^{n+1}|\alpha\rangle=0$

For some non-negative integer n.

Let $|\alpha-n\rangle=\dfrac{a^n|\alpha\rangle}{\|a^n|\alpha\|}$, so that $|\alpha-n\rangle$ is a normalized Eigenvector with Eigen value $\alpha-1$. Then from eq. (7) and (9) $\sqrt{\alpha-n}=\|a|\alpha-n\rangle\|=0$ and therefore $\alpha=n$

This shows that the Eigenvalues of a^+a must be non-negative integers, ad that there is a "ground State" $|0\rangle$ such that $a|0\rangle=0$

- By repeatedly applying a^{+} to the ground state we see that $(a^{+})^{n}|0\rangle$ has the Eigen value n, and because of Eq. (8), it is never zero. Thus the Eigen values of $a^{+}a$ are 0, 1, 2, 3…
- If $|n\rangle$ is a normalized Eigenvector with Eigenvalue n, then, from eq (8)

$|n-1\rangle = \left(\frac{1}{\sqrt{n}}\right)a|n\rangle$ is a normalized Eigenvector with Eigenvalue n-1

Also $a^{+}|n-1\rangle = \frac{1}{\sqrt{n}}a^{+}a|n\rangle = \sqrt{n}|n\rangle$

So applying a^{+} to $|n-1\rangle$ gives us back $|n\rangle$ (with a factor), rather than some other state with Eigen value n.

- We may then construct the Eigenstates of $a^{+}a$ as follows:

First we find a state $|0\rangle$ such that $a|0\rangle = 0$ (11)

Then we define

$$|1\rangle = a^{+}|0\rangle;$$

$$|2\rangle = \frac{1}{\sqrt{2}}a^{+}|1\rangle = \frac{1}{\sqrt{2}}(a^{+})^{2}|0\rangle$$

$$|3\rangle = \frac{a^{+}|2\rangle}{\sqrt{3}} = \frac{(a^{+})^{3}|0\rangle}{\sqrt{3!}}$$

and in general $\boxed{|n\rangle = \frac{1}{\sqrt{n!}}(a^{+})^{n}|0\rangle}$

(Note that we could have included arbitrary phase factor in the definition of $|n\rangle$, our convention here is to make them unity).

- With this definition, they $|n\rangle$ are orthonormal and satisfy

$$\boxed{a^{+}|n\rangle = \sqrt{n+1}|n+1\rangle} \tag{13}$$

$$\boxed{a|n\rangle = \sqrt{n}|n-1\rangle} \tag{14}$$

$$\boxed{a^{+}a|n\rangle = n|n\rangle} \tag{15}$$

- The operators a^+ and a are called ***"raising"*** and ***"lowering"*** operators respectively, a^+a will be interpreted as the observable representing the number of particles of a certain kind, in which case a^+ ***and a are called "Creation" and "Annihilation" operators***, or "emission"and "absorption" operators.

- Equations (13) and (14) may be expressed in terms of matrix elements

$$\boxed{\langle m|a^+|n\rangle = \sqrt{n+1}\delta_{m,n+1}} \tag{13'}$$

$$\boxed{\langle m|a|n\rangle = \sqrt{n}\delta_{m,n-1}} \tag{14'}$$

Note *that we can represent* a^+ **as** $\bar{a}\ or\ a^\dagger$

7.3 Illustrative Examples

Example 1: Suppose a operator a satisfies

$$[a,a^+]=1 \tag{1}$$

Then find the eigen values of the Hermitian operator a^+a .Also find eigen vectors of a^+a .

{Note that a^+ denotes the Hermitian conjugate of *a*, and $[a,a^+]$ is, of course the commutator $aa^+ - a^+a$ }.

Sol. We first note that, if $|\alpha\rangle$ is a normalized eigenvector with

$$a^+a|\alpha\rangle = \alpha|\alpha\rangle \tag{2}$$

Then $\alpha = \langle\alpha|a^+a|\alpha\rangle = \left\| a|\alpha\rangle \right\|^2 \geq 0$ $\quad$ (3)

That is, the eigenvalues are all real and nonnegative.

Using the identity $[AB,C]=A[B,C]+[A,C]B$, we observe that

$$[a^+a,a]=[a^+,a]a=-a \tag{4}$$

$$[a^+a,a^+]=a^+[a,a^+]=a^+ \tag{5}$$

Or, equivalently

$$(a^+a)a=a(a^+,a-1) \tag{6}$$

$$(a^+a)a^+=a(a^+a+1) \tag{7}$$

From (6) we have, for an eigenvector $|\alpha\rangle$,

$$\left(a^{+}a\right)a|\alpha\rangle = a\left[a^{+}a-1\right]|\alpha\rangle = a(\alpha-1)|\alpha\rangle = (\alpha-1)a|\alpha\rangle \tag{8}$$

Therefore $a|\alpha\rangle$ is an eigenvector with eigenvalue $(\alpha-1)$, unless $a|\alpha\rangle = 0$.

Similarly $a^{+}|\alpha\rangle$ is an eigenvector with eigenvalue with $(\alpha+1)$, unless $a^{+}|\alpha\rangle = 0$.

The norm of $a|\alpha\rangle$ is found from

$$\left\|a|\alpha\rangle\right\|^{2} = \left\langle\alpha\left|a^{+}a\right|\alpha\right\rangle = \alpha\langle\alpha|\alpha\rangle = \alpha$$

Or $$a|\alpha\rangle = \sqrt{\alpha} \tag{9}$$

similarly $$\left\|a^{+}|\alpha\rangle\right\| = \sqrt{\alpha+1} \tag{10}$$

Now, suppose that $a^{n}|\alpha\rangle \neq 0$ for all n. Then by repeated application of (8); $a^{n}|\alpha\rangle$ in an eigenvector of $a^{+}a$ with eigenvalue $\alpha-n$. This contradicts Eq. (3), because $\alpha-n<0$ for sufficiently large *n*. Therefore we must have

$$a^{n}|\alpha\rangle \neq 0 \quad \text{but} \quad a^{n+1}|\alpha\rangle = 0 \tag{11}$$

For some nonnegative integer *n*.

Let $|\alpha-n\rangle = \dfrac{a^{n}|n\rangle}{\left\|a^{n}|n\rangle\right\|}$, so that $|\alpha-n\rangle$ is a normalized eigenvector with eigenvalue $\alpha-n$.

Then from (9) and (11)

$$\sqrt{\alpha-n} = \left\|a|\alpha-n\rangle\right\| = 0$$

And therefore $\alpha = n$. This shows that the eigenvalues $a^{+}a$ must be nonnegative integers, and that there is a "ground state" $|0\rangle$ such that

$$a|0\rangle = 0 \tag{12}$$

By repeatedly applying a^{+} to the ground state we see that $\left(a^{+}\right)^{n}|0\rangle$ has the eigenvalue *n*, and because of Eq. (10), it is never zero.

Thus the eigenvalues of $a^{+}a$ are 0,1,2,3.

- If $|n\rangle$ is a normalized eigenvector with eigenvalue n.

then

$$\left|n-1\right\rangle = \frac{a\left|n\right\rangle}{\left\|a\left|n\right\rangle\right\|} = \frac{a\left|n\right\rangle}{\sqrt{n}}$$

Thus $a\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle$

Also $a^{+}\left|n-1\right\rangle = \frac{a^{+}a\left|n\right\rangle}{\sqrt{n}} = \frac{n\left|n\right\rangle}{\sqrt{n}} = \sqrt{n}\left|n\right\rangle$.

So applying a^{+} to $\left|n-1\right\rangle$ gives us back $\left|n\right\rangle$ (within a factor), rather than some other state with eigenvalue $\left|n\right\rangle$.

We may construct the eigenstates of $a^{+}a$ as follows :

First we find a state $\left|0\right\rangle$ such that

$$a\left|0\right\rangle = 0 \qquad (13)$$

Then we define

$$\left|1\right\rangle = a^{+}\left|0\right\rangle; \left|2\right\rangle = \frac{1}{\sqrt{2}}a^{+}\left|1\right\rangle = \frac{1}{\sqrt{2}}\left(a^{+}\right)^{2}\left|0\right\rangle;$$

And in general $\left|n\right\rangle = \frac{1}{\sqrt{n!}}\left(a^{+}\right)^{n}\left|0\right\rangle$ (14)

The $\left|n\right\rangle$ are orthonormal and satisfy

$$a^{+}\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle \qquad (15)$$

$$a\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle \qquad (16)$$

$$a^{+}a\left|n\right\rangle = n\left|n\right\rangle \qquad (17)$$

7.4 Linear Harmonic Oscillator

Hamiltonian of one dimensional harmonic oscillator

$$\boxed{H = \frac{p^{2}}{2m} + \frac{1}{2}mw^{2}x^{2}} \qquad (16)$$

- x and p are position and momentum operators for the particle and satisfy

$$\boxed{\left[x, p\right] = i\hbar} \qquad (17)$$

Our task into find the Eigen values and Eigen states of H.

- Define $\boxed{a=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{mw}{\hbar}}x+i\frac{1}{\sqrt{mw\hbar}}p\right)}$ (18)

- Because x and p are Hermitian it follows that

$$\boxed{a^{+}=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{mw}{\hbar}}x-i\frac{1}{\sqrt{mw\hbar}}p\right)} \tag{19}$$

From (17) we obtain $\boxed{\left[a,a^{+}\right]=1}$ (20)

It follows $\boxed{x=\sqrt{\frac{\hbar}{mw}}\frac{a+a^{+}}{\sqrt{2}}}$ (21)

$$\boxed{p=\sqrt{mw\hbar}\,\frac{a-a^{+}}{i\sqrt{2}}} \tag{22}$$

We get, for the Hamiltonian

$$\boxed{H=\frac{\hbar w}{2}\left(a^{+}a+aa^{+}\right)=\hbar w\left(a^{+}a+\frac{1}{2}\right)} \tag{23}$$

Thus, the Eigen states of H are those of $a^{+}a$

It now follows: $\boxed{H\left|n\right\rangle=\left(n+\frac{1}{2}\right)\hbar w\left|n\right\rangle}$ (24)

The energy levels are thus $\boxed{E_{n}=\left(n+\frac{1}{2}\right)\hbar w}$

Eigen states are given by (11) and (12)

We can easily obtain the wavefunctions $\varphi_{n}(x)=\left\langle x|n\right\rangle$ follows

$$0=a\left|0\right\rangle\sqrt{\frac{mw}{2\tau}}\left(x+\frac{i}{mw}p\right)\left|0\right\rangle \tag{25}$$

Applying $\left\langle x\right|$ and noticing that $\left\langle x\right|p\left|\varphi\right\rangle=-i\hbar\frac{d}{dx}\left\langle x|\varphi\right\rangle$ we get

$$0=\sqrt{\frac{mw}{2\hbar}}\left(x+\frac{\hbar}{mw}\frac{d}{dx}\right)\left\langle x|0\right\rangle \tag{26}$$

Solving it, we get

$$\langle x|0\rangle = Ae^{-\left(\frac{mw}{2\hbar}\right)x^2}$$

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-\left(\frac{mw}{\hbar}\right)x^2} dx$$

$$= |A|^2 \sqrt{\frac{\pi\hbar}{mw}}$$

$$\therefore A = e^{i\theta}\left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}}$$

The phase θ of A is arbitrary, and we set is equal to zero.

Then $A = \left(\frac{mw}{\pi\hbar}\right)^{1/4}$

$$\therefore \langle x|0\rangle = \left(\frac{mw}{\pi\hbar}\right)^{1/4} e^{-\left(\frac{mw}{2\hbar}\right)x^2} \tag{27}$$

For the other states we apply a^{+}

$$\langle x|n\rangle = \frac{1}{\sqrt{n!}}\langle x|\ \left(a^{+}\right)^{n}|0\rangle\langle x|\left(a^{+}\right)^{n}|0\rangle \tag{28}$$

Since $\because \langle x|a^{+} = \left(\frac{mw}{2\hbar}\right)\langle x|\left(x-\frac{i}{mw}p\right)$

$$= \sqrt{\frac{mw}{2\hbar}\left(x-\frac{\hbar}{mw}\frac{d}{dx}\right)\langle x|}$$

We have

$$\langle x|n\rangle = \frac{1}{\sqrt{n!}}\left(\frac{mw}{2\tau}\right)^{\frac{n}{2}}\left(x-\frac{\hbar}{mw}\frac{d}{dx}\right)^{n}\langle x|0\rangle$$

$$= \frac{1}{\sqrt{n!}}\left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}}\left(\frac{mw}{2\hbar}\right)^{\frac{n}{2}}\left(x-\frac{\hbar}{mw}\frac{d}{dx}\right)^{n} e^{-\left(\frac{mw}{2\hbar}\right)x^2} \tag{29}$$

7.5 Illustrative Examples

Example 2: Evaluate $\langle 0|x^4|0\rangle$, where x is the position operator of simple harmonic oscillator, $|0\rangle$ state is the ground state of simple harmonic oscillator.

Sol. $\because x = \sqrt{\frac{\hbar}{mw}}\frac{a+a^+}{\sqrt{2}}$

Therefore

$$\langle 0|x^4|0\rangle = \langle 0|\left(a+a^+\right)^4|0\rangle\left(\frac{\hbar}{2mw}\right)^2$$

Expanding $\left(a+a^+\right)^4$ gives is 16 terms, the only terms giving a non zero expectation value are those with *a*'s and two a^+'s :

$$\langle 0|\left(a+a^+\right)^4|0\rangle$$

$$= \langle 0|a^+a^+aa + a^+aa^+a + a^+aaa^+ + aa^+a^+a + aa^+aa^+ + aaa^+a^+|0\rangle$$

$$= 0+0+0+0+1+2$$

$$= 3$$

$$\therefore \langle 0|x^4|0\rangle = \left(\frac{\hbar}{2mw}\right)^2 .3 = 3\left(\frac{\hbar}{2mw}\right)^2$$

Example 3: Consider one-dimensional harmonic oscillator which has a Hamiltonian of the form :

$$H = \frac{1}{2m}p^2 + \frac{mw^2}{2}x^2$$

Where x and p are the position and momentum operators and satisfy

$$[\mathrm{x}, p] = i\hbar$$

Define $a = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{mw}{\hbar}}x + i\frac{1}{\sqrt{mw\hbar}}p\right)$ and $a+ = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{mw}{\hbar}}x - i\frac{1}{\sqrt{mw\hbar}}p\right)$

(Because x and p are Hermitian)

(1) Find H in terms of a and a^+

(2) Find eigenvalues of H

(3) Find ground state wave-function

Sol. Expressing x and p in terms of a and a^+, we have

$$a = \sqrt{\frac{\hbar}{mw}} \frac{a + a^{+}}{\sqrt{2}}$$

$$p = \sqrt{mw\hbar} \frac{a - a^{+}}{\sqrt{2}}$$

Substituting for x and p in the Hamiltonian

$$H = \frac{\hbar w}{2}\left(a^{+}a + aa^{+}\right)$$

$$= \frac{\hbar w}{2}\left(a^{+}a + a^{+}a + 1\right)$$

$$= \hbar w\left(a^{+}a + \frac{1}{2}\right)$$

Thus , the eigenstates of H are those of $a^{+}a$.

$$H\left|n\right\rangle = \hbar w\left(a^{+}a + \frac{1}{2}\right)\left|n\right\rangle$$

$$= \left(n + \frac{1}{2}\right)\hbar w\left|n\right\rangle$$

The energy levels are thus $\left(n + \frac{1}{2}\right)\hbar w$.

Also $0 = a\left|0\right\rangle = \sqrt{\frac{mw}{2\hbar}}\left(c + \frac{i}{mw}.p\right)\left|0\right\rangle$

Applying $\left\langle x\right|$ and noticing that $\left\langle x\right|p\left|\phi\right\rangle = -i\hbar\frac{d}{dx}\left\langle x|\phi\right\rangle$, we get

$$0 = \sqrt{\frac{mw}{2\hbar}}\left(x + \frac{\hbar}{mw}\frac{d}{dx}\right)\left\langle x|\phi\right\rangle$$

(Where x is now a number rather than an operator)

Solving the above differential equation, we get

$$\frac{\hbar}{mw}\sqrt{\frac{mw}{2\hbar}}\frac{d}{dx}\left\langle x|0\right\rangle = -x\sqrt{\frac{mw}{2\hbar}}\left\langle x|0\right\rangle$$

or $$\frac{d\left\langle x|0\right\rangle}{\left\langle x|0\right\rangle} = -\sqrt{\frac{mw}{2\hbar}.\frac{2\hbar}{mw}}.\frac{mw}{\hbar}xdx$$

or $$\ln\langle x|0\rangle = -\frac{mwx^2}{2\hbar} + \ln A$$

$\therefore \langle x|0\rangle = Ae^{-\frac{mwx^2}{2\hbar}}$, where A is a constant. Normalization requires

$$1 = \langle 0|0\rangle = \int_{-\infty}^{\infty} \langle x|0\rangle\langle x|0\rangle dx = |A|^2 \int_{-\infty}^{\infty} e^{-\frac{mwx^2}{2\hbar}} dx$$

$$= |A|^2 \sqrt{\frac{\pi\hbar}{mw}}$$

Thus $A = \left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}}$

7.6 The Uncertainty Product

We calculate the uncertainty product $\Delta x\ \Delta p$ for the harmonic oscillator states. The uncertainties Δx and Δp are given by :

$$\boxed{\Delta x = \left[\langle x^2\rangle - \langle x\rangle^2\right]^{1/2}}$$

and $$\boxed{\Delta p = \left[\langle p^2\rangle - \langle p\rangle^2\right]^{1/2}}$$

where

$$\langle x\rangle = \langle n|x|n\rangle,\ \langle x^2\rangle = \langle n|x^2|n\rangle$$
$$\langle p\rangle = \langle n|p|n\rangle,\ \langle p^2\rangle = \langle n|p^2|n\rangle$$

represent the expectation values of the operators in the n$^{\text{th}}$ eigenstate of the oscillator. Now,

$$\boxed{x = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} (a^+ + a)}$$

$$\boxed{p = i\left(\frac{\mu\hbar\omega}{2}\right)^{1/2} (a^+ - a)}$$

Thus $$\langle x\rangle = \langle n|x|n\rangle = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \langle n|a^+ + a|n\rangle$$

$$= \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \left[\sqrt{n+1}\langle n | n+1 \rangle + \sqrt{n}\langle n | n-1 \rangle\right]$$

$$= 0 \qquad \left\{\because \boxed{\langle n | m \rangle = \delta_{mn}}\right\}$$

and

$$\langle x^2 \rangle = \langle n | x^2 | n \rangle = \frac{\hbar}{2\mu\omega}\left[\langle n | a^+ a^+ | n \rangle + \langle n | a^+ a | n \rangle + \langle n | a a^+ | n \rangle + \langle n | a a | n \rangle\right]$$

$$= \frac{\hbar}{2\mu\omega}[0 + n + (n+1) + 0]$$

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

Similarly

$$\langle p \rangle = \langle n | p | n \rangle = 0 \text{ and } \langle p^2 \rangle = \mu\omega\hbar(n + \frac{1}{2})$$

This gives

$$\boxed{\Delta x \, \Delta p = (n + \frac{1}{2})\hbar}$$

The minimum value $(= \frac{1}{2}\hbar)$ ***occurring for the ground state.***

7.7 The Number Operator

Consider the operator

$$\boxed{N_{op} = a^+ a}$$

$$H = \left(N_{op} + \frac{1}{2}\right)\hbar\omega$$

Since $\boxed{H | n \rangle = \left(n + \frac{1}{2}\right)\hbar\omega | n \rangle}$

We have

$$\boxed{N_{op} | n \rangle = n | n \rangle}$$

Hence $|n\rangle$ are also the eigenkets of N_{op}, the corresponding eigenvalues being *n* and since *n* takes the values 0, 1, 2,………., the operator N_{op} is called the number operator. For this reason, $|n\rangle$ are often referred to as number states. Obviously

$$\boxed{\langle m | N_{op} | n \rangle = n\delta_{mn}}$$

7.8 Self Learning Exercise

Q1. Find the values of $\langle m|a^{+}|n\rangle$ and $\langle m|a|n\rangle$.

Q.2 Evaluate $\langle n|\left(a+a^{+}\right)^{4}|n\rangle$

Q.3 In the linear harmonic oscillator problem, let $|n\rangle$ represent the set of orthonormal eigenkets of H.

(a) Evaluate $\langle 4|x^{2}|6\rangle$, $\langle 5|p^{2}|6\rangle$

(b) Are $|0\rangle$, $|1\rangle$ and $|2\rangle$ eigenkets of *a* ?

(c) Evaluate (i) H $\left[a^{+}a^{+}|0\rangle\right]$ (ii) H $\left[a\,a|n\rangle\right]$

(d) If $\left|\psi(t=0)\rangle = \frac{1}{\sqrt{2}}[|1\rangle + i|3\rangle]\right|$

Then what would be $|\psi(t)\rangle$

7.9 Illustrative Examples

Example 4: For Linear harmonic Oscillator obtain the value of $\langle 3|x^{3}|2\rangle$

Sol. $\langle 3|x^{3}|2\rangle = \left(\frac{\hbar}{2m\omega}\right)^{3/2} \langle 3|\left(a+a^{+}\right)^{3}|2\rangle$

$$= \left(\frac{\hbar}{2m\omega}\right)^{3/2} \langle 3|a^{3} + a^{2}a^{+} + aa^{+}a + aa^{+}a^{+} + a^{+}aa + a^{+}aa^{+} + a^{+}a^{+}a + a^{+}a^{+}a^{+}\,)|2\rangle$$

Since *a* lowers *n* by one unit and $\bar{a}$ raises it by one unit and we want to go up by one unit from n = 2 to n = 3, the only nonzero contribution comes from $\bar{a}\,\bar{a}a$, $a\,\bar{a}\,\bar{a}$ and $\bar{a}\,a\bar{a}$. Now

$$a^{+}a^{+}a|2\rangle = 2^{1/2}\, a^{+}a^{+}|1\rangle = 2^{1/2}2^{1/2}a^{+}|2\rangle = 2^{1/2}2^{1/2}3^{1/2}|3\rangle$$

$$aa^{+}a^{+}|2\rangle = 3^{1/2}\, aa^{+}|3\rangle = 3^{1/2}4^{1/2}a|4\rangle = 3^{1/2}4^{1/2}4^{1/2}|3\rangle$$

$$a^+aa^+|2\rangle = 3^{1/2}\,a^+a|3\rangle = 3^{1/2}N|3\rangle = 3^{1/2}3|3\rangle$$

So that

$$\langle 3|\mathrm{x}^3|2\rangle = \left(\frac{\hbar}{2\mu\omega}\right)^{3/2}\left[2(3^{1/2})+4(3^{1/2})+3(3^{1/3})\right]$$

Example 5: Using equations $a^+|n\rangle = \sqrt{(n+1)}|n+1\rangle$ and $|n\rangle = \frac{(a^+)^n}{\sqrt{n!}}|0\rangle$ evaluate the matrix elements $\langle m|a|n\rangle$ and $\langle m|a^+|n\rangle$

Write the matrices representing a and $\overline{a}$ and show that they are not Hermitian.

Sol. $\langle \mathrm{m}|\mathrm{a}|\mathrm{n}\rangle = \sqrt{\mathrm{n}}\langle \mathrm{m}|\mathrm{n}-1\rangle = \sqrt{\mathrm{n}}\delta_{\mathrm{m,n-1}}$

and $\langle \mathrm{m}|\overline{\mathrm{a}}|\mathrm{n}\rangle = \sqrt{\mathrm{n}+1}\langle \mathrm{m}|\mathrm{n}+1\rangle = \sqrt{\mathrm{n}+1}\delta_{\mathrm{m,n+1}}$

Thus the matrices which represent a and $\overline{\mathrm{a}}$ are

$$\mathrm{a} = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \cdots \\ 0 & 0 & 0 & 0 & \sqrt{4} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix}$$

and

$$\overline{\mathrm{a}} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & 0 & .. \\ 0 & \sqrt{2} & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix}$$

which are non Hermitian matrices

7.10 Summary

The operators a^+ and a are called “raising” and “lowering” operators ,respectively, because they raise and lower the eigenvalues of a^+, a.

a^+a will be interpreted as the observable representing the number of particles of a certain kind ,in which case a^+ and a are called ‘Creation ’and ‘Annilhilation

’operators. As an application of this formalism we have solved the simple harmonic oscillator problem and found its eigenvalues and eigenfunctions. This formalism is highly useful in quantum field theory.

7.11 Glossary

a : Annihilation operator

a^+ : Creation operator

a^+a : Number operator

$\left[a, a^+\right] = 1$: Commutator relation

7.12 Answers to Self Learning Exercise

Ans.1: $\langle m|a^+|n\rangle = \sqrt{n+1}\langle m|n+1\rangle$

$$= \sqrt{n+1}\,\delta_{m,n+1}$$

and $\langle m|a|n\rangle = \sqrt{n}\,\langle m|n-1\rangle = \sqrt{n}\,\delta_{m,n-1}$

Ans.2:

$$\langle n|\left(a+a^+\right)^4|n\rangle = \langle n|a^+a^+aa + a^+aa^+a + a^+aaa^+ + aa^+a^+a + aa^+aa^+ + aaa^+a^+|n\rangle$$

$$= n(n-1) + n^2 n(n-1)n(n+1) + (n+1)^2 + (n+1)(n+2)$$

$$= 6\mathrm{n}^2 + 6n + 3$$

Ans.3: (b) Only $|0\rangle$ is an eigenket of a **(c)**(ii) $\sqrt{\mathrm{n}(\mathrm{n}-1)}(\mathrm{n}-\frac{5}{2})\hbar\omega|\,\mathrm{n}\rangle$

7.13 Exercise

Q.1 Show that

$$\langle \mathrm{m}\,|\,\mathrm{x}\,|\,\mathrm{n}\rangle = \begin{cases} \left(\dfrac{\hbar}{2\mu\omega}\right)^{1/2}\sqrt{\mathrm{n}+1} & \text{for } \mathrm{m}=\mathrm{n}+1 \\ \left(\dfrac{\hbar}{2\mu\omega}\right)^{1/2}\sqrt{\mathrm{n}} & \text{for } \mathrm{m}=\mathrm{n}-1 \\ 0 & \text{otherwise} \end{cases}$$

$$\langle m|p|n\rangle = \begin{cases} i\left(\frac{\mu\hbar\omega}{2}\right)^{1/2}\sqrt{n+1} \text{ for } m=n+1 \\ -i\left(\frac{\mu\hbar\omega}{2}\right)^{1/2}\sqrt{n} \quad \text{for } m=n-1 \\ 0 \qquad \text{otherwise} \end{cases}$$

Write the matrices representing x and p show that they are both Hermitian.

Q.2 Show that

$$\left\langle n\left|\frac{1}{2}\mu\omega^2x^2\right|n\right\rangle = \left\langle n\left|\frac{p^2}{2\mu}\right|n\right\rangle$$

Implying that the expectation values of the potential and kinetic energies are equal

Q.3 (a) Show that

$$\langle m|x^2|n\rangle = \begin{cases} \frac{\hbar}{2\mu\omega}\sqrt{(n+1)(n+2)} \text{ for } m=n+2 \\ \frac{\hbar}{2\mu\omega}(2n+1) \qquad \text{for } m=n \\ \frac{\hbar}{2\mu\omega}\sqrt{n(n-1)} \qquad \text{for } m=n-2 \\ 0 \qquad \text{otherwise} \end{cases}$$

(b) Similarly evaluate $\langle m|p^2|n\rangle$ and show that

$$\left\langle m\left|\frac{p^2}{2\mu}+\frac{1}{2}\mu\omega^2x^2\right|n\right\rangle = \left(n+\frac{1}{2}\right)\hbar\omega\delta_{mn}$$

Q.4 In the linear harmonic oscillator problem, let $|n\rangle$ represent the set of orthonormal eigenkets of H.

(a) Evaluate $\langle 4|x^2|6\rangle$, $\langle 5|p^2|6\rangle$

(b) Are $|0\rangle$, $|1\rangle$ and $|2\rangle$ eigenkets of a ?

(c) Evaluate (i) H $\left[a^+a^+|0\rangle\right]$ (ii) H $\left[a\,a|n\rangle\right]$

(d) If $\left|\psi(t=0)\rangle = \frac{1}{\sqrt{2}}[|1\rangle + i|3\rangle]\right|$

Q.5 Show that

$$\langle n\,|\,x^4\,|\,n\rangle = \frac{3}{2}\left(\frac{\hbar}{\mu\omega}\right)^2\left(n^2+n+\frac{1}{2}\right)$$

Then what would be $|\,\psi(t)\rangle$

7.14 Answers to Exercise

Ans.4: (b) Only $|\,0\rangle$ is an eigenket of a **(c)**(ii) $\sqrt{n(n-1)}(n-\frac{5}{2})\hbar\omega|\,n\rangle$

References and Suggested Readings

1. J. J. Sakurai, Modern Quantum Mechanics (2nd Edition), Addison-Wesley;2010
2. Quantum Mechanics "Theory and Applications" by Ajoy Ghatak & S.Lokanathan,Fourth Edition,Macmillan India Ltd,1999
3. Principles Of Quantum Mechanics by R.Shankar , Second Edition ,Springer 2012
4. Eugen Merzbacher ,Quantum Mechanics ,third Edition ,John Wiley & Sons (Asia) Pte Ltd.1999

UNIT-8

Schrodinger's Equation

Continuity Equation, Potential Well

Structure of the Unit

8.0 Objectives

This unit constitutes the basic concepts related to Schrodinger equation and probability current density. One can learn the properties of Schrodinger equation.

Applications of boundary conditions is introduced in the potential well problem.

8.1 Introduction

Schrodinger equation is the milestone in the whole mathematical formalism of quantum mechanics. In this unit we discuss the Schrodinger equation and its properties. We derive the equation of continuity for probability current density. Finally we study the potential well problem qualitatively.

8.2 Schrodinger Equation

Wave equation for a particle in an external field

$$\boxed{i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+U\psi} \tag{8.1}$$

Above equation is called ***Schrodinger's equation*** which was obtained by Schrodinger in 1926.

Here ψ is the wavefunction that describes the state of quantum mechanical system.

$U=U(\vec{r},t)$ is the potential energy of the particle in the external field.

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

Eq.(8.1) is the basic equation of nonrelativistic quantum mechanics. It must be remembered that this equation cannot be derived. Agreement between predictions and experiment gives justification for eq.(8.1). Schrodinger equation is a fundamental one in quantum mechanics.

Eq.(8.1) is known as ***time dependent Schrodinger equation***. Eq.(8.1) can be written as

$$i\hbar\frac{\partial\psi}{\partial t}=\left[-\frac{\hbar^2}{2m}\nabla^2+U\right]\psi$$

$$\Rightarrow\boxed{i\hbar\frac{\partial\psi}{\partial t}=H\psi}$$

where $\boxed{H=-\frac{\hbar^2}{2m}\nabla^2+U}$ is the ***Hamiltonian operator***

The Time Independent Schrodinger Equation & Stationary States:-

There are many problems in which the potential energy of the particle does not depend on the time i.e. $U(x,y,z,t)=U(x,y,z)$

In order to solve the Schrodinger equation ,we use the method of separation of variables.

$$\psi(\vec{r},t)=\psi(\vec{r})\phi(t) \tag{8.2}$$

Then Schrodinger equation becomes

$$i\hbar\frac{\partial}{\partial t}\left[\psi(\vec{r})\phi(t)\right]=-\frac{\hbar^2}{2m}\nabla^2\left[\psi(\vec{r})\phi(t)\right]+U\psi(\vec{r})\phi(t)$$

$$i\hbar\psi(\vec{r})\frac{d}{dt}\phi(t)=-\phi(t)\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+U\psi(\vec{r})\phi(t)$$

$$i\hbar\frac{1}{\phi(t)}\frac{d}{dt}\phi(t)=-\frac{1}{\psi(\vec{r})}\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+U \tag{8.3}$$

Here left hand side depends only on time *t* whereas right hand side only on position $\vec{r}$. Therefore we have set them equal to a constant E that is equal to the total energy of the particle.

From eq.(8.3) we have

$$i\hbar\frac{1}{\phi(t)}\frac{d}{dt}\phi(t)=E$$

$$\text{or }\frac{d\phi(t)}{\phi(t)}=-\frac{i}{\hbar}Edt$$

$\ln\phi=-i\frac{E}{\hbar}t+\ln C$ where C is an arbitrary constant.

$$\phi=Ce^{\left(-i\frac{E}{\hbar}t\right)} \tag{8.4}$$

From eq.(8.3) ,we have

$$-\frac{1}{\psi(\vec{r})}\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+U=E$$

or $$\boxed{\nabla^2\psi(\vec{r})+\frac{2m}{\hbar^2}\left(E-U\right)\psi(\vec{r})=0} \tag{8.5}$$

Eq.(8.5) is the ***time independent Schrodinger equation.***

One dimensional time independent Schrodinger equation is given by

$$\boxed{\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left(E-U\right)\psi=0} \tag{8.6}$$

One dimensional time independent Schrodinger equation for ***a free particle*** is given by $\dfrac{d^2\psi}{dx^2}+\dfrac{2m}{\hbar^2}E\psi=0$ (8.7)

Solution of the above equation has finite value in all space for any positive value of the energy E.

$$\frac{d^2\psi}{dx^2}+\frac{p^2}{\hbar^2}\psi=0 \tag{8.8}$$

where $p=\sqrt{\dfrac{2mE}{\hbar^2}}$

Solutions of the eq.(8.8) will be of the form

$$e^{i\frac{p}{\hbar}x} \tag{8.9}$$

Here p can take any real value between $-\infty$ to ∞.

From eq.(8.2),(8.4) and(8.9) the complete wave function $\psi(x,t)$ of such stationary states are

$$\psi(x,t)=\text{constant. } e^{\frac{ip}{\hbar}x}e^{-\frac{iE}{\hbar}t} \tag{8.10}$$

For three dimensional solution

$$\boxed{\psi(\vec{r},t)=\text{constant. } e^{\frac{i\vec{p}.\vec{r}}{\hbar}}e^{-\frac{iE}{\hbar}t}} \tag{8.11}$$

Eq.(8.11) can be written as

$$\boxed{\psi(\vec{r},t)=\psi(\vec{r})e^{-\frac{iE}{\hbar}t}} \tag{8.12}$$

Above wave function $\psi(\vec{r},t)$ describes a plane wave in which the particle has a definite momentum $\vec{p}$ and energy E.

From eq.(8.12) ***,it is clear*** $\psi^*(\vec{r},t)\psi(\vec{r},t)=\psi^*(\vec{r})\psi(\vec{r})$

Therefore probability density is constant in time and wavefunctions of the form (8.11) represents the stationary state.

By using $p=\hbar k$ eq.(8.10),(8.11) can be written as

$$\psi(x,t)=\text{constant. } e^{ikx}e^{-\frac{iE}{\hbar}t}$$

$$\psi(\vec{r},t) = \text{constant. } e^{i\vec{k}.\vec{r}} e^{-\frac{iE}{\hbar}t}$$

8.3 Fundamental Properties of Schrodinger Equation

The state of a quantum mechanical system is described by wavefunction $\psi(\vec{r},t)$ .We will discuss the conditions that must be satisfied by solutions of Schrodinger equation.

(i) Wavefunction $\psi(\vec{r},t)$ must be single valued .

(ii) Wavefunction $\psi(\vec{r},t)$ must be finite .

(iii) Wavefunction $\psi(\vec{r},t)$ must be ***continuous*** in all space.

(iv) Since term i is present in the Schrodinger equation , therefore, in general ,its solution will be complex.

(v) ***Derivative of wavefunction must remain continuous except when potential energy U becomes infinite*** i.e. if potential U makes a sudden jump of infinite magnitude then $\frac{\partial \psi}{\partial x}$ (in one dimensional case) has a finite discontinuity whereas ψ remains continuous. ***If potential energy U becomes infinite then*** ψ ***must be zero in that region.***

(vi)If potential energy U is finite ,then the wave function ψ must be finite in all space because $|\psi|^2$ is the probability of finding the particle .Total probability of finding the particle in the universe is one, therefore $\int \psi^2 d\tau = 1$ or $\langle \psi | \psi \rangle = 1$

Above condition is called ***normalization condition*** for wavefunction. Here $d\tau$ is infinitesimal volume element. Thus finiteness of $|\psi|^2$ implies that $\psi(\vec{r},t) \to 0$ as $\vec{r} \to \infty$.

In classical mechanics, it is impossible for a particle to penetrate into a region where $U > E$,but in quantum mechanics, solution of Schrodinger equation confirms the penetration of particle into the region where $U > E$.

(vii) ψ and its derivatives occur only linearly in the Schrodinger equation i.e. every term having ψ or one of its derivatives in the first power only. Therefore ***linear combination (superposition) of wavefunctions is also solution of Schrodinger equation.***

If a given system has wavefunctions ψ_1 and ψ_2 corresponding to two states, then linear combination $c_1\psi_1 + c_2\psi_2$ also represents a state of the system.

Hence Schrodinger equation for a free particle also gives wave packet solutions

i.e. $\psi(x,t) = \int a(p)e^{i\left(\frac{px}{\hbar}-\frac{Et}{\hbar}\right)}dp$ will also be a solution of Schrodinger equation.

(viii)If a particle is moving in time independent potential U ,then wave equation describes stationary states in which probability density $|\psi|^2$ at every point $\vec{r}$ in the space remains independent of time.

$$\psi(x,t) = \psi(x)e^{-\frac{iEt}{\hbar}}$$

$$|\psi(x,t)|^2 = |\psi(x)|^2$$

(ix) Schrodinger equation and admissibility conditions on wavefunctions give ,in general, discrete energy spectrum for system(eigenvalue spectrum of energy).

8.4 Probability Current Density

A particle is described by wave function $\psi(\vec{r},t)$,then probability density

$$\boxed{P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t) = |\Psi(\vec{r},t)|^2}$$

$P(\vec{r},t)d\tau$ ***is the probability of finding the particle in volume element*** $d\tau$ ***about its position*** $\vec{r}$ ***at time t when large number of measurements made***. Here volume element $d\tau = dxdydz$

The probability of finding the particle in a certain volume (region) τ of the space is given by $\int_\tau \psi^*\psi d\tau$ .Statistical interpretation of the normalized wavefunction says that the probability integral $\int_{\text{All space}} \psi^*\psi d\tau$ must be equal to one i.e.

$\boxed{\int_{\text{All space}} \psi^*\psi d\tau = 1}$ .Here all spatial integrations extend to over all space i.e.

$$\boxed{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(\vec{r},t)\psi(\vec{r},t)dxdydz = 1}.$$

This statement holds for all the time, because the particle will certainly be found in the universe. Thus

$$\frac{\partial}{\partial t}\int_{All\ space}\psi^*\psi\, d\tau = 0\,.$$

By Schrodinger equation, we shall verify the above statement. To study this, we consider time dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi(\vec{r},t) \tag{8.13}$$

It's complex conjugate is given by

$$\Rightarrow \qquad -i\hbar\frac{\partial}{\partial t}\psi^*(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U^*(\vec{r})\right]\psi^*(\vec{r},t)$$

$$\Rightarrow \qquad -i\hbar\frac{\partial}{\partial t}\psi^*(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi^*(\vec{r},t) \tag{8.14}$$

Here potential energy $U(\vec{r})$ is assumed to be real i.e. $U^*(\vec{r}) = U(\vec{r})$

Multiplying eq.(8.13) by $\psi^*(\vec{r})$ from left, we get

$$i\hbar\psi^*\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + U\psi^*\psi \tag{8.15}$$

Multiplying eq.(8.14) by $\psi(\vec{r})$ from left, we get

$$-i\hbar\psi\frac{\partial\psi^*(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + U\psi\psi^* \tag{8.16}$$

Subtracting eq. (8.16) from eq. (8.15)

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

$$\because \psi^*\psi = \psi\psi^*$$

$$i\hbar\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] = -\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right]$$

$$\left\{\begin{aligned}&\because \nabla\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) = \nabla\left(\psi^*\nabla\psi\right) - \nabla\left(\psi\nabla\psi^*\right)\\ &\qquad = \nabla\psi^*\nabla\psi + \psi^*\nabla^2\psi - \nabla\psi.\nabla\psi^* - \psi\nabla^2\psi^* = \psi^*\nabla^2\psi - \psi\nabla^2\psi^*\end{aligned}\right.$$

$$\therefore \frac{\partial}{\partial t}\left(\psi\psi^*\right)=\frac{i\hbar}{2m}\nabla\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right) \qquad \left\{\because -1=i^2\right\}$$

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

$$\Rightarrow \frac{\partial}{\partial t}\left(\psi\psi\, *\right)+\nabla\left[\frac{i\hbar}{2m}\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right)\right]=0$$

$$\frac{\partial}{\partial t}(\psi\psi^*)+\nabla.\vec{S}=0$$

$$\Rightarrow \boxed{\frac{\partial P}{\partial t}+\nabla.\vec{S}=0} \tag{8.17}$$

$$\Rightarrow \frac{\partial P}{\partial t}+div\,\vec{S}=0$$

Here $\vec{S}\left(\vec{r},t\right)$ is called "***probability current density***" or ***probability flux***.

$$\boxed{\vec{S}=\frac{i\hbar}{2m}\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right)} \text{ and } P\left(\vec{r},t\right)=\psi\left(\vec{r},t\right)\psi^*\left(\vec{r},t\right)$$

Eq. (8.17) is known as ***equation of continuity for probability*** that is analogous to the equation of continuity in hydrodynamics and electrodynamics. Here symbol $\vec{J}\left(\vec{r},t\right)$ can be used for $\vec{S}\left(\vec{r},t\right)$ and ρ for P, then equation of continuity takes the form $\frac{\partial\rho}{\partial t}+\nabla.\vec{J}=0$

Some Important points:

(i) Conservation of Probability

Integrating eq. (8.17), we get

$$\int\limits_{All\,space}\frac{\partial P}{\partial t}d\tau+\int\limits_{All\,space}\nabla.\vec{S}\,d\tau=0 \tag{8.18}$$

By Gauss divergence theorem

$$\int\limits_{\tau}\nabla.\vec{S}\,d\tau=\oint\limits_{A}\vec{S}.d\vec{A}$$

where volume τ is bounded by closed surface A.

We can write eq.(8.18) as

$$\int_{All\,space} \frac{\partial P}{\partial t} d\tau + \oint_{All\,space} \vec{S}.d\vec{A} = 0 \tag{8.19}$$

$$\Rightarrow \frac{\partial}{\partial t} \int_{All\,\,space} P d\tau \;+ \oint_{All\,space} \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right).d\vec{A} = 0$$

We have taken whole space i.e. for surface integral, we take surface at infinity where ψ itself is zero, so second term in above integral becomes zero. We have

$$\frac{\partial}{\partial t} \int_{All\,space} P d\tau = 0$$

$$\Rightarrow \int_{\text{All space}} \text{Pd}\tau = \text{constant}$$

i.e. probability of finding the particle in whole space is constant (conserved). Here potential U must be real- valued if conservation of probability is to hold. If U is not real then absorption of particle is possible in such complex potentials.

(ii) From eq. (8.17) we get

$$\frac{\partial P}{\partial t} = -\nabla.\vec{S}$$

Integrating over volume τ

$$\int_\tau \frac{\partial P}{\partial t} d\tau = -\int_\tau \nabla.\vec{S} d\tau$$

Using Gauss's theorem

$$\frac{\partial}{\partial t}\int_\tau P(\vec{r},t)d\tau = -\oint_A \vec{S}(\vec{r},t).d\vec{A} \tag{8.20}$$

Here area A encloses the volume τ . From eq.(8.20) it is obvious that outflow of probability current density across the surface A is equal to rate of decrease in probability in that volume τ. In other words if the probability of finding a particle in some region decreases, then the probability of finding the particle outside the region increasing by the same amount. The change of probability arises because of the change of $\psi(\vec{r},t)$ with time.

(iii) Probability current density

$$\boxed{S = \frac{\hbar}{m}\text{Im}\left(\psi^*\nabla\psi\right)}$$

We can verify this in the following way

Imaginary part of complex number is given by

$$Im(z)=\frac{z-z^*}{2i}$$

$$Im\left(\psi^*\nabla\psi\right)=\frac{\left(\psi^*\nabla\psi\right)-\left(\psi^*\nabla\psi\right)^*}{2i}$$

$$=\frac{\psi^*\nabla\psi-\psi^{**}\nabla\psi^*}{2i}$$

$$=\frac{\psi^*\nabla\psi-\psi\nabla\psi^*}{2i}$$

$$=\frac{-\left[\psi\nabla\psi^*-\psi^*\nabla\psi\right]}{2i}$$

$$=\frac{i}{2}\left[\psi\nabla\psi^*-\psi^*\nabla\psi\right]$$

Here $\vec{S}=\frac{i\hbar}{2m}\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right)$

$$\therefore S=\frac{\hbar}{m}\operatorname{Im}\left(\psi^*\nabla\psi\right)$$

(iv) Probability current density

$$\vec{S}=Re\left(\psi^*\vec{v}_{op}\psi\right)$$

where $\boxed{\vec{v}_{op}=\frac{-i\hbar}{m}\nabla}$ =velocity operator

Let’s prove the above relation

Real part of $\psi^*\vec{v}_{op}\psi$ is

$$Re\left(\psi^*\vec{v}_{op}\psi\right)=Re\left[\psi^*\frac{-i\hbar}{m}\nabla\psi\right]$$

$$=\frac{-\hbar}{m}Re\left(i\psi^*\nabla\psi\right)$$

$$= \frac{-\hbar}{m}\left[\frac{i\psi^*\nabla\psi + \left(i\psi^*\nabla\psi\right)^*}{2}\right] \qquad \left\{\because Re\,z = \frac{z+z^*}{2}\right.$$

$$= \frac{-\hbar}{m}\left[\frac{i\psi^*\nabla\psi + i^*\psi^{**}\nabla\psi^*}{2}\right]$$

$$= \frac{-\hbar}{m}\left[\frac{i\psi^*\nabla\psi - i\psi\nabla\psi^*}{2}\right]$$

$$= \frac{i\hbar}{2m}\left[\psi\nabla\psi^* - \psi^*\nabla\psi\right] = \vec{S}$$

(v) Probability ***current density is zero corresponding to real wave function*** ψ .

$\because \psi = \psi^*$ for real wavefunction

$$\vec{S} = \frac{i\hbar}{2m}\left[\psi\nabla\psi^* - \psi^*\nabla\psi\right]$$

$$= \frac{i\hbar}{2m}\left[\psi\nabla\psi - \psi\nabla\psi\right] = 0$$

(vi) Wave function ψ and its derivative $\nabla\psi$ are continuous everywhere, so equation of continuity holds at every point of the space

(vii) If $\nabla.\vec{S}$ is zero for any state, then probability density $|\psi|^2$ ***is constant with time and such states are called stationary states.***

8.5 Illustrative Examples

Example1: What is the probability current density corresponding to plane wave

$$\psi(x,t) = Ae^{ikx}e^{-i\frac{Et}{\hbar}}$$

Sol.1: For one dimensional case

$$\vec{S} = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right]$$

$$= \frac{i\hbar}{2m}\left[Ae^{ikx}e^{-\frac{iEt}{\hbar}}\frac{\partial}{\partial x}\left(A^*e^{-ikx}e^{\frac{iEt}{\hbar}}\right) - A^*e^{-ikx}e^{\frac{iEt}{\hbar}}\frac{\partial}{\partial x}\left(Ae^{ikx}e^{-\frac{iEt}{\hbar}}\right)\right]$$

$$= \frac{i\hbar}{2m}\left[AA^*e^{ikx}\frac{\partial}{\partial x}\left(e^{-ikx}\right) - A^*Ae^{-ikx}\frac{\partial}{\partial x}e^{(ikx)}\right]$$

$$= \frac{i\hbar}{2m}\left[AA^* e^{ikx}(-ik)\left(e^{-ikx}\right) - A^* A e^{-ikx}(ik)e^{(ikx)} \right]$$

$$= \frac{i\hbar}{2m} AA^* [-2ik]$$

$$= \frac{\hbar k}{m} AA^*$$

$$\vec{S} = \frac{\hbar k}{m} |A|^2$$

Note : Here $\psi\psi^* = Ae^{ikx} e^{-\frac{iEt}{\hbar}} A^* e^{-ikx} e^{\frac{iEt}{\hbar}}$

$$= AA^* = |A|^2 = \rho$$

Thus $\vec{S} = \frac{\hbar k}{m} |\psi^2|$

$$\vec{S} = \frac{\hbar k}{m} \rho$$

In fluid mechanics current density is given by $J = \rho v$ where v represents the velocity of the fluid and ρ is the density of the fluid. In this example, a similar analogy can be made by stating that probability is similar to the fluid that flows with velocity $v = \frac{\hbar k}{m}$ at point (position) $\vec{r}$ and density of fluid at the point is $\rho(\vec{r})$. But it is suggestive not to make too much similar analogy with fluid because, in quantum mechanics, simultaneous precision measurement of position and velocity violate the Heisenberg uncertainty principle.

Example 2: A wavefunction $\psi = A\sin\frac{n\pi x}{L}$ exists in a region $0 < x < L$.Potential is given by

$$V = \begin{cases} 0 & ;\ 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Here $n = 1, 2, 3, 4, ...$

By normalization condition determine the constant A.

Sol. From normalization condition

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

$$\Rightarrow \int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

$$\Rightarrow A^2 \int_0^L \left(\frac{1 - \cos\frac{2n\pi x}{L}}{2} \right) dx = 1$$

$$\Rightarrow \frac{A^2}{2} \left[x - \frac{L}{2n\pi} \sin \frac{2n\pi x}{L} \right]_0^L = 1$$

$$\Rightarrow \frac{A^2}{2} \left[L - 0 - \frac{L}{2n\pi} \sin \frac{2n\pi L}{L} + \frac{L}{2n\pi} \sin \frac{2n\pi 0}{L} \right]_0^L = 1$$

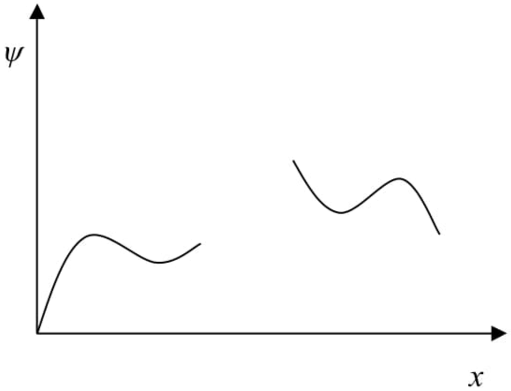
$$\Rightarrow \frac{A^2 L}{2} = 1$$

$$\therefore A = \sqrt{\frac{2}{L}}$$

8.6 Self Learning Exercise-I

Q.1 What is the value of the probability current density when the wave function is real.

Q.2 Is the given wave function admissible?

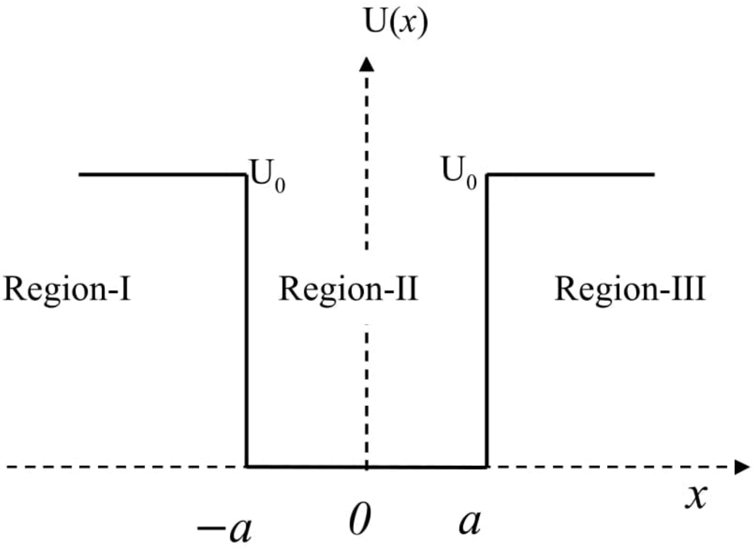


Q.3 What are stationary states ? Show that probability current density is constant in time in these states.

8.7 Potential Well

We consider a square well potential with finite walls. A particle of mass m is moving inside the one dimensional potential well. Mathematically, potential energy of the particle can be written as

$$U(x)=\begin{cases} U_0 & ; x<-a \quad (\text{Region-}I) \\ 0 & ; -a<x<a \quad (\text{Region-}II) \\ U_0 & ; x>a \quad (\text{Region-}III) \end{cases}$$



We study the bound state of the particle i.e. $E<U_0$ .We can write time independent Schrodinger equations in these three regions.

For Region -I $(x<-a)$

$$\frac{d^2\psi_1}{dx^2}+\frac{2m(E-U_0)}{\hbar^2}\psi_1=0 \tag{8.21}$$

$$\Rightarrow \frac{d^2\psi_1}{dx^2}-\frac{2m(U_0-E)}{\hbar^2}\psi_1=0$$

$$\Rightarrow \frac{d^2\psi_1}{dx^2}-\gamma^2\psi_1=0 \tag{8.22}$$

where $\gamma=\sqrt{\frac{2m(U_0-E)}{\hbar^2}}=positive$

General solution of the above equation is

$$\psi_1 = Ae^{-\gamma x} + Be^{\gamma x} \tag{8.23}$$

We apply the boundary condition on the wavefunction that wavefunction must remain finite.

If coefficient A is not zero ,then $\psi_1(x) \to \infty$ as $x \to -\infty$

Therefore ***in order to obtain the well behaved wavefunction ,A must be zero***. Hence

$$\psi_1 = Be^{\gamma x} \tag{8.24}$$

For Region II $(-a < x < a)$

Schrodinger equation

$$\frac{d^2\psi_2}{dx^2} + \frac{2m(E-0)}{\hbar^2}\psi_2 = 0$$

$$\frac{d^2\psi_2}{dx^2} + \beta^2\psi_2 = 0 \text{ where } \beta = \sqrt{\frac{2mE}{\hbar^2}} = positive$$

General solution of the above equation is

$$\psi_2 = C\sin\beta x + D\cos\beta x \tag{8.25}$$

where C and D are arbitrary constants.

For Region III $(x > a)$

Schrodinger equation

$$\frac{d^2\psi_3}{dx^2} + \frac{2m(E-U_0)}{\hbar^2}\psi_3 = 0$$

$$\Rightarrow \frac{d^2\psi_3}{dx^2} - \gamma^2\psi_3 = 0 \text{ where } \gamma = \sqrt{\frac{2m(U_0-E)}{\hbar^2}} = positive$$

General solution of the above equation is

$$\psi_3 = Fe^{-\gamma x} + Ge^{\gamma x}$$

If G is not zero ,then $\psi_3 \to \infty$ as $x \to \infty$.

Therefore G must be zero for well behaved wavefunction. Hence

$$\psi_3 = Fe^{-\gamma x} \tag{8.26}$$

Thus wavefunction for different regions

$$\psi(x)=\begin{cases} Be^{\gamma x} & ; \quad x<-a \quad (\text{Region-}I) \\ C\sin\beta x+D\cos\beta x & ; \quad -a<x<a \quad (\text{Region-}II) \\ Fe^{-\gamma x} & ; \quad x>a \quad (\text{Region-}III) \end{cases}$$

We apply the boundary conditions on wavefunction at $x=-a$

i.e. $\psi_1=\psi_2$ and $\frac{d\psi_1}{dx}=\frac{d\psi_2}{dx}$

We get

$$Be^{-\gamma a}=-C\sin\beta a+D\cos\beta a \tag{8.27}$$

and $\gamma Be^{-\gamma a}=\beta C\cos\beta a+\beta D\sin\beta a$ (8.28)

Now we apply the boundary conditions on wavefunction at $x=a$

i.e. $\psi_2=\psi_3$ and $\frac{d\psi_2}{dx}=\frac{d\psi_3}{dx}$

$$Fe^{-\gamma a}=C\sin\beta a+D\cos\beta a \tag{8.29}$$

and $-\gamma Fe^{-\gamma a}=\beta C\cos\beta a-\beta D\sin\beta a$ (8.30)

Adding and subtracting eq.(8.27)and (8.29),we get

$$(B+F)e^{-\gamma a}=2D\cos\beta a \tag{8.31}$$

and $(F-B)e^{-\gamma a}=2C\sin\beta a$ (8.32)

Adding and subtracting eq(8.28) & (8.30)

$$\gamma(B-F)e^{-\gamma a}=2\beta C\cos\beta a \tag{8.33}$$

and $\gamma(B+F)e^{-\gamma a}=2\beta D\sin\beta a$ (8.34)

From eq.(8.31&(8.34)

$$\gamma=\beta\tan\beta a \tag{8.35}$$

From eq(8.32)&(8.33)

$$-\gamma=\beta\cot\beta a \tag{8.36}$$

Equations (8.35) and(8.36) are transcendental equations. Solution of these equations(8.35)& (8.36)can be obtained graphically. Graphical solution gives certain discrete energy levels for one dimensional finite potential well. Then

We consider the special case in which $U_0\to\infty$ (i.e. potential box).

Graphically obtained condition gives

$$\beta a = \frac{n\pi}{2} \quad \text{where } n = 1, 2, 3, 4...$$

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

$$\Rightarrow E = \frac{n^2h^2}{8m(2a)^2} = \frac{n^2h^2}{8m(L)^2} \quad \text{where } L = 2a$$

We get these energy levels of the particle same as in case of one dimensional potential box.

8.8 Self Learning Exercise-II

Q.1 Define probability current density.

Q.2 A particle of mass m is moving inside the one dimensional potential box.

Potential is given by

$$V = \begin{cases} 0 & ;\ 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

The normalised wavefunction of the particle at time $t = 0$ is

$$\psi(x,0) = \alpha \sin\frac{\pi x}{a} + \beta \sin\frac{5\pi x}{a}$$

where α and β are constants. Find

(i) $\psi(x,t)$

(ii) Is this wavefunction $\psi(x,t)$ represent stationary state?

Q.3 A wavefunction of a particle in one dimensional potential box($0 < x < L$) is given by $\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}$,otherwise $\psi(x) = 0$.Find the probability of finding the particle in the region $0 < x < \frac{L}{2}$

8.9 Summary

1. Schrodinger's equation

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U\psi$$

$$i\hbar\frac{\partial\psi}{\partial t}=H\psi$$

$$H=-\frac{\hbar^2}{2m}\nabla^2+U=Hamiltonian\ operator$$

2. *Time independent Schrodinger equation*

$$\nabla^2\psi(\vec{r})+\frac{2m}{\hbar^2}(E-U)\psi(\vec{r})=0$$

3. The complete wave function $\psi(x,t)$ of stationary states are

$$\psi(x,t)=\text{constant. } e^{\frac{ip}{\hbar}x}e^{-\frac{iE}{\hbar}t}$$

4. *Probability density* $P(\vec{r},t)=\Psi^*(\vec{r},t)\Psi(\vec{r},t)=|\Psi(\vec{r},t)|^2$

Probability current density $\vec{S}=\frac{i\hbar}{2m}\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right)$

$$\frac{\partial P}{\partial t}+\nabla.\vec{S}=0 \text{ equation of continuity for probability}$$

Normalization condition $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(\vec{r},t)\psi(\vec{r},t)dxdydz=1$

8.10 Glossary

Laplacian Operator: $\nabla^2\equiv\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$

Probability density: $\psi^*(\vec{r},t)\psi(\vec{r},t)=\psi^*(\vec{r})\psi(\vec{r})$

8.11 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: Zero

Ans.2: No ,it is not continuous function.

Answers to Self Learning Exercise-II

Ans.1: $\vec{S}=\frac{i\hbar}{2m}\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right)$

Ans.2: (i) $\psi(x,t) = \alpha \sin\frac{\pi x}{a} e^{\frac{-iE_1 t}{\hbar}} + \beta \sin\frac{5\pi x}{a} e^{\frac{-iE_5 t}{\hbar}}$

where $E_1 = \frac{h^2}{8ma^2}$ and $E_5 = \frac{25h^2}{8ma^2}$

(ii) No, because $\psi^*(x,t)\psi(x,t)$ is not independent of time

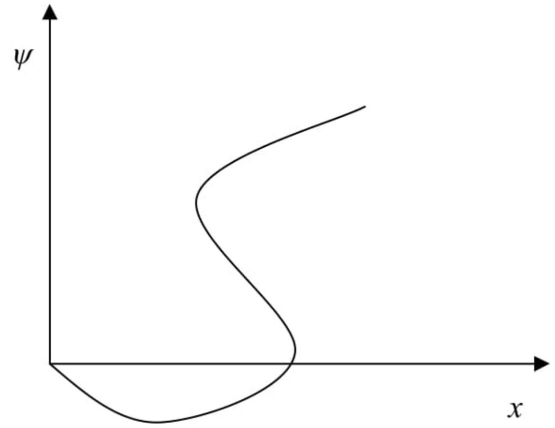
Ans.3: $\int_0^{\frac{L}{2}} P dx = \int_0^{\frac{L}{2}} \psi^* \psi \, dx$

$$= \int_0^{\frac{L}{2}} \frac{2}{L} \sin^2 \frac{2\pi x}{L} dx = \frac{1}{2}$$

8.12 Exercise

Section A:Very Short Answer Type Questions

Q.1 Is the given wave function admissible?



Q.2 "Wavefunction is always complex quantity in quantum mechanics."Is this statement true?

Section B : Short Answer Type Questions

Q.3 Deduce the time independent Schrodinger equation from time dependent Schrodinger equation.

Q.4 Assume $\psi = \frac{1}{\sqrt{r}} e^{ikr}$ where r is distance from z axis in cylindrical coordinates. Calculate the probability current density.

Q.5 Give the probability interpretation of the wavefunction and show that the probability density ρ i.e. $|\Psi|^2$ and probability current density $\vec{S}$ satisfy the continuity equation $\frac{\partial \rho}{\partial t} + \nabla.\vec{S} = 0$.

Also give the physical significance of this equation is quantum mechanics.

Q.6 Write the general properties of Schrodinger equation.

Q.7 Consider the time independent potential in which wavefunctions ψ_1, ψ_2 *and* ψ_3 that are solutions of Schrodinger equation belonging to same energy. Here these wavefunctions are linearly independent. Show that their linear combination is also solution of the Schrodinger equation belonging to same eigen value.

Q.8 Consider motion of a particle of mass *m* in three dimensional cubic potential box having side *a*. Potential for this box is given below

$$V = \begin{cases} 0 & ;\text{ inside the box} \\ \infty & \text{ otherwise} \end{cases}$$

Wavefunction of the particle is

$$\psi(x,y,z) = \sqrt{\frac{8}{a^3}} \sin\frac{n_1 \pi x}{a} \sin\frac{n_2 \pi x}{a} \sin\frac{n_3 \pi x}{a} \text{ and the eigen value}$$

$$E = \frac{h^2}{8ma^2}(n_1^2 + n_2^2 + n_3^2)$$

For state $(n_1, n_2, n_3) = (2,2,1)$,write the wavefunction for this state and also write the energy eigen value for this state. What is the degeneracy of this energy level?

Section C : Long Answer Type Questions

Q.9 Discuss the particle in one dimensional potential box. Potential is given by

$$V = \begin{cases} 0 & ;\ 0 < x < a \\ \infty & \text{ otherwise} \end{cases}$$

Obtain the eigenfunctions and eigenvalues of the particle in the box.

Q.10 Discuss the motion of the bound particle of mass m in the given one dimensional potential well

$$U(x)=\begin{cases}0 & ;\ x<-a\ \ (\text{Region-}I)\\ -U_0 & ;\ -a<x<a\ \ (\text{Region-}II)\\ 0 & ;\ x>a\ \ (\text{Region-}III)\end{cases}$$

Energy of the particle is $E=-|E|$ and $U_0>|E|$

Obtain the transcendental equations.

8.13 Answers to Exercise

Ans.1: No ,it is not single valued function

Ans.2: False

Ans.4: Probability current density

$$\vec{S}=\frac{i\hbar}{2m}\left[\psi\nabla\psi^{*}-\psi^{*}\nabla\psi\right]$$

In cylindrical coordinates

$$\nabla\psi=\left(\hat{r}\frac{\partial}{\partial r}+\hat{\phi}\frac{1}{r}\frac{\partial}{\partial\phi}+\hat{z}\frac{\partial}{\partial z}\right)\psi$$

$$\nabla\psi=\left(\hat{r}\frac{\partial}{\partial r}+\hat{\phi}\frac{1}{r}\frac{\partial}{\partial\phi}+\hat{z}\frac{\partial}{\partial z}\right)\frac{1}{\sqrt{r}}e^{ikr}$$

$$\nabla\psi=\hat{r}\frac{\partial}{\partial r}\left(\frac{1}{\sqrt{r}}e^{ikr}\right)$$

$$\nabla\psi=\hat{r}\left[-\frac{1}{2r^{\frac{3}{2}}}e^{ikr}+\frac{ik}{\sqrt{r}}e^{ikr}\right]$$

and $\nabla\psi^{*}=\hat{r}\left[-\frac{1}{2r^{\frac{3}{2}}}e^{-ikr}+\frac{ik}{\sqrt{r}}e^{-ikr}\right]$

$$\therefore\vec{S}=\frac{i\hbar}{2m}\left[\psi\nabla\psi^{*}-\psi^{*}\nabla\psi\right]$$

$$=\frac{i\hbar}{2m}\left[\left(\frac{1}{\sqrt{r}}e^{ikr}\right)\hat{r}\left\{-\frac{1}{2r^{\frac{3}{2}}}e^{-ikr}+\frac{ik}{\sqrt{r}}e^{-ikr}\right\}-\left(\frac{1}{\sqrt{r}}e^{-ikr}\right)\hat{r}\left\{-\frac{1}{2r^{\frac{3}{2}}}e^{ikr}+\frac{ik}{\sqrt{r}}e^{ikr}\right\}\right]$$

$$=\frac{i\hbar}{2m}\hat{r}\frac{-2ik}{r}$$

$$\vec{S} = \frac{\hbar k}{mr}\hat{r}$$

Ans.7: Let's consider the energy eigen value E corresponding to these eigen wavefunctions. Therefore we have

$$-\frac{\hbar^2}{2m}\nabla^2\psi_1 + U\psi_1 = E\psi_1 \qquad (1)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_2 + U\psi_2 = E\psi_2 \qquad (2)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_3 + U\psi_3 = E\psi_3 \qquad (3)$$

We consider a linear combination of wavefunction

$$\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3$$

Here $H\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + U\psi$

$$\Rightarrow H\psi = -\frac{\hbar^2}{2m}\nabla^2\left(a_1\psi_1 + a_2\psi_2 + a_3\psi_3\right) + U\left(a_1\psi_1 + a_2\psi_2 + a_3\psi_3\right)$$

$$\Rightarrow H\psi = a_1\left[-\frac{\hbar^2}{2m}\nabla^2\psi_1 + U\psi_1\right] + a_2\left[-\frac{\hbar^2}{2m}\nabla^2\psi_2 + U\psi_2\right] + a_3\left[-\frac{\hbar^2}{2m}\nabla^2\psi_3 + U\psi_3\right]$$

From eq.(1),(2)and(3)

$$\Rightarrow H\psi = a_1E\psi_1 + a_2E\psi_2 + a_3E\psi_3$$

$$\Rightarrow H\psi = E\left(a_1\psi_1 + a_2\psi_2 + a_3\psi_3\right)$$

$$\Rightarrow H\psi = E\psi \text{ Hence Proved}$$

Ans.8: For state $(n_1, n_2, n_3) = (2,2,1)$

Wavefunction $\psi(x,y,z) = \sqrt{\frac{8}{a^3}}\sin\frac{2\pi x}{a}\sin\frac{2\pi x}{a}\sin\frac{\pi x}{a}$

and energy eigen value $E = \frac{9h^2}{8ma^2}$

Degeneracy of this energy level is 3, because we have three different wavefunctions corresponding to same eigen value. We have different combinations as

$(n_1, n_2, n_3) = (2,2,1), (2,1,2), (1,2,2)$

Ans.9: $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ where $n = 1,2,3,4,...$

Energy eigen value $E = \frac{h^2}{8ma^2} n^2$

Ans.10: $\gamma = \beta \tan \beta a$ and $-\gamma = \beta \cot \beta a$

where $\beta = \sqrt{\frac{2m(U_0 - |E|)}{\hbar^2}}$ *and* $\gamma = \sqrt{\frac{2m|E|}{\hbar^2}}$

References and Suggested Readings

1. Gupta, Kumar& Sharma, Quantum Mechanics, Twenty first edition (2001),Jai Prakash Nath &Co.
2. L.D. Landau and E.M. Lifshitz, Quantum Mechanics(Non Relativistic Theory)Third Edition(2008),Butterworth –Heinemann.
3. P.M.Mathews & K.Venkatesan,A Textbook of Quantum Mechanics ,Tata McGraw Hill Publishing Company Limited.
4. Ajoy Ghatak & S.Lokanathan, Quantum Mechanics (Theory and Applications)Fourth Edition(1999),Macmillan India Limited.
5. Eugen Merzbacher, Quantum Mechanics, Third Edition(1998)John Wiley &Sons INC.
6. Mahesh C. Jain ,Quantum Mechanics,2007,PHI Learning Private Limited.

UNIT -9

The Linear Oscillator, A Rectangular Potential Wall

Structure of the unit

9.0 Objectives

We shall study the following one-dimensional problems –

- The linear harmonic oscillator (its eigen values and eigen function)
- Reflection coefficient from a rectangular potential wall.
- Transmission coefficient for a rectangular potential barrier.
- Problems related to these.

9.1 Introduction

In this chapter we solve some simple problems of one-dimensional motion. They are of interest because they illustrate some nonclassical effects and because many physical situations are effectively one-dimensional even though we live in three-dimensional world.

9.2 The Harmonic Oscillator

As an example we first consider the harmonic oscillator. We consider a particle executing small oscillations in one dimension (What is called a "linear oscillator"). The potential energy of such a particle is $\frac{1}{2}m\omega^2 x^2$, where ω is, the angular frequency of oscillation. According the Hamiltonian of the oscillator is

$$\boxed{H = \frac{1}{2}\frac{\hat{p}^2}{m} + \frac{1}{2}m\omega^2\hat{x}^2} \tag{1}$$

Since the potential energy becomes infinite for $x = \pm\infty$, the particle can have only a finite motion, and the energy eigenvalue spectrum is entirely discrete.

We shall first determine the energy levels of the oscillator by solving schrodinger's equation. For an oscillator this has the form

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2 x^2\right)\psi = 0 \tag{2}$$

Here it is convenient to introduce, instead of the coordinate x, the dimensionless variable ξ by the relation

$$\xi = \sqrt{\left(\frac{m\omega}{\hbar}\right)}x \tag{3}$$

Then we have the equation

$$\psi'' + \left[\left(\frac{2E}{\hbar\omega}\right) - \xi^2\right]\psi = 0 \tag{4}$$

Here the prime denotes differentiation with respect to ξ.

For large ξ, we can neglect $\frac{2E}{\hbar\omega}$ in comparison with ξ^2, the equation becomes

$$\psi'' - \xi^2\psi = 0$$

This equation has the asymptotic integrals

$$\psi = e^{\pm\frac{1}{2}\xi^2}$$

(for differentiation of this function gives $\psi'' = \xi^2\psi$ on neglecting terms of order less than that of the term retained).

Since the wave function ψ must remain finite as $\xi \to \pm\infty$, the index must be taken with the minus sign. It is therefore natural to make in equation (4) the substitution

$$\psi = e^{-\frac{\xi^2}{2}}\chi(\xi) \tag{5}$$

We calculate ψ'' and substitute in (4) to get the equation for the function $\chi(\xi)$:

$$\chi'' - 2\xi\chi' + \left(\frac{2E}{\hbar\omega} - 1\right)\chi = 0 \tag{6}$$

We denote the expression $\left(\frac{2E}{\hbar\omega} - 1\right)$ by *2n*, so the equation (6) becomes

$$\chi'' = 2\xi\chi' + 2n\chi = 0 \tag{7}$$

Since we already know that E>0, we have $n > -\frac{1}{2}$.

The function χ must be finite for all finite χ, and for $\chi \to \pm\infty$ must not tend to infinity more rapidly than every finite power of ξ (in order that the function ψ should tend to zero).

Such solutions of equation (7) exist only for positive integral (and zero) values of n ; this gives the relation

$$\frac{2E}{\hbar\omega} - 1 = 2n \qquad (n \geq 0)$$

or

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0,1,2,......} \tag{8}$$

The solutions of equation (7) corresponding to various integral values of n are $\chi = \{\text{Constant}\, H_n(\xi)\}$ where $H_n(\xi)$ are what are called "Hermite Polynomials". These are polynomials of the n^{th} degree in ξ, defined by the formula

$$\boxed{\mathrm{H}_n(\xi) = (-1)^n e^{\xi^2}\frac{d^n}{d\xi^n}\left(e^{-\xi^2}\right)} \tag{9}$$

Determining the constants so that the functions ψ_n satisfy the normalization condition

$$\int_{-\infty}^{\infty} \psi_n^2(x)dx = 1$$

We obtain

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{2^{n/2}\sqrt{(n!)}} e^{-\frac{m\omega x^2}{2\hbar}} H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right) \tag{10}$$

Thus the wave function of the ground state is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}} \tag{11}$$

We may write out here the first few Hermite polynomials :

$$\boxed{\begin{aligned} &H_0 = 1 \\ &H_1 = 2x \\ &H_2 = 4x^2 - 2 \\ &H_3 = 8x^3 - 12x \\ &H_4 = 16x^4 - 48x^2 + 12 \end{aligned}},$$

9.3 Illustrative Examples

Example 1: Evaluate the position-momentum uncertainty product for the n$^{\text{th}}$ state of a linear harmonic oscillator.

Solution :

$$\begin{aligned} (\Delta x)^2 &= \langle x^2\rangle - \langle x\rangle^2 \\ &= \left(n + \frac{1}{2}\right)\frac{\hbar}{m\omega} - 0 \\ &= \left(n + \frac{1}{2}\right)\frac{\hbar}{m\omega} \end{aligned} \tag{1}$$

$$\begin{aligned} (\Delta p)^2 &= \langle p^2\rangle - \langle p\rangle^2 \\ &= \left(n + \frac{1}{2}\right)\hbar m\omega - 0 = \left(n + \frac{1}{2}\right)m\omega\hbar \end{aligned}$$

By (1) & (2) We obtain the position-momentum uncertainty product

$$\boxed{\Delta x \Delta p = \left(n + \frac{1}{2}\right)\hbar}, \quad n = 0, 1, 2....$$

This is in accordance with the uncertainty relation

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

For n =0, reduces to

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

Thus the uncertainty product is minimum for the ground state.

Example 2: A harmonic oscillator has wave function which is a superposition of its ground state and first excited state eigenfunctions; that is,

$$\Psi(x) = \frac{1}{\sqrt{2}}[\Psi_0(x) + \Psi_1(x)]$$

Find the expectation value of the energy.

Solution :

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \hat{E} \ \Psi(x) dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} [\Psi_0^*(x) \ \Psi_1^*(x)] \ \hat{E} \ [\Psi_0(x) + \Psi_1(x)] dx$$

$$= \frac{1}{2}\left[\int_{-\infty}^{\infty} \Psi_0^*(x) \ \hat{E} \ \Psi_0(x)\, dx + \int_{-\infty}^{\infty} \Psi_1^*(x) \ \hat{E}\, \Psi_0(x)\, dx\right.$$

$$\left. + \int_{-\infty}^{\infty} \Psi_0^*(x) \ \hat{E}\, \Psi_1(x) dx + \int_{-\infty}^{\infty} \Psi_1^*(x) \ \hat{E}\, \Psi_1(x)\, dx\right]$$

$$= \frac{1}{2}\left[E_0 \int_{-\infty}^{\infty} \Psi_0^*(x) \Psi_0(x)\, dx + E_0 \int_{-\infty}^{\infty} \Psi_1^*(x) \ \Psi_0(x)\, dx\right.$$

$$\left. + E_1 \int_{-\infty}^{\infty} \Psi_0^*(x) \ \Psi_1(x) dx + E_1 \int_{-\infty}^{\infty} \Psi_1^*(x) \Psi_1(x)\, dx\right]$$

Since the eigenfunctions are orthonormal, we obtain

$$\langle E \rangle = \frac{1}{2}[E_0 + 0 + 0 + E_1]$$

$$= \frac{1}{2}\left[\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\omega\right] = \hbar\omega$$

9.4 Self Learning Exercise

Q.1 Write the schrodinger's equation for harmonic oscillator in p-representation.

Q.2 Determine the lower limit of the possible values of the energy of an oscillator.

Q.3 Determine the ground state energy of an oscillator using the uncertainty relation :

$$\delta x \delta p_x \geq \frac{1}{2}\hbar$$

9.5 Rectangular Potential Wall

Reflection Coefficient of a Particle from a Rectangular Potential Wall:

The energy of the particle $E > U_0$. For this problem we take (Figure-1) the form of U(x) to be

$$U(x) = 0 \qquad x < 0$$
$$= U_0 \qquad x > 0$$

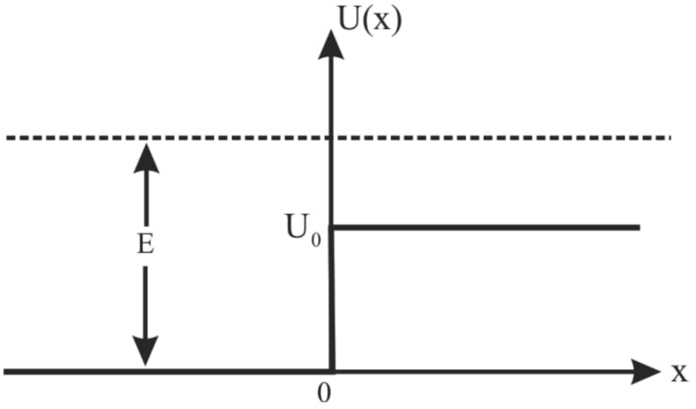


Figure 9.1

The Schrodinger equation takes the form

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[\mathrm{E} - \mathrm{U(x)}]\psi(\mathrm{x}) = 0 \tag{1}$$

We write, as usual

$$\frac{2mE}{\hbar^2} = k_1^2 \tag{2}$$

and $$\frac{2m(E-U_o)}{\hbar^2} = k_2^2 \tag{3}$$

Throughout the region x > 0 the wave function has the form for $x \to \infty$,

$$\psi \approx Ae^{ik_2x}$$

In the region x < 0 the wave function takes the form for $x \to -\infty$

$$\psi(x) \approx Ae^{ik_1x} + Be^{-ik_1x} \qquad k_1 = \frac{\sqrt{(2mE)}}{\hbar}$$

and for x > 0,

$$\psi(x) = Ce^{ik_2x}$$

The first term corresponds to a particle incident on the wall (we suppose ψ is normalized so that the coefficient of this term is unity); the second term represents a particle reflected from the wall.

The constants A and B are determined from the condition that ψ and $\frac{d\psi}{dx}$ are continuous at x = 0.

$$1 + B = A, \qquad k_1(1-B)k_2A \tag{4}$$

Therefore

$$A = \frac{2k_1}{(k_1+k_2)}, B = \frac{(k_1-k_2)}{(k_1+k_2)} \tag{5}$$

The reflection coefficient is

$$\boxed{R = |B|^2 = \left(\frac{k_1-k_2}{k_1+k_2}\right)^2} \tag{6}$$

$$= \left(\frac{p_1-p_2}{p_1+p_2}\right)^2$$

For $E = U_0$, that is $k_2 = 0$, R becomes unity, while for $E \to \infty$ it tends to zero as $\left(\frac{U_0}{4E}\right)^2$.

From the above formulae we note the following :

1. In contrast to classical mechanics, according to which a particle going over a potential wall would slow down (to conserve energy) but would never be reflected, here we do have a ***certain fraction of the incident particle reflected***. This is, of course , a consequence of the wave properties of the particle; partial reflection of light from an interface between two media is a familiar phenomenon.

2. For $E >> U_0$, that is, for $k_2 \to k_1$ from below the ratio of the reflected flux to the incident flux, that is $|R|^2$ approaches zero. This agrees with intuition which tells us that at very high energies, the presence of the 'potential wall' is but a small perturbation on the propagation of the wave.

3. If the energy E is less than U_0, then k_2 becomes imaginary. If we note that, now the solution for x > 0 must be of the form

$$\psi(x) = Ce^{-|k_2|x} \tag{7}$$

So as not to blow up at $+\infty$, we see that now

$$R = |B|^2 = \left(\frac{k_1 - i|k_2|}{k_1 + i|k_2|}\right)\left(\frac{k_1 - i|k_2|}{k_1 + i|k_2|}\right)^*$$

or
$$R = \frac{k_1^2 + |k_2|^2}{k_1^2 + |k_2|^2} = 1 \tag{8}$$

Thus as in classical mechanics ,there is now total reflection.

Note : however that the continuity of the derivatives implies

$$ik_1(1 - B) = ik_2C \tag{9}$$

Substituting for B from (5), we fin d

$$C = \frac{2k_1}{k_1 + k_2} \Rightarrow \frac{2k_1}{k_1 + i|k_2|} \tag{10}$$

does not vanish and a part of the wave penetrates into the forbidden region. This penetration phenomenon is termed as "***tunneling***" through barriers.

Transmission Coefficient for a Rectangular Potential Barrier :

We now consider

$$\begin{aligned} U(x) &= 0 \quad &&;x < 0 \\ &= U_0 &&;0 < x < a \\ &= 0 &&;a < x \end{aligned}$$

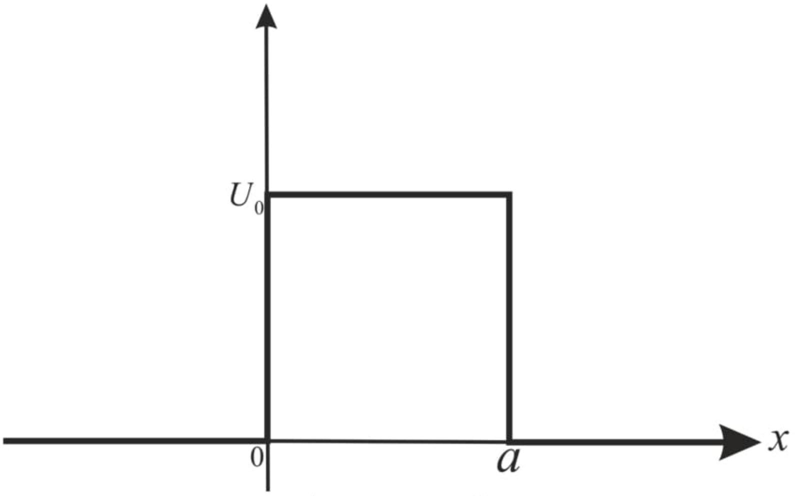


Figure 9.2

Let E be greater than U_0 and suppose that the incident particle is moving from left to right. Then we have for the wave function in the different regions expressions of the form

For x < 0, $\psi = e^{ik_1x} + Ae^{-ik_1x}$ (1)

For 0 < x < a $\psi = Be^{ik_2x} + B'e^{-ik_2x}$ (2)

For x > a $\psi = Ce^{ik_1x}$ (3)

(On the side x > a there can be only the transmitted wave, propagated in the positive diresction of x). The constants A, B, B' and C are determined from the conditions of continuity of ψ and $\frac{d\psi}{dx}$ at the points x = 0 and *a*.

The transmission coefficients is determined as

$$D = \frac{\text{transmitted flux}}{\text{incident flux}}$$

$$= \frac{\frac{\hbar k_1}{m}\left|c^2\right|}{\frac{\hbar k_1}{m}} = |c|^2 \tag{4}$$

On calculating this, we obtain

$$D = \frac{4k_1^2k_2^2}{\left(k_1^2 - k_2^2\right)\sin^2 ak_2 + 4k_1^2k_2^2} \tag{5}$$

For $E < U_0$, k_2 is a purely imaginary quantity; the corresponding expression for D is obtained by replacing k_2 by ik_2, where

$$\hbar k_2 = \sqrt{2m(\mathrm{U}_o - \mathrm{E})}$$

$$D = \frac{4k_1^2 k_2^2}{\left(k_1^2 + k_2^2\right)\sinh^2(ak_2) + 4k_1^2 k_2^2} \tag{6}$$

Thus we note that there is transmission even though the energy lies below the top of the barrier. This is a wave phenomenon and in quantum mechanics it is also one exhibited by particles. This "tunneling of a particle through a barrier is frequently encountered in physics.

9.6 Illustrative Examples

Example3: Find (a) $\langle x\rangle$, (b) $\langle x^2\rangle$, (c) $\langle p\rangle$ and (d) $\langle p^2\rangle$ for the eigenstates of a harmonic oscillator.

Solution : (a) $\langle x\rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) x \Psi_n(x) dx$ (1)

The harmonic oscillator wave functions have definite parity,We know that $\Psi_n(x)$ s either an even or an odd function of x. So we can say that the product $\Psi_n^*(x)$ $\Psi_n(x)$ will always be even.

Therefore $\langle x\rangle = 0$ Since x is odd, the integral(1) will zero

We can prove it by using recurrence relation for the Hermite polynomials.

$$2\alpha x H_n(\alpha x) = H_{n+1}(\alpha x) + 2nH_{n-1}(\alpha x) \tag{2}$$

The harmonic oscillator wave functions

$$\Psi_n(x) = \left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2}\ H_n(\alpha x), \mathrm{n} = 0,\ 1,\ 2,\ \ldots.. \tag{3}$$

Multiplying Equation (2) by

$$\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2}$$

and solving, we get

$$x\Psi_n(x) = \frac{1}{\alpha\sqrt{2}}[\sqrt{n+1}\,\Psi_{n+1}(x) + \sqrt{n}\,\Psi_{n-1}(x)] \tag{4}$$

Substituting in (1),we get

$$\langle x\rangle = \frac{\sqrt{n+1}}{\alpha\sqrt{2}} \int_{-\infty}^{\infty} \Psi_n^*(x)\ \Psi_{n+1}(x) dx + \frac{\sqrt{n}}{\alpha\sqrt{2}} \int_{-\infty}^{\infty} \Psi_n^*(x)\ \Psi_{n+1}(x) dx$$

Because the oscillator wave functions are orthonormal, both the integrals on the right hand side vanish, so

$$\langle x\rangle = 0$$

(b) $\langle x^2\rangle = \int_{-\infty}^{\infty} \Psi_n^*(x)x^2\ \Psi_n(x)dx$

$$= \frac{1}{\sqrt{2\alpha}}\int_{-\infty}^{\infty} \Psi_n^*\ x\left[\sqrt{n+1}\ \Psi_{n+1} + \sqrt{n}\Psi_{n-1}\right]dx \quad \text{(using 4)}$$

$$= \frac{1}{\sqrt{2\alpha}}\left[\sqrt{n+1}\int_{-\infty}^{\infty} \Psi_n^* x\Psi_{n+1}dx + \sqrt{n}\int_{-\infty}^{\infty} \Psi_n^*\ x\Psi_{n-1}dx\right]$$

Using (4),

$$\langle x^2\rangle = \frac{1}{\alpha}\sqrt{\frac{n+1}{2}}\left[\int_{-\infty}^{\infty}\psi^*\left\{\frac{1}{\alpha}\sqrt{\frac{n+2}{2}}\Psi_{n+2} + \frac{1}{\alpha}\sqrt{\frac{n+2}{2}}\Psi_n\right\}dx\right]$$

$$+\frac{1}{\alpha}\sqrt{\frac{n}{2}}\left[\int_{-\infty}^{\infty}\Psi_n^*\left\{\frac{1}{\alpha}\sqrt{\frac{n}{2}}\Psi_n + \frac{1}{\alpha}\sqrt{\frac{n-1}{2}}\Psi_{n-2}\right\}dx\right]$$

$$= \frac{\sqrt{(n+1)(n+2)}}{2\alpha^2}\int_{-\infty}^{\infty}\Psi_n^*\Psi_{n+2}dx + \frac{(n+1)}{2\alpha^2}\int_{-\infty}^{\infty}\Psi_n^*\Psi_n dx$$

$$+\frac{n}{2\alpha^2}\int\ \Psi_n^*\Psi_n dx + \sqrt{\frac{n(n-1)}{2\alpha^2}}\int_{-\infty}^{\infty}\Psi_n^*\Psi_{n-2}dx$$

By orthonormality of given wave functions, we get

$$\langle x^2\rangle = \frac{1}{2\alpha^2}(\text{n} + 1 + \text{n})$$

or $$\langle x^2\rangle = \frac{2n+1}{2\alpha^2} = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega} \tag{5}$$

(c) $\langle p\rangle = \int_{-\infty}^{\infty}\Psi_n^*(x)\hat{p}\Psi_n dx$

$$= \int_{-\infty}^{\infty}\Psi_n^*(x)\left[-i\hbar\frac{d\Psi_n(x)}{dx}\right]dx \tag{6}$$

If $\Psi_n(x)$ is odd, then its derivative is even, and vice versa. The integrand in the above integral is always an odd function of x. So

$$\langle p\rangle = 0\,.$$

We can also get this result using recurrence relation

$$\frac{dH_n(\alpha x)}{dx} = 2nH_{n-1}(\alpha x) \tag{7}$$

Differentiating (3)

$$\frac{d\Psi_n(x)}{dx} = \left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} \times \left[-(\alpha^2 x \exp\left(\frac{-\alpha^2 x^2}{2}\right) H_n(\alpha x) + \exp\left(\frac{-\alpha^2 x^2}{2}\right)\frac{dH_n(\alpha x)}{dx}\right]$$

$$= -\alpha^2 x\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} \exp\left(\frac{-\alpha^2 x^2}{2}\right) H_n(\alpha x) + \left(\frac{\alpha}{2^n !\sqrt{\pi}}\right)^{1/2} \times \alpha \exp\left(\frac{-\alpha^2 x^2}{2}\right)\frac{dH_n(\alpha x)}{d(\alpha x)}$$

Using (3) and (7)

$$\frac{d\Psi_n(x)}{dx} = -\alpha^2 x\Psi_n(x) + \left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} \alpha \exp\left(\frac{-\alpha^2 x^2}{2}\right)[2nH_{n-1}(\alpha x)]$$

$$= -\alpha^2 x\Psi_n(x) + (2\alpha n)\frac{1}{\sqrt{2n}}\left(\frac{\alpha}{2^{n-1}(n-1)!\sqrt{\pi}}\right)^{1/2} \exp\left(\frac{-\alpha^2 x^2}{2}\right) H_{n-1}(\alpha x)$$

$$= -\alpha^2 x\Psi_n(x) + 2\alpha\left(\frac{n}{2}\right)^{1/2} \Psi_{n-1}(x)$$

Using (4)

$$\frac{d\Psi_n(x)}{dx} = \frac{-\alpha}{\sqrt{2}}[\sqrt{n+1}\Psi_{n+1}(x) + \sqrt{n}\Psi_{n-1}(x)] + \frac{2\alpha}{\sqrt{2}}\sqrt{n}\Psi_{n-1}(x)$$

or
$$\frac{d\Psi_n(x)}{dx} = \frac{\alpha}{\sqrt{2}}[\sqrt{n}\Psi_{n-1}(x) - \sqrt{n+1}\Psi_{n+1}(x)] \tag{8}$$

By (6) and using the orthonormality of eigenfunctions, we get

$$\langle p\rangle = 0$$

(d)
$$\langle p^2\rangle = \int_{-\infty}^{\infty} \Psi_n^*(x)\hat{p}^2\, \Psi_n(x)dx$$

$$= -\hbar^2\int_{-\infty}^{\infty} \Psi_n^*(x)\frac{d^2\Psi_n(x)}{dx^2}dx$$

$$= \frac{-\hbar^2\alpha}{\sqrt{2}}\int_{-\infty}^{\infty} \Psi_n^* \frac{d}{dx}[\sqrt{n}\Psi_{n-1} - \sqrt{n+1}\Psi_{n+1}]dx \qquad \text{(using 8)}$$

$$= \frac{-\hbar^2\alpha}{\sqrt{2}}\left[\sqrt{n}\int_{-\infty}^{\infty} \Psi_n^* \frac{d\Psi_{n-1}}{dx}dx - \sqrt{n+1}\int_{-\infty}^{\infty} \Psi_n^* \frac{d\Psi_{n+1}}{dx}dx\right]$$

Using (8)

$$\langle p^2\rangle = \frac{-\hbar^2\alpha^2\sqrt{n}}{2}\int_{-\infty}^{\infty}\Psi_n^*[\sqrt{n-1}\,\Psi_{n-2}(x)-\sqrt{n}\Psi_n]dx$$

$$+\frac{h^2\alpha^2\sqrt{n+1}}{2}\int_{-\infty}^{\infty}\Psi_n^*[\sqrt{n-1}\,\Psi_n-\sqrt{n+2}\,\Psi_{n+2}]dx$$

$$=\frac{-h^2\alpha^2}{2}\Big[\sqrt{n(n-1)}\int_{-\infty}^{\infty}\Psi_n^*\Psi_{n-2}dx-n\int_{-\infty}^{\infty}\Psi_n^*\Psi_n dx$$

$$-(n+1)\int_{-\infty}^{\infty}\Psi_n^*\Psi_n dx+\sqrt{(n+1)(n+2)}\int_{-\infty}^{\infty}\Psi_n^*\Psi_{n+2}\,dx\Big]$$

Using the orthonormality this becomes

$$\langle p^2\rangle = -\frac{\hbar^2\alpha^2}{2}(0-\mathrm{n}-(\mathrm{n}+1)+0)$$

$$=\frac{2n+1}{2}\hbar^2\alpha^2$$

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

or $$\langle p^2\rangle = \left(n+\frac{1}{2}\right)m\omega\hbar$$

Example.4 : Obtain the expectation value of the kinetic and potential energies for the nth state of a linear harmonic oscillator.

Solution. $\langle T\rangle = \frac{1}{2m}\langle p^2\rangle = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega = \frac{E_n}{2}$

$$\langle V\rangle = \frac{1}{2}k\langle x^2\rangle = \frac{1}{2}(m\omega^2)\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}$$

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

9.7 Summary

In this chapter we have solved the problems of eigenvalues and eigenfunctions of simple harmonic oscillator by making use of Schrodinger equation . We have also demonstrated the basic quantum phenomena by solving the problem of reflection coefficient of a particle from a rectangular potential wall where the energy of the particle E is greater than the potential energy. Here one sees the departure from the laws of classical mechanics

9.8 Glossary

Expectation Value: expectation value of quantity A is $\langle A\rangle = \dfrac{\int \psi^{*}\hat{A}\psi\,dV}{\int \psi^{*}\psi\,dV}$

9.9 Answers to Self Learning Exercise

Ans.1: $\hat{H} = \dfrac{\hat{p}^2}{2m} - \dfrac{1}{2}m\omega^2\hbar^2\dfrac{d^2}{dp^2}$

The corresponding Schrodinger's equation.

$\hat{H}a(p) = Ea(p)$ for the wave function a(p) in the momentum representation is

$$\frac{d^2a(p)}{dp^2} + \frac{2}{m\omega^2\hbar^2}\left(E - \frac{\hat{p}^2}{2m}\right)a(p) = 0$$

This equation is of exactly the same form as in coordinate representation.

Ans.2: $E >> \dfrac{1}{2}\hbar\omega$

Ans.3: Since $\overline{(\delta x)^2} = \overline{(x-\overline{x})^2}$ where 'bar' denotes the average.

Hence $\overline{\delta x^2} = \overline{x^2} + (\overline{x})^2 - 2\overline{x\overline{x}}$

$$= \overline{x^2} + (\overline{x})^2 - 2(\overline{x})^2$$

$$\overline{\delta x^2} = \overline{x^2} - (\overline{x})^2 \qquad (1)$$

$$\therefore \overline{x^2} = (\overline{x})^2 + (\delta x)^2 \qquad (2)$$

Similarly $\therefore \overline{p^2} = (\overline{p})^2 + (\delta p)^2$ (3)

The mean value of the energy of the oscillator is given by

$$\overline{E} = \frac{1}{2}m\omega^2\overline{x^2} + \frac{\overline{p^2}}{2m} \geq \frac{1}{2}m\omega^2(\delta x)^2 + \frac{(\delta p)^2}{2m}$$

or $\overline{E} \geq \dfrac{1}{2}m\omega^2\left(\dfrac{\hbar}{2\delta p}\right)^2 + \dfrac{(\delta p)^2}{2m}$ (We have used $\delta x \delta p_x \geq \dfrac{1}{2}\hbar$)

or $$\overline{E} \geq \frac{m\omega^2\hbar^2}{8(\delta p)^2} + \frac{(\delta p)^2}{2m} \tag{4}$$

On determining the minimum value of this expression (regarded as a function δp), We find the lower limit of the mean values of the energy:

$$\frac{d\overline{E}}{d(\delta p)} = 0$$

$$\Rightarrow -\frac{m\omega^2\hbar^2}{4(\delta p)^3} + \frac{2\delta p}{2m} = 0$$

This gives $(\delta p)^4 = \dfrac{m\omega^2\hbar^2}{4}$

or $$(\delta p)^2 = \frac{m\omega\hbar}{2} \tag{5}$$

Substituting this value of $(\delta p)^2$ into (4), we get $\overline{E} \geq \frac{1}{2}\hbar\omega$

9.10 Exercise

Section A:Very ShortAnswer Type Questions

Q.1 Represent graphically the ground state wave function of harmonic oscillator. Also plot $\psi_0, \psi_1, \psi_2, \psi_3$.

Q.2 What is the ground-state energy of Simple Harmonic Oscillator.

Q.3 How much is the energy difference between two consecutive energy levels of Simple Harmonic Oscillator.

Q.4 Write the Hamiltonian for simple harmonic oscillator in momentum *p*-representation.

Section B:Short Answer Type Questions

Q.5 Find the energy levels of a particle moving in a potential field of the shape

$$V(x) = \infty \qquad (x < 0)$$

$$V(x) = \frac{m\omega^2 x^2}{2} \qquad (x > 0)$$

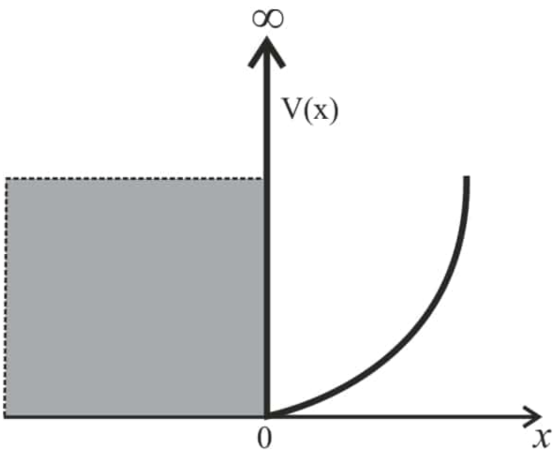


Figure 9.3

Section C:Long Answer type Questions

Q.6 Write the Schrödinger's equation for an oscillator in the p-representation and determine the probability distribution for different values of the momentum.

Q.7 Find the transmission coefficient through a potential of the form

$V(x) = -V_0\delta(x), \qquad V_0 > 0$

x is real. The corresponding wave function $\psi(x)$ is supposed to be smooth.

9.11 Answers to Exercise

Ans.1: $\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} . e^{-\frac{m\omega x^2}{2\hbar}}$

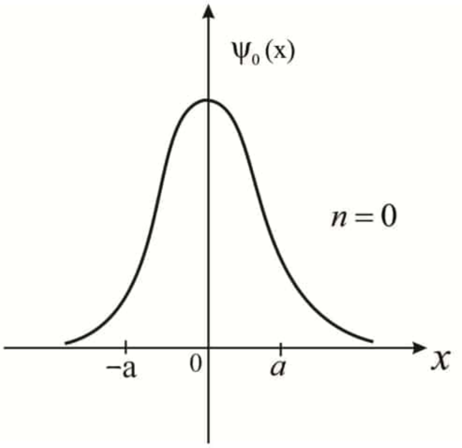


Figure 9.4a

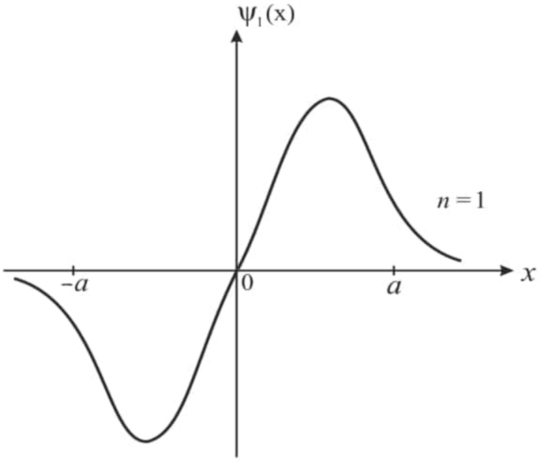


Figure 9.4b

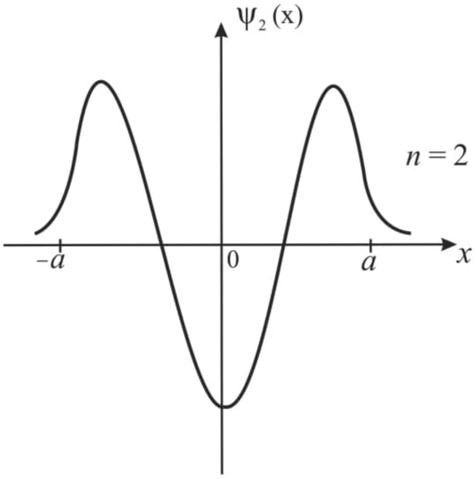


Figure 9.4c

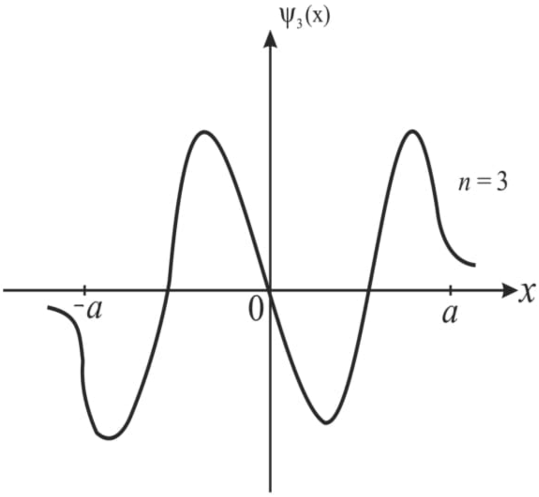


Figure 9.4d

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

$$\text{n} = 0,\ E_0 = \frac{1}{2}\hbar\omega$$

Ans.3: $\Delta E = E_{n+1} - E_n$

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

$$= \hbar\omega$$

Ans.4: $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}mw^2\hat{x}^2$. Replace the coordinate operator $\hat{x} = i\hbar\frac{d}{dp}$, we obtain

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2(i)^2\hbar^2\frac{d^2}{dp^2}$$

$$= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hbar^2\frac{d^2}{dp^2}$$

Ans.5: The wave function should tend to zero as $x \to 0$. For $x > 0$ it satisfies the differential equation of the harmonic oscillator. It should be noted that the wave functions of the oscillator for odd $n = 2k + 1$ tend to zero as $x \to 0$ (The Hermite polynomials $H_n(x) \Rightarrow 0$ for odd *n*), and in the region $x \geq 0$ give the solution to our problem. Consequently

$$E_k = \left(2k+1+\frac{1}{2}\right)\hbar\omega \qquad (\because n = 2k+1)$$

$$\mathrm{k} = 0,1,.....$$

$$E_k = \left(2k+\frac{3}{2}\right)\hbar\omega \qquad \mathrm{k} = 0,1,2,.....$$

$$\mathrm{E}_{\mathrm{min}} = \frac{3}{2}\hbar\omega$$

Ans.6: Schrodinger Equation is

$$\left(\frac{\hat{p}^2}{2m} - \frac{1}{2}m\omega^2\hbar^2\frac{\partial^2}{\partial\hat{p}^2}\right)a_n(p) = E_n a_n(p)$$

$$\left|a_n(\mathrm{p})^2\right| = \frac{1}{2^n n!}\frac{1}{\sqrt{\pi m\hbar\omega}}e^{-\frac{p^2}{m\omega\hbar}}H_n^2\left(\frac{p}{\sqrt{m\omega\hbar}}\right)$$

References and Suggested Readings

1. L.D.Landau and E.M.Lifshitz ,Quantum Mechanics(Non relativistic theory) Vol-3 ,third edition, Butterworth Heinmann
2. Mahesh C. Jain ,Quantum Mechanics, Eastern Economy Edition, PHI 2014
3. Stephan Gasiorowicz ,Quanatum Physics ,Second edition, John Wiley &Sons

UNIT-10

Angular Momentum

Structure of the Unit

10.0 Objectives

After interacting with the material presented here students will be able to

a. Relate rotation and angular momentum operator

b. Law of conservation of angular momentum

c. Commutation relation of orbital angular momentum operator with momentum and position operator

d. Eigen values and eigen vectors of L_x, L_y, L_z, L^2

10.1 Introduction

Angular momentum is one of the basic features of quantum mechanics. Its conservation is a universal phenomenon independent of the nature of the reference frame that allows calculation of energy values of the system under different conditions.

Angular momentum ***L*** for a particle of momentum ***p*** is defined through

$$\boxed{\vec{L} = \vec{r} \times \vec{p}}$$

(To understand it classically it is to be considered as moment of momentum).

In its fully expanded form

$$\boxed{\vec{L} = \hat{i}L_x + \hat{j}L_y + \hat{k}L_z}$$

$$= (\boldsymbol{i}\,x + \boldsymbol{j}\,y + \boldsymbol{k}\,z) \times (\boldsymbol{i}\,p_x + \boldsymbol{j}\,p_y + \boldsymbol{k}\,p_z)$$

$$= \boldsymbol{i}\,(y\,p_z - z\,p_y) \;+ \boldsymbol{j}(z\,p_x - x\,p_z) \;+ \boldsymbol{k}(x\,p_y - y\,p_x)$$

Here we have expressed vectors ***r***, ***p*** and ***L*** in their components along the Cartesian axes. We have also used the orthogonal properties of vectors viz.,

$$\boldsymbol{i} \times \boldsymbol{i} = \boldsymbol{j} \times \boldsymbol{j} = \boldsymbol{k} \times \boldsymbol{k} = 0\,;$$

$$\boldsymbol{i} \times \boldsymbol{j} = \mathbf{k},\;\; \boldsymbol{j} \times \boldsymbol{k} = \boldsymbol{i},\;\; \boldsymbol{k} \times \boldsymbol{i} = \boldsymbol{j} \text{ and } \boldsymbol{j} \times \boldsymbol{i} = -\,\boldsymbol{k} \text{ etc.}$$

Let us concentrate on the z-component of angular momentum (equating coefficients of ***k***) we have

$$\boxed{L_z = (x\,p_y - \;y\,p_x)}$$

We can express this relation in operator form by writing a cap (^ symbol) on each of the letter under consideration.

We find

$$\boxed{\hat{L}_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})}$$

$$\hat{L}_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$$

$$\hat{L}_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

The magnitude (*L*, a scalar quantity) of the angular momentum is related to its components in the same way that any vector magnitude can be constructed

$$\boxed{L^2 = L_x^2 + L_y^2 + L_z^2}$$

We now establish the ***commutation relationships*** of the L operators. First the commutator of the operators L_x and L_y can be found:

$$
\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= [(yp_z - zp_y), (zp_x - xp_z)] \\
&= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\
&= y[p_z, z]p_x - 0 - 0 + p_y[z, p_z]x = i\hbar(-yp_x + xp_y) \\
&= i\hbar\hat{L}_z
\end{aligned}
$$

The other two commutators can be found in the same way, or can be simply written down using cyclical permutation. In summary then

$$\boxed{\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z}$$

$$\boxed{\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x}$$

$$\boxed{\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y}$$

The remaining operator we need is that corresponding to the square of the magnitude of the angular momentum, $\hat{L}^2$. We need to know whether it commutes with the L_q components

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_z] = [\hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2, \hat{L}_z] &= [\hat{L}_x{}^2, \hat{L}_z] + [\hat{L}_y{}^2, \hat{L}_z] + [\hat{L}_z{}^2, \hat{L}_z] \\
&= [\hat{L}_x{}^2, \hat{L}_z] + [\hat{L}_y{}^2, \hat{L}_z] + 0
\end{aligned}
$$

Now we examine each of the two non-zero terms in turn

$$
\begin{aligned}
[\hat{L}_x{}^2, \hat{L}_z] &= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x \\
&= \hat{L}_x\hat{L}_x\hat{L}_z(-\hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x) - \hat{L}_z\hat{L}_x\hat{L}_x \\
&= \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x \\
&= -i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)
\end{aligned}
$$

The parenthesis placed in line 2 is the overall addition of zero to the RHS. Similarly

$$[\hat{L}_y^2, \hat{L}_z] = i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$$

Therefore $\hat{L}^2$ and $\hat{L}_z$ ***commute.***

Moreover, L_x, L_y, and L_z all occur symmetrically in L^2 and therefore all must commute with L^2, if any one of them does. In other words

$$\boxed{\left[\hat{L}^2, \hat{L}_x\right] = \hat{0}}$$

$$\boxed{\left[\hat{L}^2, \hat{L}_y\right] = \hat{0}}$$

$$\boxed{\left[\hat{L}^2, \hat{L}_z\right] = \hat{0}}$$

The commutation relations expressed are fundamental to the theory of angular momentum, and are quite general. In fact we can usually say that an observable is an angular momentum if its operators satisfy the above commutation relationships.

10.2 Relation between Rotation Operator and Angular Momentum Operator

If $R_z(\theta)$ represents an operator corresponding to an infinitesimal rotation θ about z-axis then

$$R_z(\theta)\,\Psi(x,y,z) = \Psi(x',y',z')$$

$$= \Psi(x+y\theta, y-x\theta, z)$$

Now by Taylor expansion we can write

$$R_z(\theta)\,\Psi(x,y,z) = \Psi(x,y,z) + y\theta\frac{\partial}{\partial x}\Psi(x,y,z) - x\theta\frac{\partial}{\partial y}\Psi(x,y,z)$$

Or $$R_z(\theta)\,\Psi(x,y,z) = (1 + \theta[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}])\,\Psi(x,y,z)$$

$$= [1 + \frac{\theta}{i\hbar}L_z]\,\Psi(x,y,z)$$

It suggests that

$$R_z(\theta) \;=\; [1 + \frac{\theta}{i\hbar} L_z]$$

and similarly we can show that

$$R_x(\theta) = [1 + \frac{\theta}{i\hbar} L_x]$$

and

$$R_y(\theta) \;= [1 + \frac{\theta}{i\hbar} L_y]$$

In other words L_x, L_y and L_z are the generator of rotations about z-axis.

The matrices rotating a vector by θ about the x, y and z axes are

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix},$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix},$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In the limit of rotations about infinitesimal angles (ignoring higher order terms),

$$R_x(\varepsilon) = 1 + \varepsilon \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$R_y(\varepsilon) = 1 + \varepsilon \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix},$$

$$R_z(\varepsilon) = 1 + \varepsilon \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

It is easy to check that

$$[R_x(\varepsilon), R_y(\varepsilon)] = \varepsilon^2 \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$= R_z(\varepsilon^2) - 1$$

10.3 Rotational Invariance and Conservation of Angular Momentum

Invariance dictates no change under some operation and conservation dictates commutation with energy operator.

Rotational invariance is the property of a system such that after undergoing rotation, the new system still obeys Schrodinger equation. Thus for any rotation, the rotation operator and energy operator commutes.

i.e.

$$[R, (E\text{-}H)] = 0$$

Since rotation does not depend explicitly on the time, it commutes with energy operator.

Thus

$$\boxed{\left[\hat{R}, \hat{H}\right] = \hat{0}}$$

here H represents energy operator or the Hamiltonian of the system.

Let the system be rotated (in x-y plane) by an infinitesimal angle $d\theta$ then the rotation operator is

$$R = 1 + L/i\hbar\, d\theta$$

Then from

$$[R, (E\text{-}H)] = 0$$

we find that

$$[(1 + L/i\hbar\, d\theta), \frac{d}{dt}] = 0$$

$$\frac{d}{dt}(L) = 0$$

It suggests that angular momentum in such rotations is conserved.

10.4 Self Learning Exercise -I

Short Answer Type Questions

Q. 1 Calculate $\left[L^{+}, L_{z}\right]$

Q. 2 Calculate $\left[L^{-}, L_{z}\right]$

Q.3 Prove that $\boxed{J \times \mathrm{J} = i\hbar \mathrm{J}}$

Hint – Write $\boldsymbol{J} = \boldsymbol{i}J_x + \boldsymbol{j}J_y + \boldsymbol{k}J_z$, then find $\boldsymbol{J} \times \boldsymbol{J}$ and find if the sum of all the three commutations produce the desired result.

Q.4 Prove that $[J_x, \boldsymbol{J}^2] = 0$

Long Answer Type Questions

Q. 5 Calculate the angular momentum for the following particles. Find the angle between the position and the momentum vectors.
(a) r=(4,-5,3)and p =(1,4,-2)
(b) r =(1,-2,3)and p =(7,-1,1)

Q.6 Show that the wave function $\psi = (\sin\theta)(e^{i\phi})$ is an eigenfunction of $\hat{L}_z$.
What is the eigenvalue? (Hint: $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$)

10.5 Commutation Relations

When two operators $\hat{A}$ and $\hat{B}$ are written as $\hat{A}\,\hat{B}$ and $\hat{B}\,\hat{A}$ we have an important relation

$$\boxed{\hat{A}\hat{B} - \hat{B}\hat{A} = [\hat{A}, \hat{B}]}$$

The operator [$\hat{A}$, $\hat{B}$] is called commutation operator.

Example 1 : To find what the operator $[\hat{x}\hat{\mathrm{p}}_{\mathrm{x}} - \hat{\mathrm{p}}_{\mathrm{x}} x]$ represents?

Sol. We must remember that an operator without an operand hardly conveys any meaning. Hence we write $[\hat{x}\hat{\mathrm{p}}_{\mathrm{x}} - \hat{\mathrm{p}}_{\mathrm{x}} x]\Psi(\mathrm{x})$ to find what the operator is like.

Writing these operators in their usual form gives

$$[x\,(-i\hbar\,\frac{\partial}{\partial x}) - (-i\hbar\,\frac{\partial}{\partial x})x]\,\Psi(x) = -\,[x\,(i\hbar\,\frac{\partial \psi(x)}{\partial x}) - (i\hbar\,\frac{\partial \psi(x)}{\partial x})x]$$

$$= -\,[x\,(i\hbar\,\frac{\partial \psi(x)}{\partial x})\ -i\hbar\,\Psi(x) - xi\Psi(x)\,\frac{\partial \psi(x)}{\partial x}]$$

$$= -i\hbar\,\Psi(x)$$

or $$[x\,(-i\hbar\,\frac{\partial}{\partial x}) - (-i\hbar\,\frac{\partial}{\partial x})x]\,\Psi(x) = i\hbar\Psi(x)$$

Corollary $$[x\,(-i\hbar\,\frac{\partial}{\partial x}) - (-i\hbar\,\frac{\partial}{\partial x})x]) = i\hbar$$

Example 2: To show that the operator $[x, d/dx] = -1$

Sol. Let us operate this operator on Ψ,

we have

$$x\,\frac{d}{dx}\Psi - \frac{d}{dx}x.\Psi = x\,\frac{d}{dx}\Psi - \Psi - x\,\frac{d}{dx}\Psi = -\Psi$$

Thus $[x, d/dx]\,\Psi = -\Psi$

Example 3: Find $[L_x, x]$

Sol. Since $L_x = (\mathbf{r}\times\mathbf{p})_x = yp_z - zp_y$ here subscript suggests that the component along that direction is considered.

Thus p_y is component of $\boldsymbol{p}$ along y direction.

Writing L_x in operator form $\hat{L}_x = \hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})$

But $[L_x,x] = L_x x - xL_x$ hence

$$[L_x,x] = \{\,\hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})\,\}\,\hat{x} - \hat{x}\,\{\,\hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})\,\}$$

$$[L_x,x] = -\,\hat{x}\,\{\,\hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})\,\}$$

As the first bracket is zero because it is either differentiation of x with respect to z or with respect to y.

Example 4 Find $[L_x,y]$

Sol.

We have [L_x,y] $= \{ \hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})\}\ \hat{y}$ - $\hat{y}\{ \hat{y}(-i\hbar\frac{\partial}{\partial z}) - \hat{z}(-i\hbar\frac{\partial}{\partial y})\}$

Second term is meaningless.

First term gives 0 + $i\hbar$ z$\frac{\partial y}{\partial y}$.

Hence [L_x,y] $= i\hbar$ z.

Important Note: The commutators between linear and angular momentum are very similar to the ones between position and angular momentum:

$$\boxed{[p_x, L_x] = [p_y, L_y] = [p_z, L_z] = 0}$$

$$[p_x, L_y] = [L_x, p_y] = i\hbar p_z$$

$$[p_y, L_z] = [L_y, p_z] = i\hbar p_x$$

$$[p^2, L_x] = [p^2, L_y] = [p^2, L_z] = [p^2, L] = 0$$

$$[p, L^2] = -2\hbar^2 p - 2i\hbar p \times L = 2\hbar^2 p + 2i\hbar(r.p)p - 2i\hbar r(p.p)$$

The following commutators are also useful:

$$[r \times L, L^2] = 2i\hbar r L^2$$

$$[[r, L^2], L^2] = 2\hbar^2(rL^2 + L^2 r)$$

10.6 Eigen values and Eigen Vectors of L_x, L_y, L_z, L^2

Operators in polar form

To express various operators in polar form we will use following set of relations:

Set I

$$\boxed{\begin{aligned} x &= r\ sin\theta cos\theta \\ y &= r\ sin\theta sin\theta \\ z &= r\ cos\theta \end{aligned}}$$

Set II $r^2 = x^2 + y^2 + z^2$

Set III $tan^2\ \theta = [x^2 + y^2]/z^2$

Set IV $tan\ \phi = y/x$

Now our task is to find $\frac{\partial r}{\partial x}$, $\frac{\partial r}{\partial y}$, $\frac{\partial r}{\partial z}$, $\frac{\partial \theta}{\partial x}$, $\frac{\partial \theta}{\partial y}$, $\frac{\partial \theta}{\partial z}$ and $\frac{\partial \phi}{\partial x}$, $\frac{\partial \phi}{\partial y}$, $\frac{\partial \phi}{\partial z}$

Once this is done their substitution in appropriate formulae would yield angular momentum operator in polar form.

Step I

From $r^2 = x^2 + y^2 + z^2$

$$2r\frac{\partial r}{\partial x} = 2x$$

$$\frac{\partial r}{\partial x} = x/r$$

$$or \qquad \frac{\partial r}{\partial x} = r \sin\theta \cos\phi / r$$

$$or \qquad \frac{\partial r}{\partial x} = \sin\theta \cos\phi$$

It can be shown that

$$\frac{\partial r}{\partial y} = \sin\theta \sin\phi$$

$$\frac{\partial r}{\partial z} = \cos\theta$$

Step II

From $\tan^2\theta = [x^2 + y^2]/z^2$

we have

$$2\tan\theta \sec^2\theta\,[\partial\theta/\partial x] = 2x/z^2$$

$$\text{or} \qquad \frac{\partial\theta}{\partial x} = \frac{x}{z^2\ \tan\theta\ \sec^2\theta}$$

$$\text{or} \qquad \frac{\partial\theta}{\partial x} = \frac{r\sin\theta\cos\phi}{z^2\ \cos^2\theta\ \ \tan\theta\ \sec^2\theta}$$

$$\text{or} \qquad \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}$$

Similarly

$$\frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r}$$

and $$\frac{\partial\theta}{\partial z} = -\frac{\cos\theta}{r}$$

Step III

From $tan\,\phi = y/x$

we find that

$$sec^2\phi\,\frac{\partial\phi}{\partial x} = -y/x^2$$

$$= -\frac{r\sin\theta\sin\phi}{\mathrm{r}^2\cos^2\phi\,\sin^2\theta}$$

or $$\frac{\partial\phi}{\partial x} = -\frac{r\sin\theta\sin\phi}{\mathrm{r}^2\sec^2\phi\cos^2\phi\,\sin^2\theta}$$

or $$\frac{\partial\phi}{\partial x} = -\frac{\cos ec\theta\sin\phi}{\mathrm{r}}$$

Proceeding in a similar manner we find that

$$\frac{\partial\phi}{\partial y} = \frac{\cos\phi\cos ec\theta}{r}$$

and $$\frac{\partial\phi}{\partial z} = 0$$

We know that x is a function of r, θ, and ϕ. In mathematical notation we express this fact as

$$x = x(r, \theta, \phi)$$

Recognizing this fact we can write

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial x}$$

Substituting values of $\frac{\partial r}{\partial x}$, $\frac{\partial \theta}{\partial x}$ and $\frac{\partial \phi}{\partial x}$ in this equation we get

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}[\sin\theta\cos\phi] + \frac{\partial}{\partial \theta}[\frac{\cos\theta\cos\phi}{r}] + \frac{\partial}{\partial \phi}[-\frac{\cos ec\theta\sec\phi\tan\phi}{\mathrm{r}}$$

$$]$$

or $$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial \theta} - \frac{\cos ec\theta\sin\phi}{\mathrm{r}}\frac{\partial}{\partial \phi}$$

Similarly

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial \phi}$$

and

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}$$

We know that

$$\hat{L}z = -i\hbar[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}]$$

we have

$$\hat{L}z\psi = -i\hbar[x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}]$$

$$= -i\hbar[x(\frac{\partial\psi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial y}) - y(\frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x})]$$

$$= -i\hbar[r\sin\theta\cos\phi(\frac{\partial\psi}{\partial r}\sin\theta\sin\phi + \frac{\partial\psi}{\partial\theta}\frac{\cos\theta\sin\phi}{r} + \frac{\partial\psi}{\partial\phi}\frac{\cos\phi\cos ec\theta}{r})$$

$$-r\sin\theta\sin\phi(\frac{\partial\psi}{\partial r}\frac{\sin\theta\cos\phi}{1} + \frac{\partial\psi}{\partial\theta}\frac{\cos\theta\cos\phi}{r} - \frac{\partial\psi}{\partial\phi}\frac{\sin\phi\cos ec\theta}{r})]$$

Or $\hat{L}_z\psi = -i\hbar\frac{\partial\psi}{\partial\phi}$

It suggests that

$$\boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}}$$

In a similar fashion we can find

$$\boxed{\hat{L}_x = -i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cos\theta\cos\phi\frac{\partial}{\partial\phi}\right]}$$

and

$$\boxed{\hat{L}_y = -i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]}$$

Once we have determined all components of $\hat{L}$ we can find the operator $\hat{L}$

(use $\hat{L} = \mathbf{i}\,\hat{Lx} + \mathbf{j}\,\hat{Ly} + \mathbf{k}\,\hat{Lz}$) and also another important operator $\hat{L^2}$ using the fact that

$$\hat{L^2} = \hat{Lx}^2 + \hat{Ly}^2 + \hat{Lz}^2$$

$$\hat{L^2} = -\hbar^2\left[\nabla^2 - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})\right]$$

$$\hat{L^2} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\theta^2}\right]$$

Eigen values and Eigen functions of *Lz* :

(*Eigen functions are also called Eigen vectors)

The relation

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

indicates that the corresponding Eigen function could be $\Phi = \phi(\phi)$.

Writing Eigen value equation as

$$\hat{L}_z\,\Phi(\phi) = E\Phi(\phi)$$

A trial solution could be

$$\Phi(\phi) = Ae^{-im\phi}$$

$$-i\hbar\frac{\partial}{\partial\phi}(\mathrm{A}e^{-im\phi}) = E\mathrm{A}e^{-im\phi}$$

or $$i\hbar A(-im)\,e^{-im\phi} = EAe^{-im\phi}$$

suggesting that Eigen value

$$E = m\hbar$$

Eigen function

$$\boxed{\Phi = Ae^{-im\phi}}$$

Eigen values of L_z for Eigen vector $(L_x \pm iL_y)\ \Psi(m)$

From $\quad L_yL_z = i\hbar L_x + L_zL_y$

and $\quad L_zL_y = -i\hbar L_x + L_zL_y$

we have

$$\begin{aligned} L_z(L_x \pm iL_y) &= L_zL_x \pm iL_zL_y \\ &= L_zL_x \pm i[-i\hbar L_x + L_zL_y] \\ &= \pm\hbar(L_x \pm iL_y) + L_z(L_x \pm iL_y) \\ &= (L_x \pm iL_y)(L_z \pm \hbar) \end{aligned}$$

So $\; L_z(L_x \pm iL_y)\,\Psi(m) = (L_x \pm iL_y)(L_z \pm \hbar)\,\Psi(m)$

But $\quad (L_z \pm \hbar)\,\Psi(m) = (m \pm 1)\hbar\,\Psi(m)$

Hence $\; L_z(L_x \pm iL_y)\,\Psi(m) = (m \pm 1)\hbar\,(L_x \pm iL_y)\,\Psi(m)$

Thus if $\Psi(m)$ is a wave function of L_z with an Eigen value of $m\hbar$, then $(L_x \pm iL_y)$ $\Psi(m)$ are also Eigen functions of L_z with Eigen values of $(m \pm 1)\hbar$.

Eigen function and Eigen values for L^2

Let μ represent the largest Eigen value for L_z when operated on $(L_x + iL_y)$ and μ' its maximum negative value for L_z when operated upon $(L_x - iL_y)$. Then

$$L_z(L_x + iL_y)\,\Psi(\mu) = 0$$

and

$$L_z(L_x - iL_y)\,\Psi(\mu') = 0$$

Consider

$$L^2\Psi(\mu) = (L_x^2 + L_y^2 + L_z^2)\,\Psi(\mu)$$

$$= [L_z^2 + (L_x - iL_y)(L_x + iL_y) - i(L_xL_y - L_y L_x)]\,\Psi(\mu)$$

$$= [L_z^2 + (L_x - iL_y)(L_x + iL_y) - i.i\,L_z]\,\Psi(\mu)$$

$$= [\mu^2\hbar^2 - (L_x - iL_y).0 + \mu\hbar]\,\Psi(\mu)$$

or $$L^2\Psi(\mu) = \mu(\mu + 1)\hbar^2\,\Psi(\mu)$$

Similarly we can obtain

$$L^2\Psi(\mu') = \mu'(\mu' - 1)\hbar^2\,\Psi(\mu')$$

Both equations must be valid at all the time hence $\mu(\mu + 1)$ must be equal to $\mu'(\mu' - 1)$

Two possible situations would be

$$\mu = \mu' \text{ and } (\mu + 1) = \mu'$$

We would disregard second solution as we have assumed that μ' cannot have larger value than μ. Hence we take $\mu' = \mu$,to be the acceptable result.

Let us call this value of μ as *l*. then the ***Eigen value of L^2 are $l(l+1)\hbar^2$*** .

Example. What is the magnitude for the Eigen value of L?

Sol. We can claim that it must be square root of the Eigen value for L^2. Recall that quantum number related to L is written as $\sqrt{l(l+1)}$

10.7 Self Learning Exercise -II

Very Short Answer Type Questions

Q.1 Write down eigenvalue for $\mathbf{J^2}$ **.**

Q.2 Write down eigenvalue for $\mathbf{J_z}$ **.**

Short Answer Type Questions

Q.3 What is $[L_x, x]\,\Psi(x)$?

Q. 4 Show that

1. $[L_x, z] = -i\hbar y$

2. $[L_x, p_x] = 0$

3. $[L_x, p_y] = i\hbar p_z$

Q.5 Show that

1. $[L_y, L_z] = -i\hbar L_x$

2. $[L_x, L_x] = 0$

10.8 Summary

The unit starts with the introduction of angular momentum followed by relation of rotation and angular momentum operator. In this unit we also discussed law of conservation of angular momentum, Commutation relation of orbital angular momentum operator with momentum and position operator and Eigen values and eigen vectors of L_x, L_y, L_z, L^2

10.9 Glossary

Angular Momentum :also called moment of momentum, it is the cross product of position vector and momentum.

Orbital angular momentum: an angular momentum that corresponds to the quantum analog of classical angular momentum

Momentum **:**A measure of how much effort is required to stop a body, defined as the body's mass multiplied by its velocity. Thus, a large heavy body (e.g. a train) going relatively slowly may have more momentum than a smaller body going very fast (e.g. a racing car). The Law of Conservation of Momentum rules that the total momentum of an isolated system (one in which no net external force acts on the system) does not change.

Uncertainty Principle**:**

The principle in quantum theory, formulated by Werner Heisenberg in 1926, which holds that the values of certain pairs of variables cannot both be known exactly, so that the more precisely one variable is known, the less precisely the other can be known. For example, if the speed or momentum of a particle is known exactly, then its location must remain uncertain; if its location is known with certainty, then the particle's speed or momentum cannot be known. Formulated another way, relating the uncertainties of energy and time, the uncertainty principle permits the existence of ultra-short-lived microscopic particles (virtual particles) in apparently empty space, which briefly blink into existence and blink out again.

Eigen Value: An allowed value of the constant *a* in the equation *Au=au*

Where *A* is an operator acting on a function *u* (which is called eigenfunction). Also called characteristic value.

Commute: Two operators commute with each other if their commutator is equal to zero. The commutator of operators A and B is

$$[A,B]=AB-BA$$

Hermitian operator: Operators that are equal to their Hermitian adjoints, in other words, an operator is Hermitian if

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

Hilbert Space: Infinite-dimensional complete vector space over the complex numbers endowed with a metric induced by a scalar product that satisfies Schwartz's inequality

State :A mechanical system is at any given time completely characterized in quantum mechanics by the state Ψ. The projection onto coordinate space, Ψ(r), is called a wave function. States are vectors in Hilbert space.

Superposition Principle :Any superposition in Hilbert space, $\Psi = a\,\Psi_1 + b\,\Psi_2$, of two states Ψ_1 and Ψ_2 forms another physically realizable state of a physical system.

Wave Function **:**The representation of the state $|\Psi>$ in coordinate space, $\Psi(r)=<r|\Psi>$.

10.10 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1 : $\left[L^{+},L_{z}\right]=\left[L_{x}+iL_{y},L_{z}\right]=-i\hbar L_{y}-\hbar L_{x}=\hbar L^{+}$

Ans. 2: $\left[L^{-},L_{z}\right]=\left[L_{x}-iL_{y},L_{z}\right]=-i\hbar L_{y}+\hbar L_{x}=\hbar L^{-}$

Ans. 3 :

$$J \times J = \mathbf{i}(J_yJ_z-J_zJ_y) + \mathbf{j}(J_zJ_x-J_xJ_z) + \mathbf{k}(J_xJ_y-J_yJ_x)$$

$$= \mathbf{i}[J_y,J_z] + \mathbf{j}[J_z,J_x] + \mathbf{k}[J_x,J_y]$$

$$= \mathbf{i}(i\hbar J_x) + \mathbf{j}(i\hbar J_y) + \mathbf{k}(i\hbar J_z)$$

$$= i\hbar(\mathbf{i}J_x + \mathbf{j}J_y + \mathbf{k}J_z) = i\hbar J.$$

Ans. 4: $[J_x, J^2] = [J_x,(J_x^2 + J_y^2 + J_z^2]$

$$= [J_x,J_x^2] + [J_x,J_y^2] + [J_x, J_z^2]$$

$$= 0$$

Ans.5: (a)

$$L = \begin{vmatrix} i & j & k \\ 4 & -5 & 3 \\ 1 & 4 & -2 \end{vmatrix}$$

$$= i[(-5)(-2)-(4)(3)] - j[(4)(-2)-(1)(3)] + k[(4)(4)-(1)(-5)]$$

$$= -2i+11j+21k$$

$L = [(-2)^2 + (11)^2 + (21)^2]^{½} = 23.791$ kg-m^2/s

$r = [(4)^2 + (-5)^2 + (3)^2]^{½} = 7.0711$ m

$p = [(1)^2 + (4)^2 + (-2)^2]^{½} = 4.5826$ kg-m/s

$\varphi = \sin^{-1}(L/rp) = \sin^{-1}[23.791 / (7.0711 \times 4.5826)] = 47.2°$

(b)

$$L = \begin{vmatrix} i & j & k \\ 1 & -2 & 3 \\ 7 & -1 & 1 \end{vmatrix}$$

$$= i[(-2)(1)-(-1)(3)] - j[(1)(1)-(7)(3)] + k[(1)(-1)-(7)(-2)]$$

$$= i+20j+13k$$

$L = [(1)^2 + (20)^2 + (13)^2]^{½} = 23.875$ kg-m^2/s

$r = [(1)^2 + (-2)^2 + (3)^2]^{½} = 3.7417$ m

$p = [(7)^2 + (-1)^2 + (1)^2]^{½} = 7.1414$ kg-m/s

$$\varphi = \sin^{-1}(L/rp) = \sin^{-1}[\,23.875 / (3.7417 \times 7.1414)] = 63.3°$$

Ans. 6:

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\left[(\sin\theta)\left(e^{i\phi}\right)\right]$$

$$\hat{L}_z = \frac{\hbar}{i}(\sin\theta)\left(e^{i\phi}\right)(i)$$

$$\hat{L}_z = \hbar(\sin\theta)\left(e^{i\phi}\right)$$

$$\hat{L}_z = \hbar\psi$$

The eigenvalue is $\hbar$.

Answers to Self Learning Exercise-II

Ans. 1: The eigenvalue for $\mathbf{J}^2$ is given by $j(j + 1)\,(h/2\pi)^2$. That is,

$\mathbf{J}^2|j, m> = j(j + 1)\,(h/2\pi)^2|j, m>$.

Ans. 2 : The eigenvalue for $\mathbf{J}_z$ is given by $m(h/2\pi)$.That is,

$\mathbf{J}_z|j, m> = m(h/2\pi)|j, m>$.

Ans. 3: It is zero since $\Psi(x)$ is function of x and not y or z.

10.11 Exercise

Long Answer Type Questions:

Q.1 Show that if any operator commutes with two of the components of an angular momentum operator, it commutes with the third.

Q.2 Prove that

$$L^2 = L_+L_- + L_z^2 - L_z \text{ and } L^2 = L_+L_- + L_z^2 - L_z .$$

Q.3 Show that $L_\pm\,|\,Y_{\alpha\beta} >$ has the same eigenvalues for L^2 that $|\,Y_{\alpha\beta} >$ does.

Q.4 Show that $L_-\,|\,Y_{\alpha\beta} >$ has $\beta - 1$ as an eigenvalue for L_z.

Q.5 Use $L_i = \varepsilon_{ijk} x_j p_k$ to show that $x_j p_k - x_k p_j = \varepsilon_{ijk} L_i$.

References and suggested Readings

1. J. D. Griffiths Introduction to Quantum Mechanics, 2004.
2. N. Zettili, Quantum Mechanics, John Wiley and Sons, 2001.
3. Ghatak, Basic Quantum Mechanics, Macmillian India Ltd 2009.
4. Walter Greiner, Quantum Mechanics : An Introduction , Springer 2007.

UNIT-11

Eigenvalues and Eigenfunctions of J^2 and J_z, Spin Half Angular Momentum

Structure of the Unit

11.0 Objectives

At the end of this chapter the students should:

1. have understood Eigenvalues and eigenfunctions of J^2 and $J_{z.}$
2. have learned the notion of spin half angular momentum and Pauli spin half matrices.

11.1 Introduction

In quantum mechanics, the total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin).

If ***s*** is the particle's spin angular momentum and ***l*** its orbital angular momentum vector, the total angular momentum ***j*** is

$$j=l+s$$

The associated quantum number is the main ***total angular momentum quantum number j***. It can take the following range of values, jumping only in integer steps:

$$\boxed{l-s\le j\le l+s}$$

where l is the azimuthal quantum number (parameterizing the orbital angular momentum) and *s* is the spin quantum number (parameterizing the spin).

The relation between the total angular momentum vector **j** and the total angular momentum quantum number *j* is given by the usual relation (see angular momentum quantum number)

$$\boxed{\|\mathrm{j}\|=\sqrt{j(j+1)}\hbar}$$

the vector's *z*-projection is given by

$$\boxed{j_z=m_j\hbar}$$

where m_j is the secondary total angular momentum quantum number. It ranges from −j to +j in steps of one. This generates 2j + 1 different values of m_j.

11.2 Eigen Vectors of J^2 and J_z

Let us assume that the simultaneous Eigen functions for J^2 and J_z are $\Psi(\lambda,m)$ such that

$$J^2\ \Psi(\lambda,m)=\hbar^2\,\lambda\,\Psi(\lambda,m)$$

and

$$\boxed{J_z\psi(\lambda,m)=\hbar m\psi(\lambda,m)}$$

to find values of λ and m, we use ladder operators with some well known relations given below:

$$\boxed{[J_z,J_+]=\hbar J_+}$$

$$\boxed{[J_z,J_-]=-\hbar J_-}$$

$$\boxed{[J_+, J_-] = 2\hbar J_z}$$

and

$$\boxed{J_+^\dagger = J_-} \; and \; \boxed{J_+ = J_-^\dagger}$$

(† is spelt as dagger and so the above quantities are spelt as J plus dagger equals J minus etc. Dagger represents complex conjugate of the quantity over which it is super scripted.)

We will also use

$$\boxed{J_+J_- = J^2 - J_z^2 + \hbar J_z}$$

and

$$\boxed{J_-J_+ = J^2 - J_z^2 - \hbar J_z}$$

Total angular momentum is defined as sum of the orbital component and spin component of angular momenta

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

J follows the same commutation rules as do **L**. if that is so **S** will also behave similarly.

Thus

$$\boxed{[J_x, J_y] = i\hbar J_z}$$

$$\boxed{[J_y, J_z] = i\hbar J_x}$$

$$\boxed{[J_z, J_x] = i\hbar J_y}$$

Ladder Operators:

The operators $\boxed{J_+ \equiv (J_x + iJ_y)}$ and $\boxed{J_- \equiv (J_x - iJ_y)}$ are called ***ladder*** operators. This will become clear in the following sections when we operate those on appropriate Eigen functions.

1. $[J_z, J_+] = \hbar\, J_+$

$[J_z, J_+] = J_zJ_{+}, -J_+J_z$

$= J_z(J_x + iJ_y) - (J_x + iJ_y) J_z$

$= J_zJ_x + i J_z J_y - J_xJ_z - iJ_yJ_z$

$= J_zJ_x - J_xJ_z + i (J_z J_y - J_yJ_z)$

$= [J_z,J_x] + i[J_z,J_y]$

$= i \hbar J_y + i(-i \hbar J_x)$

$= \hbar (J_x + iJ_y)$

$= \hbar J_+$

Similarly

2. $[J_z,J_-]= - \hbar J_-$

$[J_z,J_-] = J_zJ_-,-J_-J_z$

$= J_z(J_x - iJ_y) - (J_x -iJ_y) J_z$

$= J_zJ_x - i J_z J_y - J_xJ_z + iJ_yJ_z$

$= J_zJ_x - J_xJ_z - i (J_z J_y - J_yJ_z)$

$= [J_z,J_x] - i[J_z,J_y]$

$= i \hbar J_y - i(-i \hbar J_x)$

$= \hbar (-J_x + iJ_y)$

$= - \hbar J_-$

3. $[J_+,J_-]$

$[J_+,J_-] = J_+,J_- - J_-J_+$

$= (J_x +iJ_y) (J_x - iJ_y) - (J_x -iJ_y) (J_x +iJ_y)$

$= J_x^2 + iJ_yJ_x - iJ_xJ_y +J_y^2 - J_x^2 +iJ_yJ_x - J_xJ_y - J_y^2$

$= i[J_y,J_x] + i[J_y,J_x]$

$= 2i [J_y,J_x]$

$=2 \hbar J_z$

Let the eigenstates of J^2 and J_z be denoted by $|j,m >$. The action of the various operators on these states (vectors) is:

(1) $\boxed{J^2\,|\,j,m>= j\left(j\,+\,1\right)\hbar^2\,|\,j,m>}$ with $j \in [0,1/2,\ 1,3/2,\ ...]$.

(2) $\boxed{J_z\,|\,j,m>=\ m\hbar\,|\,j,m>}$ where $-j \le\ m \le\ j$. Total of $2j + 1$ values for m.

(3) $\boxed{J_-\,|\,j,m>=\hbar\sqrt{j\left(j\,+\,1\right)\ -\ m\left(m\ -\ 1\right)}\ |\,j,\ m-1>}$ if $m>-j$ and 0 if $m=-j$

(4) $\boxed{J_+\,|\,j,m>=\hbar\sqrt{j\left(j\,+\,1\right)\ -\ m\left(m\ +\ 1\right)}\ |\,j,\ m+1>}$ if $m<j$ and 0 if $m=j$

We introduce simultaneous eigenstates $\left|\lambda,m\right\rangle$ of the two commuting operators J^2 and J_z

$$J^2\left|\lambda,m\right\rangle=\lambda\hbar^2\left|\lambda,m\right\rangle$$

$$J_z\left|\lambda,m\right\rangle=m\hbar\left|\lambda,m\right\rangle$$

and we note that the states $J_\pm\ \left|\lambda,m\right\rangle$ are also eigenstates of J^2 with eigenvalue λ. $J_\pm\ \left|\lambda,m\right\rangle$ are also eigenstates of J_z with eigenvalue $m\pm1$.

$$J^2\ J\pm\left|\lambda,m\right\rangle=\lambda\hbar^2J\pm\left|\lambda,m\right\rangle$$

Thus we can write

$$J_\pm\left|\lambda,m\right\rangle=c_\pm\hbar\left|\lambda,m\right\rangle$$

Where $c_\pm$ are constants of proportionaity

We now observe that, for a given λ, m^2 $\hbar$ λ so that m must have both a maximum value, m_{max} and a min value m_{min}.

Proof

$$(J^2\text{-}J_z^2)\ \left|\lambda,m\right\rangle=(J_x^{\,2}+J_y^{\,2})\ \left|\lambda,m\right\rangle$$

$$(\lambda\text{-}m^2)\hbar^2\ \left|\lambda,m\right\rangle=(J_x^{\,2}+J_y^{\,2})\ \left|\lambda,m\right\rangle$$

$$(\lambda\text{-}m^2)\hbar^2=(J_x^{\,2}+J_y^{\,2})\geq0$$

So that

$$(\lambda\text{-}m^2)>0$$

$$-\sqrt{\lambda}\leq m\leq\sqrt{\lambda}$$

Hence the spectrum of J_z is bounded above and below, for a given value λ.

$$J_+ \left|\lambda, m_{\max}\right\rangle = 0$$

$$J_- \left|\lambda, m_{\min}\right\rangle = 0$$

To proceed further, we will use identity

$$J_+J_- = J^2 - J_z^2 + \hbar J_z$$

Hence $$(J^2 - J_z^2 + \hbar J_z) \left|\lambda, m_{\min}\right\rangle = 0$$

Since $$J_- \left|\lambda, m_{\min}\right\rangle = 0$$

$$(\lambda - m_{min}^2 + m_{min}) \left|\lambda, m_{\min}\right\rangle = 0$$

$$\lambda = m_{min}(m_{min} - 1)$$

Similarly with second identity

$$J_-J_+ = J^2 - J_z^2 - \hbar J_z$$

Hence $(J^2 - J_z^2 - \hbar J_z) /\lambda, m_{max}> = 0$

Since $J_+ \left|\lambda, m_{\max}\right\rangle = 0$

$$(\lambda - m_{max}^2 - m_{max}) /\lambda, m_{max}> = 0$$

$$\lambda = m_{max}(m_{max} + 1)$$

Usually m_{max} is denoted by *j* then

$$\lambda = m_{min}(m_{min} - 1) = m_{max}(m_{max} + 1)$$

$$= m_{min}(m_{min} - 1)$$

$$= j(j+1)$$

This is a quadratic equation for m_{min}

$$m_{min}^2 - m_{min} - j^2 - j = 0$$

which can be factorized as

$$(m_{min} + j)(m_{min} - j - 1) = 0$$

And we see that, since $m_{min} \leq j$

By definition, the only acceptable root is

$$m_{min} = -j$$

Now since m_{max} and m_{min} differ by some integer k, we can write

$$m_{max}-m_{min}=k, \quad k=0,1,2,3,..$$

$$j-(-j)=2j=k, \quad k=0,1,2,3,..$$

so that the allowed values of j are

$$j=0,1/2,1,3/2,2,5/2,3,\ldots$$

For a given value of j, we see that **m ranges** over the values

$$j,j-1,\ldots.,-j+1,-j$$

a total of $(2j+1)$ values.

From the results presented above we can draw the following conclusions.

1. ***The eigenvalue of J^2 are $j(j+1)\hbar^2$***
Where $j=0,1/2,1,3/2,2,5/2,3,\ldots$

2. Since $\lambda= j(j+1)$, we can equally well label the simultaneous eigenstates of J^2 and J_z by j rather than by λ so that,

$$\boxed{J^2 \mid j,m >= j\left(j+1\right)\hbar^2 \mid j,m >}$$

$$\boxed{J_z \mid j,m >= m\hbar \mid j,m >}$$

3. ***Thus for every value of j, there are 2j+1 values of m, thus there are 2j+1 corresponding eigenfunctions (degeneracy).***

11.3 Self Learning Exercise -I

Short Answer Type Questions

Q.1 With $J_{\pm} = J_x \pm iJ_y$, express J_+J_- and J_-J_+ in terms of the operators J^2 and J_z.

Q.2 Compute the following commutators:

a. $[J_+,J_-]$
b. $[J_{\pm},J^2]$
c. $[J_{\pm},J_z]$
d. $[J_{\pm},J_x]$
e. $[J_{\pm},J_y]$

Q.3 Consider a system described by the Hamiltonian

$$H = AJ_z + B(J_x^2+J_y^2)$$

where J_x, J_y, and J_z are the three components of a generalized angular momentum operator, and *A* and *B* are constants. What are the energy levels of this system?

Q.4 Let $|j,m>$ be the standard simultaneous eigenstate of J^2 and J_z.

a. What are $J^2|j,m>$ and $J_z|j,m>$ in terms of *j* and *m*?

b. What are the allowed values of *j*?

c. For a given *j*-value, what are the allowed values of *m*?

Q.5 Compute matrix elements of J^2, J_z, $J_\pm$, J_x, J_y.

Long Answer Type Questions

Q.6 Show explicitly that J^2 commutes with J_z, then use a symmetry argument to show that J^2 must also commute with J_x and J_y. Then, answer the following (be sure to explain your reasoning):

Do simultaneous eigenstates of J_x and J_z exist?

- Do simultaneous eigenstates of J^2 and J_z exist?
- Do simultaneous eigenstates of J^2 and J_y exist?
- Do simultaneous eigenstates of J^2 J_z and J_y exist?
- Do simultaneous eigenstates of J^2 and J_x exist?

11.4 Spin Half Angular Momentum

If electron were a spin less particle and only described an orbital motion about the nucleus, its magnetic dipole moment would have been

$$\boxed{\mu = -\frac{e}{2\text{m}_0}L}$$

where m_0 is the mass of the electron. This magnetic moment then should be the source of permanent magnetism of the ferromagnetic substance. But the observed magnetic moment of a magnetic specimen gives a factor e/m_0 and not $e/2m_0$. This has been attributed partially to gyro magnetic effect. Further for S ($l = 0$) state atom should have no magnetism. This is again against the observed fact.

Fine structure of the spectrum is also inconsistent with the orbital angular momentum concept. Sodium D lines are well known example. Fine structure is possible only if there were additional energy levels. Zeeman and Paschen-Back effects too cannot be explained without attributing spin to electron.

For S state there should be no splitting of atomic beam in Stern-Gerlach experiment, but this also goes against the experimental observations.

To explain all above anomalies ***Uhlenback and Goudsmit postulated that electron possesses an intrinsic angular momentum***. He named it electron spin, which for brevity we simply call spin. Ultimately it was noted that protons and even neutrons possess spin.

The spin associated with an electron is quantized. For explaining doublet fine structure of alkali atoms it was sufficient to ascribe a spin of $\frac{1}{2}\hbar$ to the electron. Associated ***spin quantum number, s has only one value for the electron namely ½.*** We describe the quantum state of electron by $\hbar\,\sigma$. Assuming σ to be related to quantum number s, ***the multiplicity of energy levels would be (2s + 1). According to Stern-Gerlach the atomic beam with S = 0, splits into two beams, i.e., the multiplicity is 2. It suggests that s = ½.***

Recall that the angular momentum commutation relations

$$\boxed{\begin{array}{l}[L^2, L_z] = 0\ , \\ [L_i\ ,\ L_j] = i\hbar L_k\end{array}} \quad \text{(i j k cyclic)}$$

were derived from the definition of the orbital angular momentum operator:

$$\boxed{\vec{L} = \vec{r} \times \vec{p}}\ .$$

The spin operator $\vec{S}$ does not exist in Euclidean space (it doesn't have a position or momentum vector associated with it), so we cannot derive its commutation relations in a similar way. Instead we boldly ***postulate*** that the same commutation relations hold for spin angular momentum:

$$\boxed{[S^2, S_z] = 0}\ ,$$

$$\boxed{[S_i\ ,\ S_j] = i\hbar S_k}\ .$$

From these, we derive, that

$$\boxed{S^2\left|s,m_s\right\rangle = \hbar^2 s(s+1)\left|s,m_s\right\rangle}$$

$$\boxed{S^2\left|s,m_s\right\rangle = \frac{3}{4}\hbar^2\left|s,m_s\right\rangle}$$ (since s = ½)

$$\boxed{S_z\left|s,m_s\right\rangle = \hbar m_s\left|s,m_s\right\rangle}$$

$$\boxed{S_z\left|s,m_s\right\rangle = \pm\frac{1}{2}\hbar\left|s\,m_s\right\rangle}$$

(since $m_s = -s, +s = -1/2, +1/2$)

Notation: since s = ½ always, we can drop this quantum number, and specify the eigenstates of L^2 , L_z by giving only the m_s quantum number. There are various ways to write this:

$$\left|s\,m_s\right\rangle = \left|m_s\right\rangle = \begin{matrix} \left|+\tfrac{1}{2}\right\rangle, \left|-\tfrac{1}{2}\right\rangle \\ \left|+\right\rangle, \left|-\right\rangle \\ \left|\uparrow\right\rangle, \left|\downarrow\right\rangle \end{matrix}$$

These states exist in a 2D subset of the full Hilbert Space called *spin space*. ***Since these two states are eigenstates of a hermitian operator, they form a complete orthonormal set (within their part of Hilbert space)*** and any, arbitrary state in spin space can always be written as

$$\left|\chi\right\rangle = a\left|\uparrow\right\rangle + b\left|\downarrow\right\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

Matrix notation: $\left|\uparrow\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \left|\downarrow\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$

If we were working in the full Hilbert Space of, say, the H-atom problem, then our basis states would be $\left|n\ \ell\ m_\ell\ m_s\right\rangle$. Spin is another degree of freedom, so that the full specification of a basis state requires 4 quantum numbers. (More on the connection between spin and space parts of the state later.)

The matrix form of S^2 and S_z in the $\left|m^{(z)}\right\rangle$ basis can be worked out element by element.

(Recall that for any operator $\hat{A}$, $A_{mn} = \langle m|\hat{A}|n\rangle$.)

$$\boxed{\langle\uparrow|S^2|\uparrow\rangle = \frac{3}{4}\hbar^2, \quad \langle\uparrow|S^2|\downarrow\rangle = 0}, \text{ etc.}$$

$$\boxed{\langle\uparrow|S_z|\uparrow\rangle = +\frac{1}{2}\hbar, \quad \langle\uparrow|S_z|\downarrow\rangle = 0}, \text{ etc.}$$

$$\boxed{S^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}}$$

$$\boxed{S_z = \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}}$$

Operator equations can be written in matrix form, for instance,

$$\boxed{S_z|\uparrow\rangle = +\frac{\hbar}{2}|\uparrow\rangle}$$

$$\Rightarrow \quad \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = +\frac{\hbar}{2}\begin{pmatrix}1\\ 0\end{pmatrix}$$

Raising and lowering operators:

$$\boxed{\begin{aligned} S_+ &= S_x + iS_y \\ S_- &= S_x - iS_y \end{aligned}}$$

$$\Rightarrow \quad \begin{aligned} S_x &= \tfrac{1}{2}(S_+ + S_-) \\ S_y &= \tfrac{1}{2i}(S_+ - S_-) \end{aligned}$$

In matrix representation

$$\boxed{\begin{aligned} S_+|s,m_s\rangle &= \hbar\sqrt{s(s+1)-m(m+1)}\ |s,\ m_s+1\rangle \\ S_-|s,m_s\rangle &= \hbar\sqrt{s(s+1)-m(m-1)}\ |s,\ m_s-1\rangle \end{aligned}}$$

For the case s = ½, the square root factors are always 1 or 0.

For instance, s = ½, m = −1/2

gives

$$s(s+1) - m(m+1) = \tfrac{1}{2}\left(\tfrac{3}{2}\right) - \left(-\tfrac{1}{2}\right)\left(\tfrac{1}{2}\right)$$
$$= 1$$

Consequently,

$$\boxed{S_+|\downarrow\rangle = \hbar|\uparrow\rangle, \quad S_+|\uparrow\rangle = 0}$$

and $\boxed{S_-|\uparrow\rangle = \hbar|\downarrow\rangle, \quad S_-|\downarrow\rangle = 0}$

leading to

$$\langle\uparrow|S_+|\uparrow\rangle = 0,$$
$$\langle\uparrow|S_+|\downarrow\rangle = \hbar, \text{ etc.}$$

and

$$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Notice that S_+, S_- are not Hermitian.

Using $\boxed{S_x = \tfrac{1}{2}(S_+ + S_-) \quad \text{and} \quad S_y = \tfrac{1}{2i}(S_+ - S_-)}$ yields

$$\boxed{S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}$$

$$\boxed{S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

These are Hermitian, of course.

11.5 Pauli Spin Half Matrices

The Pauli spin matrices σ_i are simply defined and have the following properties

$$\boxed{\vec{S}_i = \frac{\hbar}{2}\vec{\sigma}_i},$$

where

$$\boxed{\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}$$

$$\boxed{\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

$$\boxed{\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

Properties

1. $[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k$
2. $\boxed{\sigma_i^2 = 1}$
3. They also ***anticommute***

$$\boxed{\sigma_x\sigma_y = -\sigma_y\sigma_x}$$

$$\boxed{\sigma_x\sigma_z = -\sigma_z\sigma_x}$$

$$\boxed{\sigma_z\sigma_y = -\sigma_y\sigma_z}$$

4. ***These matrices are the Hermitian matrices***
5. Pauli matrices are ***traceless*** matrices of dimension 2.
6. Any 2×2 matrix can be written as a linear combination of the sigma matrices and identity.

11.6 Self Learning Exercise- II

Q.1 Which of the following spin wave functions are symmetric with respect to the exchange of electrons?

$$\varphi_1 = \alpha(1)\alpha(2)$$

$$\varphi_2 = \beta(1)\beta(2)$$

$$\varphi_3 = \frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

$$\varphi_4 = \frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

Q.2 Show that the following spin function

$$\phi = \frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

is an eigenfunction of the total *z* component of spin angular momentum for a two-electron system. What is the eigenvalue?

Q.3 Use the Slater determinant to arrive at a wave function to describe the ground state of a two-electron system such as He. Express the resulting wave function in terms of the 1s spatial wave function for each electron [$\phi_{1s}(1)$ and $\phi_{1s}(2)$], and of the spin wave functions for each electron $[\alpha(1), \alpha(2), \beta(1), \text{and } \beta(2)]$.

Q.4 The quantum number *J* represents the total angular momentum, and describes the Russel-Saunders coupling between *L* and *S.* Determine the values of *J* for two *d* electrons.

(*Hint:* the allowed values of *J* are given by $J = L + S, L + S - 1, \ldots, |L - S|$)

Q.5 Write the complete term symbols for the following states

(a) L = 4, S = 1, J = 5;

(b) L = 2, S = 0, J = 2;

(c) L = 0, S = 0, J = 0

Q.6 List the quantum numbers L, S, and J for the following terms symbols:

- $^4G_{5/2}$
- $^3P_2$
- $^2D_{3/2}$.

Q.7 Determine the electronic configuration for an atom with the term symbol $^4S_{3/2}$.

Q.8 Derive the ground state term symbol for the following configuration $(5s)^1(4d)^4$, if given that *J* = 1/2.

Q.9 Give the term symbol for Li:$1s^2 2s^1$.

11.7 Summary

In this unit we continued our previous chapter. In this chapter we firstly discussed eigenvalues and eigenfunctions of J^2 and J_z followed by Spin half angular momentum and Pauli spin half matrices.

11.8 Glossary

Spin: The intrinsic angular momentum of an electron, classified as up or down.

Quantum numbers: the values of quantized entities, such as energy and angular momentum.

Angular Momentum: also called moment of momentum, it is the cross product of position vector and momentum.

Orbital angular momentum: an angular momentum that corresponds to the quantum analog of classical angular momentum

Spin projection quantum number: quantum number that can be used to calculate the intrinsic electron angular momentum along the *z*-axis.

Spin quantum number: the quantum number that parameterizes the intrinsic angular momentum (or spin angular momentum, or simply spin) of a given particle.

Magnitude of the intrinsic (internal) spin angular momentum :given by

$$S = \hbar\sqrt{s(s+1)}$$

Pauli exclusion principle :A principle that states that no two electrons can have the same set of quantum numbers; that is, no two electrons can be in the same state.

Eigen Value **:**An allowed value of the constant *a* in the equation

$$Au=au$$

Where *A* is an operator acting on a function *u* (which is called eigenfunction). Also called characteristic value.

Commute :Two operators commute with each other if their commutator is equal to zero. The commutator of operators A and B is

$$\boxed{[\mathrm{A},\mathrm{B}]=\mathrm{AB}-\mathrm{BA}}$$

Hermitian operator :Operators that are equal to their Hermitian adjoints, in other words, an operator is Hermitian if

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

Hilbert Space :Infinite-dimensional complete vector space over the complex numbers endowed with a metric induced by a scalar product that satisfies Schwartz's inequality

11.9 Answers to Self Learning Exercises

Answers to Self learning Exercise I

Ans.1:

$$J_+J_- = (J_x + iJ_y)(J_x - iJ_y)$$
$$= J_x^2 + J_y^2 + i[Jy,Jx]$$
$$= J^2 - J_z^2 + \hbar J_z$$

Similarly

$$J_-J_+ = J^2 - J_z^2 - \hbar J_z$$

Ans.2:

a. $[J_+,J_-]=[J_+,J_-]$

$$= J_+J_- - J_-J_+$$
$$= 2\hbar J_z$$

b. $[J_\pm,J^2]= [J_x,J^2] \pm i[J_y,J^2]$

$$= 0$$

c. $[J_\pm,J_z] = [J_x,J_z] \pm i[J_y,J_z]$

$$= -\mathrm{i}\,\hbar J_y \pm (-\hbar J_x)$$
$$= -\hbar J_\pm$$

d. $[J_\pm,J_x] = \pm i[J_y,J_x]$

$$= \pm \hbar J_z$$

e. $[J_\pm,J_y] = [J_x,J_y]$

$$= i\hbar J_z$$

Ans. 3: With $J_x^2 + J_y^2 = J^2 - J_z^2$, the Hamiltonian becomes

$$H = B\,(J^2 - J_z^2) + AJz$$

The eigenstates of this are the standard $|j,m>$ states, with eigenvalues given by

$$H\,|j,m> \;=\; B(J^2 - J_z^2)\,|j,m> + AJz|j,m>$$

$$=\; B\,\hbar^2(j^2+j-m^2)\,|j,m> + A\,\hbar\, m|j,m>$$

Ans. 4:

a. $J^2|j,m> = \hbar^2(j^2+j)\,|j,m>$

and $J_z|j,m> = \hbar\, m|j,m>$

b. $j \in \{0, 1/2, 1, 3/2, 2, 5/2, \ldots\}$

c. $m \in \{-j, -j+1, \ldots, j\}$

Ans. 5:

- $<j,m|J^2|j',m'> = \hbar^2 j(j+1) <j,m|j',m'>$

  $= \hbar^2 j(j+1)\,\delta_{j,j'}\delta_{m,m'}$
- $<j,m|J_z|j',m'> = \hbar\, \mathrm{m} <j,m|j',m'>$

  $= \hbar\, m\,\delta_{j,j'}\delta_{m,m'}$
- $<j,m|J_\pm|j',m'> = \hbar\sqrt{j'(j'+1)-m'(m'\pm 1)}\;\delta_{j,j'}\delta_{m,m'\pm 1}$
- $<j,m|J_x|j',m'> = 1/2\;\; <j,m|(J_+ + J_-)|j',m'>$
- $<j,m|J_y|j',m'> = 1/2\;\; <j,m|(J_+ - J_-)|j',m'>$

Ans. 6:

$$[J_x^2, Jz] = J_x^2 J_z - J_z J_x^2$$

$$= J_x^2 J_z - J_x J_z J_x + J_x J_z J_x - J_z J_x^2$$

$$= J_x\,[J_x, J_z] + [J_x, J_z] J_x$$

$$= -i\hbar\, J_x J_y - i\hbar\, J_y J_x$$

$$[J_y^2, Jz] = J_y^2 J_z - J_z J_y^2$$

$$= i\,\hbar\, J_y J_x + i\,\hbar\, J_x J_y$$

$$\boxed{\left[J_z^{\,2}, J_z\right] = 0}$$

Adding these results together gives

$[J^2,J_z] = 0$

- No, because J_x and J_z do not commute.
- Yes, ***because J^2 and J_z commute***.
- Yes, because if J^2 commutes with J_z, then by symmetry, it must commute with J_y.
- No, because J_z and J_y do not commute.
- Yes, simultaneous eigenstates of J^2 and J_x exist because J^2 and J_x commute. Clearly an eigenstate of J_x is also an eigenstate of J^2.

Answers to Self Learning Exercise- II

Ans.1 : The results of the permutator operator on the above wave functions are as follows

$$\hat{P}\varphi_1 = \hat{P}\left[\alpha(1)\alpha(2)\right] = \alpha(2)\alpha(1) = \varphi_1$$

$$\hat{P}\varphi_2 = \hat{P}\left[\beta(1)\beta(2)\right] = \beta(2)\beta(1) = \varphi_2$$

$$\hat{P}\varphi_3 = \hat{P}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right] = \alpha(2)\beta(1)+\beta(2)\alpha(1) = \varphi_3$$

$$\hat{P}\varphi_4 = \hat{P}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right] = \alpha(2)\beta(1)-\beta(2)\alpha(1) = -\varphi_4$$

The wave functions ϕ_1, ϕ_2, ϕ_3 are symmetric because the eigenvalue of the permutator operator is +1. The wave function ϕ_4 is antisymmetric because the eigenvalue of the permutator operator is -1.

Ans. 2: For a two-electron system, the total z component is given by

$$\hat{S}_z = \hat{S}_z(1) + \hat{S}_z(2)$$

where the spin operators and wave functions are related by

$$\hat{S}_z(i)\alpha(i) = \frac{\hbar}{2}\alpha(i)$$

$$\hat{S}_z(i)\beta(i) = -\frac{\hbar}{2}\beta(i)$$

Therefore

$$\hat{S}_z\varphi_3 = \left[\hat{S}_z(1) + \hat{S}_z(2)\right]\left[\frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]\right]$$

$$\hat{S}_z\varphi_3 = \frac{\sqrt{2}}{2}\left[\beta(2)\hat{S}_z(1)\alpha(1) + \alpha(1)\hat{S}_z(2)\beta(2) + \alpha(2)\hat{S}_z(1)\beta(1) + \beta(1)\hat{S}_z(2)\alpha(2)\right]$$

$$\hat{S}_z\varphi_3 = \frac{\sqrt{2}}{2}\left[\beta(2)\frac{\hbar}{2}\alpha(1) + \alpha(1)\left(-\frac{\hbar}{2}\right)\beta(2) + \alpha(2)\left(-\frac{\hbar}{2}\right)\beta(1) + \beta(1)\frac{\hbar}{2}\alpha(2)\right]$$

$$\hat{S}_z\varphi_3 = \frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2)\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right) + \beta(1)\alpha(2)\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)\right]$$

$$\hat{S}_z\varphi_3 = \frac{\sqrt{2}}{2}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right) = \varphi_3\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)$$

φ_3 is an eigenfunction of $\hat{S}_z$ with an eigenvalue of $\frac{\hbar}{2} - \frac{\hbar}{2} = 0$

Ans. 3:

$$\psi = \frac{1}{\sqrt{2!}}\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(2)\alpha(2) \\ \varphi_{1s}(1)\beta(1) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

$$\psi = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2) - \varphi_{1s}(1)\beta(1)\varphi_{1s}(2)\alpha(2)\right]$$

Ans. 4 :

L = 4, S = 0, J = 4

L = 4, S = 1, J = 5, 4, 3

L = 3, S = 0, J = 3

L = 3, S = 1, J = 4, 3, 2

L = 2, S = 0, J = 2

L = 2, S = 1, J = 3, 2, 1

L = 1, S = 0, J = 1

L = 1, S = 1, J = 2, 1, 0

L = 0, S = 0, J = 0

L = 0, S = 1, J = 0, 1

Ans. 5:

The format for the term symbols is $^{2S+1}X_J$.

The value of L determines the letter symbol as follows,

L = 0 ***for S;***

L = 1 ***for P;***

L = 2 ***for D;***

L = 3 ***for F;***

L = 4 ***for G;*** etc.

This leads to the following term symbols:

- $^3G_5$
- $^1D_2$
- $^1S_0$

Ans. 6:

The format for the term symbols is $^{2S+1}X_J$,

where S is the spin quantum number,

(2S + 1) is the multiplicity, and

J is the total angular momentum quantum number.

The value of L determines the letter symbol *X* as follows,

L = 0 for S;

L = 1 for P;

L = 2 for D;

L = 3 for F;

L = 4 for G; etc.

- $L = 4; S = \frac{4-1}{2} = \frac{3}{2}; J = \frac{5}{2}$
- $L = 1; S = \frac{3-1}{2} = 1; J = 2$
- $L = 2; S = \frac{2-1}{2} = \frac{1}{2}; J = \frac{3}{2}$

Ans.7: The value of the quantum number S can be determined from the multiplicity.

$$2S+1=4$$

$$S=\frac{3}{2}=M_S$$

This implies that there are three unpaired electrons. The S letter symbol gives $L=M_L=0$. This indicates that there is one electron in each of the p orbitals because $M_L=(+1)+0+(-1)=0$. The configuration is $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$

Ans. 8:

$$M_L=L=0+(+2)+(+1)+0+(-1)=+2$$

$$M_S=S=\left(+\frac{1}{2}\right)+\left(+\frac{1}{2}\right)+\left(+\frac{1}{2}\right)+\left(+\frac{1}{2}\right)+\left(+\frac{1}{2}\right)=\frac{5}{2}$$

$$2S+1=2\left(\frac{5}{2}\right)+1=6$$

The term symbol is $^6D_{1/2}$.

Ans. 9:

$$S=\frac{1}{2}, L=0, J=\frac{1}{2}$$

so the term is $^2S_{1/2}$. Note that we are only considering the unpaired electron.

11.10 Exercise

Q.1 Prove that $(\sigma.A)\ (\sigma.B)\ = A.B + i\sigma.(A x B)$ where σ 's are the Pauli spin matrices , if the components of **A** and **B** commute with those of σ .

Q.2 Determine the value of $(\sigma_x + i\sigma_y)^2$.

Q.3 Determine the eigenvalue spectrum of the angular momentum operators J^2, J_z ,J_+ and J_-, starting with the postulate $[J_x, J_y] = i\hbar J_z$ and its cyclic.

Q.4 Prove that the Pauli spin matrices anticommute.

Q.5 Given that $[J_X, J_Y] = i\hbar J_Z$ and its cyclic, verify that

$[J_+, J_-] = 2\hbar J_Z$,

where $J_+ = J_X + iJ_Y$ and $J_- = J_X - iJ_Y$.

Q.6 Prove that

$J_-|j,m> = \hbar\sqrt{\{j(j+1) - m(m-1)\}}\ |j, m-1>$ if $m > -j$

Q.7 Prove that

$J_+|j,m> = \hbar\sqrt{\{j(j+1) - m(m+1)\}}\ |j, m+1>$ if $m < j$

Q.8 Calculate the matrix elements of S_x and S_y and S_z for S=1, 3/2 and 2 in the basis set where S_z is diagonal.

References and Suggested Readings

1. J. D. Griffiths Introduction to Quantum Mechanics, 2004.
2. N. Zettili, Quantum Mechanics, John Wiley and Sons, 2001.
3. Ghatak, Basic Quantum Mechanics, Macmillian India Ltd 2009.
4. Walter Greiner, Quantum Mechanics : An Introduction , Springer 2007.

UNIT-12

Centrally Symmetric Coulomb Field

Structure of the Unit

12.0 Objectives

Quantum mechanical methods are a powerful tool for explaining the structure of many electron systems as atoms and molecules. The problem of ground state of Helium-atom has solved by perturbation theory and variational techniques. The main objective of this unit is to study about the solution of ground state problem of hydrogen atom and the approximations by which we solve potential energy of any molecule.

12.1 Introduction

In this unit first of all we shall discuss the methods to handle the problems of atoms particularly the central field approximation and finally we shall discuss the methods to handle the problems of molecules with Hydrogen molecule ion because they supply intersecting and instructive applications of quantum mechanics.

12.2 Central Field Approximation

We know about the problem of ground state of helium atom which consists of the electrostatic interaction between a pair of electrons. The problem was solved by the method of perturbation by considering the interaction term $\frac{e^2}{r_{12}}$ as perturbation term and separating the general equation (excluding the term $\frac{e^2}{r_{12}}$) into two separate equations one for each electron. If we have extend the equation for N-electron atom, we write

$$\left[\sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}\right) + \sum_{i>j}\frac{e^2}{r_{ij}}\right]\Psi = E\Psi \qquad (12.1)$$

This equation cannot be solved by the method of separation of variables due to presence of interaction terms; moreover this equation as such can also not be solved by perturbation method. Since the mutual interaction tern is too large to be treated as perturbation term. In such a case we consider a modified field in which all the electrons experience centrally symmetric field by superimposing the radial components of interaction between the electrons in the coulomb interaction term

$$\sum_{i=1}^{n}\frac{-Ze^2}{r_i}$$

The remaining part of interaction may then be treated as small interaction term and the problem can be handled by the perturbation theory or variation techniques.

Let the mutual repulsion term $\sum_{i>j} \frac{e^2}{r_{ij}}$ be divided into two parts (1) $\sum_i S(r_i)$ directed away from the nucleus (central part) and (2) remainder

$$\sum_i R_i = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i S(r_i)$$

The first part weakens the coulomb potential when superimposed on the latter. Therefore the central part is

$$\sum_{i=1}^{n} [\frac{-Ze^2}{r_i} + S(r_i)]$$

It is often, called the screened coulomb potential. The total Hamiltonian is now expressed as

$$H = H_0 + H'$$

where H_0 is the Hamiltonian of the problem with central potential, i.e.

$$H_0 = \sum_i [-\frac{\hbar^2}{2m} \nabla_i + V(r_i)]$$

where $V(r_i) = \frac{-Ze^2}{r_i} + S(r_i)]$

and $H' = \sum_i R_i = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i S(r_i)$

$$= \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i \left[V(r_i) + \frac{Ze^2}{r_i}\right]$$

When in zeroth order approximation the interaction term H' is negligibly small; we are left with only the problem containing the central field and hence the approximation method is called the central field approximation.

There are two approaches which have been employed to evaluate the central field.

1. Thomas-Fermi statistical model,
2. Hartee's self-consistent field method.

12.3 Thomas Fermi Statistical Method

This model assumes that the potential function V(r), produced by the nucleus and all the other electrons except the one whose motion is under

consideration is spherically symmetric and varies so slowly in comparison with electron wavelength that many electrons may be allowed in a volume over which the potential changes by a small fraction of itself(i.e. the potential is sensibly constant over this volume). The electrons can then are treated by statistical mechanics and obey the Fermi-Dirac statistics. This number of electron states in a cube of edge length L at the walls of which the wave functions obey the periodic boundary condition is given by

$$\left(\frac{L}{2\pi\hbar}\right)^3 dp_x dp_y dp_z$$

If the spin states are also included, the Pauli principle allows us at most two electrons per state for two possible spin orientations, therefore above number of states is modified to

$$2\left(\frac{L}{2\pi\hbar}\right)^3 dp_x dp_y dp_z$$

Since electrons obey Fermi-Dirac statistics, these states are filled in order of increasing momentum up to some maximum value p_0 and considering the spherical symmetry the total number of can be expressed as

$$2\left(\frac{L}{2\pi\hbar}\right)^3 \int_0^{p_0}\int_0^{\pi}\int_0^{2\pi} p^2 dp\ sin\theta\ d\theta\ d\phi = \frac{p_0^3 L^3}{3\pi^2\hbar^3} \qquad (12.3.1)$$

Each state expressed by above relation will be able to accommodate one electron and if we assume that all these states are occupied, then expression (12.3.1) would represent the total number of electrons in volume L^3. Hence the number of electrons per unit volume or volume density of electrons is

$$n=\frac{p_0^3}{3\pi^2\hbar^3} \qquad (12.3.2)$$

We know that for an electron to remain in an atom, the maximum kinetic energy at any distance r from the nucleus is -V(r) i.e.

$$\frac{p_0^2}{2m} = -V(r) i.e. p_0^2 = -2mV(r)$$

Hence the electron density at distance r is

$$n(r)=\frac{p_0^3}{3\pi^2\hbar^3}=\frac{[-2mV(r)]^{\frac{3}{2}}}{3\pi^2\hbar^3} \qquad (12.3.3)$$

According to the classical Poisson's equation $(\nabla^2\phi = -4\pi\rho)$ the electrostatic potential $\phi=\frac{V(r)}{e}$ in terms of charge density ρ=e n(r) is given by

$$\nabla^2\left(\frac{V(r)}{e}\right) = -4\pi \mathrm{e}\ \mathrm{n(r)}$$

or $$\frac{1}{e}\cdot\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial V(r)}{\partial r}\right) = -4\pi \mathrm{e}\ \mathrm{n(r)} \tag{12.3.4}$$

Equation (12.3.3) and (12.3.4) may be solved to give the values of n(r) and V(r).

For a neutral atom as r→0, as field must become the coulomb field of nucleus, so that V(r) = $\frac{-Ze^2}{r}$. As r→∞, there must be no net charge inside the sphere of radius r or r V(r)→0, which implies that V(r) falls off more rapidly than 1/r.

12.3.1 Evaluation of Potential

Eliminating n(r) from (12.3.3) and (12.3.4), we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial(-V)}{\partial r}\right] = \frac{4e^2[-2mV(r)]^{\frac{3}{2}}}{3\pi^2\hbar^3} \tag{12.3.1.1}$$

If we put the approximate form of the solution as

$$\left.\begin{aligned} &\mathrm{V(r)} = \frac{-Ze^2}{r}\chi \text{ and } r = bx \\ &\mathrm{b} = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{\frac{2}{3}}\frac{\hbar^2}{me^2Z^{\frac{1}{3}}} = \frac{0.885}{Z^{\frac{1}{3}}}\left(\frac{\hbar^2}{me^2}\right) = \frac{0.885a_0}{Z^{\frac{1}{3}}} \\ &\text{where } \mathrm{a_0} = \frac{\hbar^2}{me^2} \end{aligned}\right\} \tag{12.3.1.2}$$

With these substitutions equation (12.3.1.3) becomes

$$x^{\frac{1}{2}}\frac{d^2\chi}{dx^2} = \chi^{\frac{3}{2}} \tag{12.3.1.3}$$

The boundary conditions are

$$\left.\begin{aligned} &\chi = 1 \; at \; x = 0 \\ &\chi = 0 \; at \; x = \infty \end{aligned}\right\} \tag{12.3.1.4}$$

Equation (12.3.1.3) involves no parameters and thus defines a universal function $\chi(x)$. The most accurate by Bush and Caldwell.

We have $r = bx = \frac{0.885a_0x}{Z^{\frac{1}{3}}}$

Thus we have the following important results:

(1) The radius of an atom is inversely proportional to the cube root of atomic number.

(2) This model is applicable to atoms with large atomic number Z where the number of electrons in a small volume are comparatively greater so that the statistical calculations are valid.

(3) Electronic charge density n(r) gives smooth charge variation over atomic dimensions and does not involve the shells structure (*l*-dependence).

(4) The form of potential energy function in this model is useful in the self-consistent field calculations.

12.4 Hartee's Self-Consistent Field Method

A more accurate method for obtaining central field for large Z-atoms is due to D. R. Hartee. This method ignores the effect of spin on the wave function and assumes that in a multi electron atom each electron moves in the central field that can be calculated from the nuclear potential and the wave functions of all the other electrons, by assuming that the charge density associated with an electron is (-e) times the position probability density. Then Schrodinger wave equation is formulated for the system and solved to determine the Eigen functions belonging to different quantum states and then charged densities are calculated. ***These charge densities should be consistent with initially chosen ones. This is known as the condition of self-consistency***. If the charge densities so calculated do not agree with initially chosen ones then the above procedure is repeated by choosing better wave functions (which determine the probability density) again and again until the condition of self consistency is fulfilled.

In this method the wave functions Ψ is assumed to be a simple product of one-electron functions i.e. for a Z-electron system

$$\Psi\,(r_1, r_2, \ldots\ldots, r_z) = \Psi(r_1)\Psi(r_2)\ldots\ldots(r_z) \qquad (12.4.1)$$

If Ψ is normalised, then

$$\int \Psi^*(r_k)\Psi(r_k)d\tau_k = 1 \qquad (12.4.2)$$

Here k=1, 2, ..., Z.

The Hamiltonian of Z-electron system is

$$H=\sum_{i=1}^{n}\{-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}\}+\sum_{i>j}\frac{e^2}{r_{ij}} \qquad (12.4.3)$$

where $r_{ij} = | r_i - r_j |$

In order to find the wave equation for kth electron first of all we find potential energy of kth electron in the field of remaining (Z-1) electrons as follows:

The term $e\Psi_j^{*}\Psi_j = e|\Psi_j(r_j)|^2$ represents the charge distribution of jth electron; therefore the potential due to jth electron at the vicinity of kth electron is

$$\int\frac{e|\Psi_j(r_j)|^2}{r_{jk}}d\tau_j \qquad (12.4.4)$$

Therefore the potential due to all other electrons in the vicinity of kth electron is

$$\sum_{j\neq k}\int\frac{e|\Psi_j(r_j)|^2}{r_{jk}}d\tau_j \qquad (12.4.5)$$

So the potential energy of kth electron in the field of all other electrons is

$$\sum_{j\neq k}\int\frac{|\Psi_j(r_j)|^2}{r_{jk}}d\tau_j \qquad (12.4.6)$$

Then the Schrodinger equation for kth electron is

$$\left[\frac{-\hbar^2}{2m}\nabla_k^2-\frac{Ze^2}{r_k}+\sum_{j\neq k}e^2\int\frac{|\Psi_j(r_j)|^2}{r_{jk}}d\tau_j\right]\Psi_k(r_k)=E_k\Psi_k(r_k)$$

(12.4.7)

The kth electron is described by normalised wave function $\Psi_k(r_k)$ which has been made self-consistent. Thus each electron in the system is being considered as moving in the self consistent field due to the nucleus together with all other electrons.

For Z-electrons the Z-functions $\Psi_k(r_k)$ are obtained by Z-simultaneous non-linear integro-differential equations similar to equation (12.4.7). These equations cam not be solved directly. Hartee suggested the following method of successive approximation:

(1) From the previous knowledge of the atom a reasonable guess is made of approximate wave function Ψ_j of each electron.

(2) The electrostatic potential throughout the space, $V_j(r_j)$ due to the charge distribution is calculated and these potentials are summed over all values of j excluding that for a particular value k.

(3) This potential plus nuclear potential is substituted into Schrodinger wave equation and resulting equation is solved numerically for the wave function$\Psi_k{}'(r_k)$. The process is repeated for all values of k.

(4) In general the initially guessed wave functions $\Psi_j{}'$ do not agree with final ones $\Psi_j{}'$. Then using $\Psi_k{}'$ as initial wave functions, the whole process is repeated to get $\Psi_j{}'$’’ and so on. The process is repeated until the initial and final wave functions are identical. If this is done the field is self-consistent i.e. it is identical with the filed produced by charge distribution of electrons.

12.4.1 Equivalence of Hartee method to variational Principle

The Schrodinger wave equation in operator form is

$$H\Psi = E\Psi \qquad (12.4.1.1)$$

If wave function Ψ of whole atom represented by (12.4.1) is properly normalised then

$$E = \int \Psi^* H \, \Psi \, d\tau \qquad (12.4.1.2)$$

In variation method the best wave function Ψ is such that the variational integral (12.4.1.2) tends to minimum i.e.

$$\delta E = \delta \int \Psi^* H \, \Psi \, d\tau = 0 \qquad (12.4.1.3)$$

For normalised function $\Psi_k(r_k)$

$$H = \sum_{i=1}^{Z} \{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \} + \sum_{i>j} \frac{e^2}{r_{ij}}$$

$$= \sum_{i=1}^{Z} H_i^0 + \sum_{i>j} \frac{e^2}{r_{ij}} \qquad (12.4.1.4)$$

Therefore for normalised functions Ψ_k equation (12.4.1.2) gives

$$E = \sum_k \int \Psi_k^* (r_k) \left[\frac{-\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} \right] \Psi_k(r_k) d\tau +$$

$$\sum_{j>k} \int \int \Psi_j^* (r_j) \Psi_k{}^* (r_k) \frac{e^2}{e_{jk}} \Psi_j(r_j) \Psi_k(r_k) d\tau_j d\tau_k \qquad (12.4.1.5)$$

$$\delta\text{E}=\delta \int \Psi_k^* (r_k)\, H_k^0\, \Psi_k(r_k) d\tau + \sum_{j\neq k} \int \int \Psi_j^*(r_j)\Psi_k{}^*(r_k) \frac{e^2}{e_{jk}} \Psi_j(r_j)\Psi_k(r_k) d\tau_j d\tau_k$$

$$=\int \Psi_k^* (r_k)\, H_k^0\, \Psi_k(r_k) d\tau_k \qquad (12.4.1.6)$$

where $\text{H}_k = H_k^0 + \sum_{j\neq k} \int \Psi_j{}^*(r_j) \frac{e^2}{e_{jk}} \Psi_j(r_j) d\tau_j$

$$= H_k^0 + V_k \qquad (12.4.1.7)$$

where H_k is the *effective Hamiltonian* and V_k is the effective potential energy function for the k^{th} electron due to the its interaction with the rest of electrons. From the fundamental concepts it is known that δE is expectation value of operator H_k in the state Ψ_k which is zero. This is possible only if H_k is an Eigen operator of corresponding to lowest Eigen value ϵ_k

$$\text{H}_k\Psi_k = \epsilon_k \Psi_k \qquad (12.4.1.8)$$

The comparison of equation (12.4.7) and (12.4.1.8) shows that equation (12.4.1.8) is identical with Hartee's equation that we conclude that Hartee's method is equivalent to variation approximation provided the trial function in the variation method is chosen as the Hartee's product type wave functions (12.4.1).

12.5 The Hydrogen Atom

Hydrogen atom may be regarded as a system of two interacting point charges, the positively charged nucleus consisting of a proton and negatively charged electron.

For a system of two or more particles the equation of motion can be more conveniently written in the form

$$\text{H}\Psi = \text{E}\Psi \qquad (12.5.1)$$

where H is Hamiltonian operator, Ψ is the Eigen function and E is the energy of the whole system.

If $(x_1, y_1, z_1), (x_2, y_2, z_2)$ are the Cartesian co-ordinates of the nucleus and electron and $m_1 and\ m_2$ their masses respectively. The Hamiltonian of the system is given by

$$H=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial {x_1}^2}+\frac{\partial^2}{\partial {y_1}^2}+\frac{\partial^2}{\partial {z_1}^2}\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial {x_2}^2}+\frac{\partial^2}{\partial {y_2}^2}+\frac{\partial^2}{\partial {z_2}^2}\right)+V \tag{12.5.2}$$

where V is the potential energy.

So the Schrodinger wave equation for the whole system is written as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial {x_1}^2}+\frac{\partial^2}{\partial {y_1}^2}+\frac{\partial^2}{\partial {z_1}^2}\right)\Psi_T-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial {x_2}^2}+\frac{\partial^2}{\partial {y_2}^2}+\frac{\partial^2}{\partial {z_2}^2}\right)\Psi_T+V\Psi_T=E_T\Psi_T \tag{12.5.3}$$

where Ψ_T *and* E_T are total Eigen function and total energy respectively.

Equation (12.4.3) may be written as

$$\frac{1}{m_1}\left(\frac{\partial^2\Psi_T}{\partial {x_1}^2}+\frac{\partial^2\Psi_T}{\partial {y_1}^2}+\frac{\partial^2\Psi_T}{\partial {z_1}^2}\right)-\frac{1}{m_2}\left(\frac{\partial^2\Psi_T}{\partial {x_2}^2}+\frac{\partial^2\Psi_T}{\partial {y_2}^2}+\frac{\partial^2\Psi_T}{\partial {z_2}^2}\right)+\frac{2}{\hbar^2}(E_T-V)\Psi_T=0 \tag{12.5.4}$$

In general the potential energy V of the system may be written as

$$\begin{aligned} V&=\frac{(Ze)(-e)}{|\,r\,|}=\frac{(Ze)(-e)}{|\,r_2-r_1\,|}\\ &=\frac{-Ze^2}{\sqrt{x_2-x_1+(y_2-y_1)^2+(z_2-z_1)^2\}}} \end{aligned} \tag{12.5.5}$$

Equation (12.5.4) can be separated into two equations one of which represents the translation motion of the whole system that means the centre of mass and the relative motion of the two particles. In order to separate the two equations let us introduce the new variables x', y', z' and the Cartesian co-ordinates of the centre of mass of the system and (r,,) the polar co-ordinates of the electron relative to the nucleus. These new co-ordinates are related to the Cartesian co-ordinates of the two particles by the equations.

$$\left.\begin{aligned} x'&=\frac{m_1x_1+m_2x_2}{m_1+m_2}\\ y'&=\frac{m_1y_1+m_2y_2}{m_1+m_2}\\ z'&=\frac{m_1z_1+m_2z_2}{m_1+m_2} \end{aligned}\right\} \tag{12.5.6}$$

$$\left.\begin{aligned} x_2-x_1&=r\sin\theta\,\cos\phi\\ y_2-y_1&=r\sin\theta\,\cos\phi\\ z_2-z_1&=r\cos\theta \end{aligned}\right\} \tag{12.5.7}$$

Introducing these new variables in equation (12.5.4), we get

$$\frac{1}{m_1+m_2}\left(\frac{\partial^2\Psi_T}{\partial x'^2}+\frac{\partial^2\Psi_T}{\partial y'^2}+\frac{\partial^2\Psi_T}{\partial z'^2}\right)$$
$$+\frac{1}{\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi_T}{\partial r}\right)+\frac{1}{r^2\, sin\theta}\left(\sin\theta\,.\frac{\partial\Psi_T}{\partial\theta}\right)+\frac{1}{r^2\, sin^2\theta}\frac{\partial^2\,\Psi_T}{\partial\phi^2}\right\}$$
$$+\frac{2}{\hbar^2}(E_T-V)\Psi_T=0$$

(12.5.8)

When $\mu=\frac{m_1m_2}{m_1+m_2}$ = ***reduced mass*** of the system. (12.5.9)

Now we apply the principle of separation of variables to separate the two equations. For the purpose we consider

$$\Psi_T(x',y',z',r,\theta,\phi)=\ f(x,y,z)(r,\theta,\phi) \quad (12.5.10)$$

Substituting this value of Ψ_T in equation (12.5.8) and dividing by fΨ, we get

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial x'^2}+\frac{\partial^2 f}{\partial y'^2}+\frac{\partial^2 f}{\partial z'^2}\right)$$
$$+\frac{1}{\mu\Psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\, sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\, sin^2\theta}\frac{\partial^2\,\Psi}{\partial\phi^2}\right\}$$
$$+\frac{2}{\hbar^2}(E_T-V)=0$$

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial x'^2}+\frac{\partial^2 f}{\partial y'^2}+\frac{\partial^2 f}{\partial z'^2}\right)+\frac{2}{\hbar^2}E_T=$$
$$-\frac{1}{\mu\Psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\, sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\, sin^2\theta}\frac{\partial^2\,\Psi}{\partial\phi^2}\right\}+\frac{2}{\hbar^2}V$$

(12.5.11)

In above equation L.H.S. in a function of (x',y',z') while R.H.S. is a function of (r,,) and is independent of (x',y',z'). Therefore if above equation is to be satisfied both sides must be equal to a constant, $\frac{2}{\hbar^2}E_T$, i.e.

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial x'^2}+\frac{\partial^2 f}{\partial y'^2}+\frac{\partial^2 f}{\partial z'^2}\right)+\frac{2}{\hbar^2}E_T=\frac{2}{\hbar^2}E$$

or

$$\left(\frac{\partial^2 f}{\partial x'^2}+\frac{\partial^2 f}{\partial y'^2}+\frac{\partial^2 f}{\partial z'^2}\right)+\frac{2}{\hbar^2}(E_T-E)(m_1+m_2)f=0$$

(12.5.12)

and

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

or

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

(12.5.13)

Equation (12.5.12) represents the equation of motion of a free particle of mass (m_1+m_2) and en energy(E_T-E); thus the translational motion of the centre of mass is the same as that of a free particle of mass (m_1+m_2) and energy (E_T-E). This result corresponds to the classical result that the centre of mass moves in a straight line with constant speed. Equation (12.5.13) is identical with the Schrodinger wave equation for a single particle of mass μ and total energy E (exclusive of the translational energy) moving under the influence of a potential function

$V(r) = -e^2/r$ since for hydrogen atom Z=1. The energy E of the relative motion is determined as the Eigen value of this equivalent problem.

In order to solve equation (12.5.13), let us assume Eigen function $\Psi(r,\theta,\phi)$ as the product of three functions $R(r)\,\Theta(\theta)\,\Phi(\phi)$ each of which is function of the one indicated variable: thus

$$\boxed{\Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)} \qquad (12.5.14)$$

Substituting this in equation (12.5.13) and dividing by R$\Theta\Phi$, we get

$$\left\{\frac{1}{r^2 R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{r^2\,sin\theta\,\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{r^2\,sin^2\theta\,\Phi}\frac{\partial^2\,\Phi}{\partial\phi^2}\right\}+\frac{2\mu}{\hbar^2}\{E-V(r)\}=0 \qquad (12.5.15)$$

Multiplying this equation by $r^2\,sin^2\theta$ and rearranging, we get

$$\left\{\frac{sin\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Theta}{\partial\theta}\right)\right\}+r^2\,sin^2\theta\,\frac{2\mu}{\hbar^2}\{E-V(r)\}=-\frac{1}{\Phi}\frac{\partial^2\,\Phi}{\partial\phi^2} \qquad (12.5.16)$$

In this equation L.H.S. is function of r and θ and is independent of ϕ, while R.H.S

. is function of ϕ alone. Therefore if this equation is to be satisfied each side must be equal to same constant m² i.e.

$$\left\{\frac{sin\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Theta}{\partial\theta}\right)\right\}+r^2\,sin^2\theta\,\frac{2\mu}{\hbar^2}\{E-V(r)\}\;=m^2 \tag{12.5.17}$$

and $$-\frac{1}{\Phi}\frac{\partial^2\,\Phi}{\partial\phi^2}=m^2$$

or $$\boxed{\frac{\partial^2\Phi}{\partial\phi}+m^2\Phi=0} \tag{12.5.18}$$

Dividing equation (12.5.17) by $sin^2\theta$ and rearranging, we get

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2\mu}{\hbar^2}\{E-V(r)\}=\frac{m^2}{sin^2\theta}-\frac{1}{\Theta sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,.\frac{\partial\Theta}{\partial\theta}\right) \tag{12.5.19}$$

The L.H.S. of this equation is a function of variable r only while R.H.S. is a function of the variable θ only. Therefore if above equation is to be satisfied each side must be equal to the same constant, β, i.e.

$$\boxed{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2\mu}{\hbar^2}\{E-V(r)\}=\beta}$$

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\beta R}{r^2}+r^2\frac{2\mu}{\hbar^2}\{E-V(r)\}R=0 \tag{12.5.20}$$

and

$$\boxed{\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0} \tag{12.5.21}$$

12.5.1 The Solution of Φ equation

As discussed in last article the solution of equation (12.5.18) can be written as

$$\boxed{\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}} \tag{12.5.1.1}$$

where the constant ***m= 0, ±1, ±2, ±3,........ and is called the magnetic quantum number.***

12.5.2 The Solution of Θ Equation:

Now for the solution we substitute a new variable x such that

$$x = \cos\theta \tag{12.5.2.1}$$

In equation (12.5.21), then we have

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\} + \left(\beta - \frac{m^2}{1-x^2}\right)\Theta = 0 \tag{12.5.2.2}$$

his equation is same as equation (12.5.3.1) of last article.

Therefore we must have

$$\boxed{\beta = l(l+1)} \tag{12.5.2.3}$$

where $l = 0, 1, 2, 3,$........and is called the ***azimuthal quantum number***.

Also solution of equation (12.5.21) may be written as

$$\Theta_{ml}(\theta) = \sqrt{\left\{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right\}}\, P_l^{|m|}(cos\theta) \tag{12.5.2.4}$$

where $P_l^{|m|}$ is called the *associated Legendre function.*

12.5.3 Solution of Radial Equation

Substituting value of β in equation (12.5.20), we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{l(l+1)R}{r^2} + \frac{2\mu}{\hbar^2}\{E - V(r)\}R = 0$$

or

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[-\frac{l(l+1)R}{r^2} + \frac{2\mu}{\hbar^2}\{E - V(r)\}\right]R = 0 \tag{12.5.3.1}$$

This equation with V(r) = $\frac{-Ze^2}{r}$ is called the *radial equation for hydrogen-like atoms* and for Z=1 it is radial equation for hydrogen atom.

Substituting V(r) = $\frac{-Ze^2}{r}$ in equation (12.5.3.1), we get

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[-\frac{l(l+1)R}{r^2} + \frac{2\mu}{\hbar^2}E + \frac{2\mu Ze^2}{\hbar^3 r}\right]R = 0 \tag{12.5.3.2}$$

According to classical mechanics E<0, i.e. negative energies correspond to elliptical orbits representing bound states in atomic system: while E>0, i.e. positive energies correspond to hyperbolic orbits representing unbound states.

In this case let us assume that the electron is bound in the hydrogen atom, i.e. E<0. Then let us substitute

$$\left.\begin{aligned} \alpha^2 &= \frac{-2\mu E}{\hbar^2} \\ \text{and} \qquad \lambda &= \frac{\mu Z e^2}{\hbar^2 \alpha} \end{aligned}\right\} \tag{12.5.3.3}$$

In this equation (12.5.3.2), so that we have

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[-\frac{l(l+1)R}{r^2} + \alpha^2 + \frac{2\lambda\alpha}{r}\right]R = 0 \tag{12.5.3.4}$$

Now we consider a new independent variable ρ such that

$$\rho = 2\alpha r \tag{12.5.3.5}$$

So that we have $\frac{\partial R}{\partial r} = \frac{\partial R}{\partial \rho} . \frac{\partial \rho}{\partial r} = 2\alpha \frac{\partial R}{\partial \rho}$ (12.5.3.6)

$$\frac{\partial^2 R}{\partial r^2} = \frac{\partial}{\partial r}\left\{\frac{\partial R}{\partial r}\right\} = \frac{\partial}{\partial r}\left\{2\alpha \frac{\partial R}{\partial \rho}\right\}\frac{\partial \rho}{\partial r} = 4\alpha^2 \frac{\partial^2 R}{\partial \rho^2} \tag{12.5.3.7}$$

Substituting these values of $\frac{\partial R}{\partial r}$ and $\frac{\partial^2 R}{\partial r^2}$ in equation (12.5.3.4) and dividing by $4\alpha^2$, we get

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[-\frac{l(l+1)R}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right]R = 0 \tag{12.5.3.8}$$

12.5.4 Asymptotic behaviour

If $\rho \rightarrow \infty$ equation (12.5.34) approaches the form

$$\frac{\partial^2 R(\rho)}{\partial \rho^2} + \frac{1}{4}R(\rho) = 0$$

The solution of above equation is

$$R(\rho) = e^{\frac{+\rho}{2}} \; and \; R(\rho) = e^{\frac{-\rho}{2}}$$

As ρ may vary from 0 to ∞, former of these solutions will increase as ρ increases and so it will lead to an unacceptable wave-function. On the other hand second solution decreases to zero as ρ and hence r increases to infinity. Consequently second solution is satisfactory.

12.5.5 Recursion Formula

To seeing the asymptotic solution, the exact solution of equation (12.5.3.8) must be form $R(\rho) = F(\rho)e^{\frac{-\rho}{2}}$ (12.5.5.1)

where $F(\rho)$ is another function of variable ρ .

Substituting this in equation (12.5.3.8), we get

$$F'' + \left\{\frac{2}{\rho} - 1\right\}F' + \left[-\frac{l(l+1)R}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{\rho}\right]F = 0$$

(12.5.5.2)

where $F' = \frac{dF}{d\rho}$ $and\ F'' = \frac{d^2F}{d\rho^2}$

Let us now find a solution for F in the form

$$F(\rho) = \rho^s G(\rho) \qquad (12.5.5.3)$$

where G(ρ) is a power series in ρ, beginning with a non-vanishing constant, i.e.

$$G(\rho) = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\ldots\ldots = \sum_{k=0}^{\infty} a_k\rho^k, a_0 \neq 0$$

(12.5.5.4)

Differentiating equation (12.5.5.3) with respect to ρ, we get

$$F(\rho) = s\rho^{s-1}G + \rho^s G'$$

or $$F^{\prime\prime(\rho)} = s(s-1)\rho^{s-2}G + 2s\rho^{s-1}G + \rho^s G''$$

Substituting these values of F, F' and F'' in equation (12.5.5.2), we get

$s(s-1)\rho^s G + 2s\rho^{s+1}G' + \rho^{s+2}G'' + 2\rho^{s+1}G' + 2s\rho^s G - \rho^{s+2}G^2 + s\rho^{s+1}G + (\lambda - 1)\rho^{s+1}G - l(l+1)\rho^s G = 0$

Dividing above equation by ρ^s and arranging the terms, we get

$$\rho^2 G'' + [2(s+1) - \rho]G' + [\rho(\lambda - s - 1) + s(s+1) - l(l+1)G] = 0$$

(12.5.5.5)

If ρ is a set equal to zero in above equation, we get

$$\{s(s+1) - l(l+1)\}a_0 = 0$$

$$s(s+1) - l(l+1) = 0 \qquad (12.5.5.6)$$

This gives us $s = l\ or - (l+1)$ (12.5.5.7)

The boundary condition that R(ρ) be finite at $\rho = 0$ requires that $s = l$ so that

$$\rho G'' + [2(l+1) - \rho]G' + (\lambda - l - 1)G = 0 \qquad (12.5.5.8)$$

Differentiating equation (12.5.5.4) with respect to ρ, we get

$$G' = a_1 + 2a_2\rho + 3a_3\rho^2 + \dots\dots\dots = \sum_{i=1}^{\infty} a_i i \rho^{i-1}$$
$$= \sum_{k=0}^{\infty} a_{k+1}(k+1)\rho^k \qquad (12.5.5.9)$$

and $$G'' = 2a_2 + 6a_3\rho + 12a_3\rho^2 \dots\dots\dots = \sum_{i=2}^{\infty} a_i(i-1)\rho^{i-2}$$
$$= \sum_{k=0}^{\infty} a_{k+2}(k+1)(k+2)\rho^k \qquad (12.5.5.10)$$

Substituting value of G, G' and G'' from (12.5.5.4), (12.5.5.9) and (12.5.5.10), we get

$$\sum_{k=0}^{\infty} a_{k+2}(k+1)(k+2)\rho^{k+1} + [2(l+1) - \rho]\sum_{k=0}^{\infty} a_{k+1}(k+1)\rho^k$$
$$+ (\lambda - l - 1)\sum_{k=0}^{\infty} a_k\rho^k = 0$$

or

$$\sum_{k=0}^{\infty} a_{k+2}(k+1)(k+2)\rho^{k+1} - \sum_{k=0}^{\infty} a_{k+1}(k+1)\rho^{k+1} + 2(l+1)\sum_{k=0}^{\infty} a_{k+1}(k+1)\rho^k$$
$$+ (\lambda - l - 1)\sum_{k=0}^{\infty} a_k\rho^k \qquad = 0$$

(12.5.5.11)

If this equation is to be satisfied the coefficients of various powers of ρ must vanish separately.

Now equating zero the coefficients of ρ^k and equating them to zero, we get

$$a_{k+1}k(k+1) - a_k k + 2(l+1)a_{k+1} + (\lambda - l - 1)a_k = 0$$

or

$$a_{k+1}\{k(k+1) + (k+1)(2l+2)\} + (\lambda - l - 1 - k)a_k = 0$$

or $$a_{k+1} = \frac{k+l+1-\rho}{(k+l)(2l+k+2)} a_k \qquad (12.5.5.12)$$

This expression is called as *recursion formula*. Here k is an integer or zero.

For any value of λ and l the series for F(ρ) consists of infinite number of terms and does not correspond to a satisfactory wave function ; because value of the series as shown below, increases rapidly with increasing ρ and consequently with increasing r, with the result that the function R(ρ), i.e. $e^{\frac{\rho}{2}}\rho^s$ G(ρ) increases without limit as ρ increases.

To prove this consider the series

$$\rho^s e^\rho = \rho^s[1+\rho+\frac{\rho^2}{2!}+\frac{\rho^3}{3!}+\ldots\ldots\ldots\ldots+\frac{\rho^k}{k!}+\frac{\rho^{k+1}}{(k+1)!}+\ldots\ldots\ldots]$$

So that $\frac{a_{k+1}}{a_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$

If k is large $k+1 \cong k$, then

$$\lim_{k\to\infty}\frac{a_{k+1}}{a_k} \to \frac{1}{k}$$

Also from (12.5.5.12), we have

$$\lim_{k\to\infty}\frac{a_{k+1}}{a_k} \to \frac{1}{k}$$

Hence the series for F(ρ) i.e. $\rho^s G(\rho)$, for large values of ρ behaves like $\rho^s e^\rho$. If this is the case, the function R(ρ) for large values of ρ will behave like $e^{\frac{-\rho}{2}}\rho^s e^\rho = e^{\frac{\rho}{2}}\rho^s$; which approaches infinity: thus making the wave function physically unacceptable. Thus the series governed by the recursion formula (12.5.5.12) does not lead to a satisfactory wave function unless some restriction is introduced which makes the series break off finite number of terms.

12.6 Energy Eigen Values for Hydrogen Atom

We know from the previous knowledge that in order to obtain a satisfactory wave function the series will break off after a finite number of terms. The series will break off after ρ^k if we set the nominator in the recursion formula(12.5.5.12) equal to zero, i.e.

$$k+l+1-\lambda = 0$$

$$\text{or } \lambda = k+l+1 = n(say) \qquad (12.5.6.1)$$

Here k is called the radial quantum number and can have the values 1, 2, 3, ..., while ***n is called the total quantum number and can have the values 1, 2, 3,......***

$$\lambda^2 = \frac{\mu^2 Z^2 e^4}{\hbar^4 \alpha^2} = \frac{\mu^2 Z^2 e^4}{\hbar^4\left(\frac{-2E\mu}{\hbar^2}\right)^2}$$

$$\text{or} \qquad E_n = -\frac{\mu Z^2 e^4}{2\hbar^2\lambda^2}$$

$$\text{So that } E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad (12.5.6.1)$$

This equation gives the energy Eigen values for hydrogen atom with Z=1 and is in agreement with the old quantum theory and experiment.

12.6.1 Radial wave function

Substituting λ=n in equation (12.5.5.8), we get

$$\rho G'' + [2(l+1) - \rho]G' + (n - l - 1)G = 0 \tag{12.5.6.2}$$

Now substituting

$$\left.\begin{aligned} 2l + 1 &= p \\ n + l &= n' \end{aligned}\right\} \tag{12.5.6.3}$$

in equation(12.5.6.2), we have

$$\rho G'' + [p + 1 - \rho]G' + (n' - p)G = 0 \tag{12.5.6.4}$$

The solution of this equation will be the associated Laguerre polynomial or more correctly the associated Laguerre polynomial multiplied by a constant factor i.e.

$$\begin{aligned} G(\rho) &= C\, L_{n'}^{p}(\rho) \\ &= C\, L_{n+l}^{2l+1}(\rho) \end{aligned} \tag{12.5.6.5A}$$

where C is a constant and may be made equal to the normalization factor

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1}\{(n+l)!\}^{2\rho^{k}}}{[(n-l-1-k)]!\,[(2l+1+k)]!\,k!} \tag{12.5.6.5B}$$

Thus the total wave-function R(r) is given by

$$R_{nl}(r) = e^{\frac{-\rho}{2}}\rho^{l}G(\rho) = Ce^{\frac{-\rho}{2}}\rho^{l}\, L_{n+l}^{2l+1}(\rho) \tag{12.5.6.6}$$

The normalization condition, for the physically significant interval of zero to infinity is

$$\boxed{\int_{0}^{\infty} R(r)R^{*}(r)r^{2}dr = 1} \tag{12.5.6.7}$$

Here the factor r^2 is necessary to convert the length dr into an element of volume.

We have $\rho = 2\alpha r = 2.\frac{\mu Z e^{2}}{\hbar^{2} n}.r = \frac{2\mu Z e^{2}}{\hbar^{2} n}.r$

$$= \frac{2Zr}{n}.\frac{1}{a_0} \tag{12.5.6.8}$$

where $\frac{1}{a_0} = \frac{\mu e^2}{\hbar^2}$, a_0 being Bohr's radius.

From (12.5.6.8) $\quad r = \frac{na_0}{2Z}\rho$

So that $\quad dr = \frac{na_0}{2Z}d\rho$

Substituting this values R(r), $R^*(r)$, r and dr in equation (12.5.6.7), we get

$$C^2 \int_0^\infty e^{-\rho}\,\rho^{2l}\,\left[L_{n+l}^{2l+1}(\rho)\right]^2 \left(\frac{na_0}{2Z}\rho\right)^2 \left(\frac{na_0}{2Z}\right) d\rho = 1$$

i.e.

$$C^2\left(\frac{na_0}{2Z}\right)^3 \int_0^\infty e^{-\rho}\,\rho^{2l+2}\,\left[L_{n+l}^{2l+1}(\rho)\right]^2 d\rho = 1$$

$$C^2\left(\frac{na_0}{2Z}\right)^3 \left[\frac{2n\{(n+l)!\}^3}{(n-l-1)!}\right] = 1$$

$$C = \sqrt{\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}$$

Substituting this value of C in (12.5.6.8), the radial wave-function may be represented by

$$R_{nl}(r) = \sqrt{\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}\, e^{\frac{-Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \tag{12.5.6.9}$$

The first three radial functions. Found from equation (12.5.6.9) are

$$\left.\begin{aligned} R_{100}(r) &= \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2e^{-\frac{Zr}{a_0}} \\ R_{200}(r) &= \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{a_0}} \\ R_{210}(r) &= \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0\sqrt{3}}\, e^{-\frac{Zr}{a_0}} \end{aligned}\right\} \tag{12.5.6.10}$$

12.6.2 Complete wave function

The complete wave-function or the normalised Eigen functions for hydrogen atoms are

$$\boxed{\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\Theta_{ml}(\theta)\Phi_{mn}(\phi) = 0} \qquad (12.5.6.11)$$

With $\quad \Theta_{ml}(\theta) = \sqrt{\left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}\right]}\; P_l^{|m|}(cos\theta)$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

and

$$R_{nl}(r) = \sqrt{\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}\, e^{\frac{-Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

The real forms of the complete Eigen functions Ψ_{nlm}, exclusive of spin, for various values of $n, l\ and\ m$ are given below:

n	*l*	*m*	*State*	Eigen function
1	*0*	*0*	*1s*	$\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2e^{-\frac{Zr}{a_0}}$
2	*0*	*0*	*2s*	$\Psi_{200} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{a_0}}$
2	*1*	*0*	*2p*	$\Psi_{210} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} e^{-\frac{Zr}{a_0}} rcos\theta$
2	*1*	*1*	*2p*	$\Psi_{211} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} e^{-\frac{Zr}{a_0}} sin\theta\, e^{i\phi}$

If Z=1, these wave functions represent specifically the Eigen functions of hydrogen atom.

12.7 Self Learning Exercise

Q.1 Determine the energy levels of a particle moving in a centrally symmetric field with potential energy

$$V(r) = \frac{A}{r^2} - \frac{B}{r}$$

Q.2 Obtain the energy levels and corresponding Eigen functions for an infinitely deep spherically potential well defined as

$$V(r) = \left.\begin{array}{ll} 0 & r<a \\ \infty & r>a \end{array}\right\}$$

Q.3 Show that the addition of a small $1/r^2$term to the coulomb potential removes the degeneracy of states with different l.

Q.4 Find an expression for the electron density n(r) in the Thomas-Fermi model in terms of the Thomas-Fermi function χ(x).

Q.5 For hydrogen atom in an stationary state defined by quantum numbers $n, l\ and\ m,$ prove that

$$<r> = \int_0^\infty r^3 |\ R_{nl}\ |^2 dr$$

12.8 Summary

In this unit we study various knowledgeable topic and about the ground state of the atoms. This unit contains some very important topic named as Central field approximation, and its two approaches

1. Thomas-Fermi statistical model,
2. Hartee's self-consistent field method.

Mainly we study about the Hydrogen atom and its Eigen values and Eigen functions, radial wave equation etc.

12.9 Glossary

Electronic charge density: Charge per unit area is known as Electronic Charge density.

Radial equation for hydrogen-like atoms: V(r) =$\frac{-Ze^2}{r}$

Hamiltonian Operator: The expression for the classical Hamiltonian function of a particle of mass m, moving with a momentum p in a potential field $V(r)$ is

$$H = \frac{p^2}{2m} + V(r)$$

Orthonormal Functions: These are the functions which hold good for both conditions of orthogonality and normalisation.

Operator: An operator is a rule by means of which the element of one linearspace may be mapped on elements of other linear space.

12.10 Answer to Self Learning Exercise

Ans.1: For the given potential the radial equation becomes

$$\frac{d^2u}{dr^2}+\left[\frac{2m}{\hbar^2}\left\{E-\frac{A}{r^2}+\frac{B}{r}\right\}-\frac{l(l+1)}{r^2}\right]u=0$$

or $$\frac{d^2u}{dr^2}+\left[\frac{2m}{\hbar^2}\left\{E+\frac{B}{r}\right\}-\frac{s(s+1)}{r^2}\right]u=0 \qquad (1)$$

where $\frac{2m}{\hbar^2}A+l(l+1)=s(s+1)$ (2)

Equation(1)is similar to equation $\frac{d^2u}{dr^2}+\left[\frac{2m}{\hbar^2}\left\{E+\frac{K}{r}\right\}-\frac{l(l+1)}{r^2}\right]u=0$ with replaced $l \; and \; by \; s$. Substituting $(q+s+1)^{-1}=\frac{1}{n} \; and \; K=B$ in equation $E=-\frac{mK^2}{2\hbar^2n^2}$, we get

$$E=-\frac{mB^2}{2\hbar^2}(q+s+1)^{-2}$$

Where s is the positive root of equation. Thus we get

$$E_q=-\frac{2mB^2}{\hbar^2}\left[\left[2q+1+\{2l+1\}^2+8m\frac{A}{\hbar^2}\right]^{-\frac{1}{2}}\right]^2$$

The radial Eigen function may then be written

$$R_{nl}(r)=B_{nl}\left(\frac{2r}{\alpha n}\right)^s F\left(-n+s+1,2s+2,\frac{2r}{n\alpha}\right)e^{-\frac{r}{n\alpha}}$$

where $\alpha=\frac{\hbar^2}{mB}$

Ans. 2: In the region r<a, the radial equation is given as

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left[1-\frac{l(l+1)}{r^2}\right]R=0$$

With $\rho=kr \; and \; k=\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$, may be solved under the boundary condition that R→0 at r=0

Since potential well is infinitely deep. Thus the solution i.e.

$$R_l(kr)=A_l j_l(kr)$$

Vanishes at r=a. It gives

$$j_l(ka)=0$$

Its root for first few values of l may be determined as follows:

For l=0, $j_0(r) = \frac{\sin\rho}{\rho}$ (1)

And hence equation (1) reduces to $\sin ka = 0$

Which has the roots as ka = nπ

Giving $\varepsilon_n = \frac{n^2\hbar^2\pi^2}{2ma^2}$

For $l = 1$ $j_l(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}$

Hence equation (1) becomes

$$\tan ka = ka$$

Solution of which gives the energy Eigen values. Similarly, energy Eigen values may be obtained for the higher values of l.

Ans.3: The potential, referred here, has been used in question 1 with the Eigen energy given by equation which is Balmer-like formula but here n differs from an integer by $l - dependent$ quantity (i.e. quantum defect in the terminology of one electron spectra). It shows that states corresponding to different values of l will have different Eigen energies in this case and hence the degeneracy of states with different l in coulomb potential is removed by the addition of 1/r^2 term to the potential.

Ans.4: We already know,

The electron density n(r) = $\frac{[-2mV(r)]^{\frac{3}{2}}}{3\pi^2\hbar^3}$

Substituting the value of V(r) from equation V(r) = $-\frac{Ze^2\chi(r)}{r}$, we get

$$n(r) = \frac{\left[2m\frac{Ze^2\chi(r)}{r}\right]^{\frac{3}{2}}}{3\pi^2\hbar^3}$$

Replacement of r with the help of equation r=bx, gives

$$n(r) = \frac{[2mZe^2]^{\frac{3}{2}}}{3\pi^2\hbar^3}\left(\frac{\chi}{bx}\right)^{\frac{3}{2}}$$

Substitution of the value of b from equation b=$\frac{0.885a_0}{Z^{\frac{1}{3}}}$ gives

$$n(r) = \frac{32Z^2}{9\pi^3 a_0{}^3}\left(\frac{\chi}{x}\right)^{\frac{3}{2}}$$

Where a_0 is the Bohr radius. This is the required result.

Ans.5: In a stationary state,

$$<r> = \int\int\int \Psi^*_{nlm}\, r\, \Psi_{nlm}\, d\tau$$

$$= \int_0^{\infty} |R_{nl}|^2 r^3\, dr \int_0^{\pi}\int_0^{2\pi} |Y_{lm}|^{2\sin\theta}\, d\theta\, d\phi$$

Since the spherical harmonics are normalized, the value of angular integral is unity, i.e.

$$<r> = \int_0^{\infty} |R_{nl}|^2 r^3 dr$$

12.11 Exercise

Q.1 What is central field approximation method for evaluation potential energy function of many electron atoms?

Q.2 Find an expression for the electron density in Fermi-Thomas model and show that the radius of sphere enclosing a fixed fraction of all electrons is proportional $Z^{-\frac{1}{3}}$.

Q.3 Discuss Hartee's self consistent method for determining the potential energy V(r) in central field approximation.

Q.4 Why Hartee's method of determining the potential energy is called as self consistent method? Give answer with reason.

Q.5 Solve the Schrodinger wave equation for the case of hydrogen atom and discuss its radial wave equation.

Q.6 Solve the radial wave function of hydrogen atom to obtain the expression for bound state.

Q.7 Solve the radial wave equation of hydrogen atom and obtain an expression for Eigen value and normalised wave functions for the lowest state.

Q.8 Obtain the Eigen values and Eigen functions for the hydrogen atom.

Q.9 Obtain ground state wave functions for hydrogen atom using Schrodinger wave equation. Obtain the most probable distance of electron from nucleus.

Q.10 The wave function of the hydrogen atom for 1s state is

$$(1s)= \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$

where $a_0=\hbar^2/me^2$ is the Bohr radius. Calculate the expectation vale of energy of the electron in the 1s state.

Given

$$\int_0^\infty x^n e^{-\infty} dx = n!$$

Q.11 Calculate the expectation value of the radius vector r of the electron for the ground state hydrogen atom.

Q.12 Calculate the size, i.e. $<r^2>$, for the hydrogen atom in its ground state.

12.12 Answers to Exercise

Ans. 11: The wave function of the ground state is given by

$$\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$

$$<r>= \int \Psi_{100}\, r\, \Psi_{100}^*\, d\tau$$

$$<r>= \frac{1}{\pi a_0{}^3}\int_0^\infty r^3 \exp\left(\frac{-2r}{a_0}\right) dr \int_0^\pi\int_0^{2\pi} sin\theta\, d\theta\, d\phi$$

The integration over the angular coordinates gives 4π. Using the relation in the appendix, the r-integral can be evaluated. Thus

$$<r>= \frac{4}{a_0{}^3}\frac{3!}{(2/a_0)^4} = \frac{3}{2}a_0$$

Hence the expectation value of r in the ground state of hydrogen atom is $\frac{3}{2}a_0$.

Ans.12:

$$\Psi_{100} = \left(\frac{1}{\pi a_0}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}}$$

$$<r^2>= \frac{1}{\pi a^{03}}\int\int\int \exp\left(\frac{-2r}{a_0}\right) r^4\, sin\theta\, d\theta\, d\phi\, dr$$

The angular integration gives 4π. Use of the integrals in the appendix gives

$$< r^2 > = \frac{4}{{a_0}^3}\int\int\int \exp\left(\frac{-2r}{a_0}\right) r^4 \ dr$$

$$= 3a_0^2$$

$$< r^2 >^{\frac{1}{2}} = \sqrt{3}\, a_0$$

References and Suggested Readings

1. Modern Physics by Arthur Beiser.
2. Quantum Mechanics by Schiff.
3. Quantum Mechanics Concepts and applications by Nouredine Zettili.
4. Quantum Mechanics by David Griffiths.

UNIT-13

Time Independent Perturbation Theory : First and Second Order Correction

Structure of the Unit

13.0 Objectives

The potential energy of most of the real systems are different from those considered, and an exact solution is not possible different approximate methods have therefore been developed to obtain approximate solutions of systems. One such method is the time-independent perturbation theory. The objective of this unit is to define time independent perturbation theory and it's properties. We also study the use of Schrodinger wave equation.

13.1 Introduction

In quantum mechanics as in classical mechanics exact solution of problems are rare and one must frequently resort to approximation. Approximations are therefore expected to play an important role. Therefore, various methods of approximate solution of the wave equation have been explained, leading to the more or less accurate approximate evaluation of energy values and wave functions. The simple wave mechanics perturbation is developed by Schrodinger. Perturbation theories are of two kinds: time independent or stationary perturbation theory and time dependent perturbation theory

13.2 Stationary Perturbation theory

The stationary perturbation theory is related with finding the change in the energy levels and Eigen functions of a system when a small disturbance is applied. In such cases ,the Hamiltonian can be split up into two parts, one of which is large and represents a system for which the Schrodinger equation can be solved exactly, while the other part is small and can be treated as perturbation term. If the potential energy is distributed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly: of course the arrangement remains the same. Mathematically the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may be constant or it may be function of space or both space and the momentum co-ordinates.

In other words, the Hamiltonian H in the Schrodinger equation can be written as the sum of two parts ;one of these parts H^0 represents to unperturbed system and other part H' represents to perturbation effect. Let us write Schrodinger wave equation

$$\boxed{H\Psi = E\Psi} \qquad (13.2.1)$$

In which Hamiltonian *H* represents the operator

$$H = \frac{-\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + V \qquad (13.2.2)$$

E is the Eigen value and Ψ is the eigen function of operator H.

H is the sum of two terms H_0 and H' already defined

$$\boxed{H = H^0 + H'} \qquad (13.2.3)$$

Here H' is ***small perturbation*** term.

Let Ψ_k^0 and E_k^0 be a particular orthonormal eigenfunction and eigenvalue of unperturbed Hamiltonian H_0, i.e.

$$\boxed{H^0 \Psi_k^0 = E_k^0 \Psi_k^0}$$

Let us consider non-degenerate system that is system for which there is one eigenfunction corresponding to each eigen value. In the stationary system, the ***Hamiltonian H does not depend upon time*** and it is possible to expand H in terms of some parameter yielding the expression

$$\boxed{H = H^0 + \lambda H' + \lambda^2 H'' + \dots} \qquad (13.2.4)$$

In this λ has been chosen in such a way that equation (13.2.1) for λ=0 reduces to the form

$$H^0\Psi^0 - E^0\Psi^0 = 0 \qquad (13.2.5)$$

It is to be remembered that there is one eigen function Ψ^0 and energy level E^0 corresponding to operator H^0. Equation (13.2.5) can be directly solved. This equation is said to be the "*wave equation to unperturbed system*" while the terms $\lambda H' + \lambda^2 H'' + \dots\dots$ are called the *perturbation terms.*

The unperturbed equation (13.2.5) has solutions

$$\Psi_0^0, \Psi_1^0, \Psi_2^0, \dots\dots\dots\dots, \Psi_k^0, \dots\dots\dots$$

called the unperturbed eigen functions and corresponding eigen values are

$$E_0^0, E_1^0, E_2^0, \dots\dots\dots\dots, E_k^0, \dots\dots\dots\dots$$

The functions Ψ_k^0 form a complete orthonormal set, i.e. they satisfy the condition

$$\int \Psi_i^0 \Psi_j^0 d\tau = \delta_{ij} \tag{13.2.6}$$

where δ_{ij} is Kronecker delta symbol defined as

$$\delta_{ij} = 0 \text{ for } i \neq j$$
$$= 1 \text{ for } i = j$$

Now let us consider the effect of perturbation. The application of perturbation does not cause large changes :hence the energy values and wave functions for the perturbed system will be near those for the unperturbed system. We can expand the energy E and the wave function Ψ for the perturbed system in terms of λ, so

$$\boxed{\Psi_k = \Psi_k^0 + \lambda \Psi_k' + \lambda^2 \Psi_k'' + \ldots} \tag{13.2.7}$$

$$\boxed{E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots} \tag{13.2.8}$$

If the perturbation is small, then terms of the series (13.2.7)and (13.2.8) will become rapidly smaller i.e. the series will be convergent.

Now substituting (13.2.6),(13.2.7) and (13.2.8) in equation (13.2.1), we get

$$(H^0 + \lambda H' + \lambda^2 H'' \ldots\ldots)(\Psi_k^0 + \lambda \Psi'_k + \lambda^2 \Psi''_k + \ldots\ldots)$$
$$= (E_k^0 + \lambda E'_k + \lambda^2 E''_k + \ldots\ldots)(\Psi_k^0 + \lambda \Psi'_k + \lambda^2 \Psi''_k + \ldots\ldots)$$

On collecting the coefficients of like powers of λ

$$(H^0\Psi_k^0 - E_k^0\Psi_k^0) + (H^0\Psi'_k + H'\Psi_k^0 - E_k^0\Psi'_k - E'_k\Psi_k^0)\lambda +$$
$$(H^0\Psi''_k + H'\Psi'_k + H''\Psi_k^0 - E_k^0\Psi''_k - E'_k\Psi'_k - E''_k\Psi_k^0)\lambda^2 + \ldots\ldots\ldots = 0$$

(13.2.9)

If this series is properly convergent i.e., equal to zero for all possible values of λ, then coefficients of powers of λ must vanish separately. These equations will have successively higher orders of perturbation . The coefficient of λ^0 gives

$$(H^0 - E_k^0)\,\Psi_k^0 = 0 \tag{13.2.10a}$$

The coefficient of λ gives equation

$$(H^0\Psi'_k + H'\Psi_k^0 - E_k^0\Psi'_k - E'_k\Psi_k^0) = 0$$

or $$(H^0-E_k^0)\,\Psi'_k+(H'-E'_k)\,\Psi_k^0=0 \qquad (13.2.10b)$$

The coefficient of λ^2 gives the relation

$$(H^0\Psi''_k+H'\Psi'_k+H''\Psi_k^0-E_k^0\Psi''_k-E'_k\Psi'_k-E''_k\,\Psi_k^0)=0$$

$$(H^0-E_k^0)\,\Psi''_k+(H'-E'_k)\,\Psi'_k+(H''-E''_k)\,\Psi_k^0=0 \qquad (13.2.10c)$$

Similarly, the coefficients of λ^3 yield

$$(H^0-E_k^0)\,\Psi'''_k+(H'-E'_k)\,\Psi''_k+(H''-E''_k)\,\Psi'_k+(H'''-E''')\,\Psi_k^0=0 \qquad (13.2.10d)$$

But if we limit the total Hamiltonian H upto $\lambda H'$, i.e. if we put $H=H^0+H'$, then equations (13.2.10) will be modified as

$$\left.\begin{aligned}
&(H^0-E_k^0)\,\Psi_k^0=0 && (a)\\
&(H^0-E_k^0)\,\Psi'_k+(H'-E'_k)\,\Psi_k^0=0 && (b)\\
&(H^0-E_k^0)\,\Psi''_k+(H'-E'_k)\,\Psi'_k-E''_k\,\Psi_k^0=0 && (c)\\
&(H^0-E_k^0)\,\Psi'''_k+(H'-E'_k)\,\Psi''_k-E''_k\,\Psi'_k-E'''_k\,\Psi_k^0=0 && (d)
\end{aligned}\right\} \qquad (13.2.11)$$

13.3 First order Perturbation

Equation (13.2.11b) is

$$(H^0-E_k^0)\,\Psi'_k+(H'-E'_k)\,\Psi_k^0=0$$

For solving this equation here we use *expansion theorem.* As perturbation is very small, therefore deviations from unperturbed state are small. So, the first order perturbation correction function Ψ'_k can be expanded in terms of unperturbed functions

$\Psi_1^0, \Psi_2^0, \ldots\ldots\ldots\ldots, \Psi_l^0, \ldots\ldots$; since Ψ_l^0 form a normalized orthonormal set. Hence we write

$$\Psi'_k=\sum_{l=0}a_l\Psi_l^0 \qquad (13.3.1)$$

Substituting Ψ'_k from (13.2.12) in (13.2.11b), we get

$$(H^0-E_k^0)\sum_{l=0}a_l\Psi_l^0+(H'-E'_k)\Psi_k^0=0$$

i.e. $$\sum_{l=0} a_l H^0 \Psi_l^0 - E_k^0 \sum_{l=0} a_l \Psi_l^0 + (H' - E'_k)\Psi_k^0 = 0$$

Using equation $H^0\Psi_l^0 = E_l^0 \Psi_l^0$,we get

$$\sum_{l=0} a_l E_l^0 \Psi_l^0 - E_k^0 \sum_{l=0} a_l \Psi_l^0 + (H' - E'_k)\Psi_k^0 = 0$$

$$\sum_{l=0} a_l (E_l^0 - E_k^0)_l^0 = (E'_k - H')\,\Psi_k^0 \tag{13.3.2}$$

Multiplying above equation by Ψ_m^{0*} and integrating over configuration space, we get

$$\sum_{l=0} a_l (E_l^0 - E_k^0) \int \Psi_m^{0*}\, \Psi_l^0 d\tau = \int \Psi_m^{0*} (E'_k - H')\, \Psi_k^0 d\tau$$

Using orthonormal condition of orthonormalisation of $_i^0$ is

$$\int \Psi_i^{0*} \Psi_j^0 d\tau = \delta_{ij} \begin{cases} \delta_{ij} = 0 \text{ for } i \neq j \\ \quad = 1 \text{ for } i = j \end{cases}$$

We get $\sum_{l=0} a_l (E_l^0 - E_k^0)\delta_{ml} = \int \Psi_m^{0*} E'_k \Psi_k^0 d\tau - \int \Psi_m^{0*} H' \Psi_k^0 d\tau$

$$\sum_{l=0} a_l (E_l^0 - E_k^0)_{ml} = E'_k \delta_{mk} - \int \Psi_m^{0*} H' \Psi_k^0 d\tau$$

Using the notations

$$\int \Psi_m^{0*} H' \Psi_k^0 d\tau = \langle m \,|\, H' \,|\, k \rangle$$

We get

$$\sum_{l=0} a_l (E_l^0 - E_k^0)_{ml} = E'_k \delta_{mk} - \langle m \,|\, H' \,|\, k \rangle \tag{13.3.3}$$

13.4 Calculation of first order energy

Setting m=k in equation (13.3.3), we observe that

$$\sum_{l=0} a_l (E_l^0 - E_k^0)\, \delta_{kl} = E'_k - \langle k \,|\, H' \,|\, k \rangle \qquad \text{always.}$$

Since for l=k, $E_l^0 - E_k^0 = 0$ and for $l \neq k$, $\delta_{kl} = 0$ so that,

We get $0 = E'_k - \langle k \,|\, H' \,|\, k \rangle$

or $$\boxed{E'_k = \langle k | H' | k \rangle = \int \Psi_k^{0*} H' \Psi_k^0 d\tau} \tag{13.4.1}$$

Above equation gives first order perturbation energy correction. Accordingly the "*first order perturbation energy correction for a non-degenerate system is just* *the expectation value of first order perturbed Hamiltonian* (H') *over the unperturbed state of the system.*"

13.5 Calculation of first order correction to wave function

Equation (13.3.3) may be expressed as

$$a_m(E_m^0 - E_k^0) = E'_k \delta_{mk} - \langle m \mid H' \mid k\rangle \qquad (13.5.1)$$

since $\sum_{l=0} a_l (E_l^0 - E_k^0)\, \delta_{ml} = 0 + a_m(E_m^0 - E_k^0) + 0$

$$\text{Since } \delta_{mk} \begin{cases} =0 \text{ for } k \neq m \\ =1 \text{ for } k = m \end{cases}$$

For m≠k, equation (13.5.1) gives

$$a_m(E_m^0 - E_k^0) = -\langle m \mid H' \mid k\rangle$$

or $\quad a_m = -\langle m \mid H' \mid k\rangle / (E_m^0 - E_k^0)$

$$a_m = \langle m \mid H' \mid k\rangle / (E_k^0 - E_m^0)$$

Setting $\quad m = l$, $a_l = +\langle l \mid H' \mid k\rangle / (E_k^0 - E_l^0) \quad$ *for* $l \neq k$ $\qquad$ (13.5.2)

If we retain only first order correction terms, then

$$\left.\begin{aligned} E_k &= E_k^0 + \lambda E'_k \quad \text{....(a)} \\ \Psi_k &= \Psi^0_k + \lambda \Psi'_k \quad \text{....(b)} \end{aligned}\right\} \qquad (13.5.3)$$

∴ Keeping in view equations (13.3.1) and (13.5.3), we get form (13.5.3.b)

$$\Psi_k = \Psi_k^0 + \lambda \textstyle\sum'_l a_l \Psi_l^0$$

$$\Psi_k = \Psi_k^0 + \lambda \textstyle\sum'_l \{\langle l | H' | k\rangle \Psi_l^0 / (E_k^0 - E_l^0)\} + \lambda a_k \Psi_k^0 \qquad (13.5.4)$$

where prime (or dash) on summation indicates that the term l=k has been omitted from the summation (or it reminds that $l \neq$k)

The value of constant a_k may be evaluated by requiring that Ψ_k is normalised, i.e.

$$\int \Psi_k^* \Psi_k \, d\tau = 1 \qquad (13.5.5)$$

Substituting Ψ_k from 13.5.4 into 13.5.5and retaining only first order terms in ; we get

$$\int\Psi_k^{0*}\Psi_k^{0}\,d\tau+\lambda a_k\int\Psi_k^{0*}\Psi_k^{0}\,d\tau+\lambda a_k{}^*\int\Psi_k^{0*}\Psi_k^{0}\,d\tau+$$
$$\lambda{\textstyle\sum'_l}\{\langle l\,|\,H'|\,k\rangle\,\delta_{lk}/(E_k^0-E_l^0)\}+\lambda{\textstyle\sum'_l}\{[\langle l\,|H'|\,k\rangle]^*\delta_{lk}/(E_k^0-E_l^0)\}=1$$

or $\quad 1+\lambda a_k+\lambda a_k{}^*+0+0=1 \qquad$ i.e. $\qquad a_k+a_k{}^*=0 \qquad\qquad (13.5.6)$

{Since $\int\Psi_l^{0*}\Psi_k^{0}\,d\tau=\delta_{lk}$, $\int\Psi_k^{0*}\Psi_l^{0}\,d\tau=\delta_{lk}$, $\int\Psi_k^{0*}\Psi_k^{0}\,d\tau=1$ }

This equation indicates that the real part of a_k is zero and still it leaves an arbitrary choice for the imaginary part.

Let us take $a_k=i\gamma$.

From 13.5.4 The wave function Ψ_k can then be expressed as

$$\Psi_k=\Psi_k^0+\lambda\, i\gamma\,\Psi_k^0+\lambda{\textstyle\sum'_l}\{\langle l\,|\;H'\,|\,k\rangle\,\Psi_l^0/(E_k^0-E_l^0)\}$$
$$={}_k^{0}(1+\lambda\, i\gamma)+\lambda{\textstyle\sum'_l}\{\langle l\,|\;H'\,|\,k\rangle\,\Psi_l^0/(E_k^0-E_l^0)\}$$

(13.5.7)

The term containing γ merely gives a phase shift in the unperturbed function Ψ_k^0 and for normalisation , this shift can be put equal to zero, so that equation (13.5.7) gives

$$\Psi_k=\Psi_k^0+\lambda{\textstyle\sum'_l}\{\langle l\,|\;H'\,|\,k\rangle\,\Psi_l^0/(E_k^0-E_l^0)\} \qquad (13.5.8)$$

$$\left.\begin{aligned}&\boxed{E_k=E_k^0+\langle k|H'|k\rangle} &&....(a)\\ &\boxed{\Psi_k=\Psi_k^0+\lambda\sum_{\substack{l=0\\ l\neq k}}^{\infty}\frac{\langle l|H'|k\rangle\Psi_l^0}{\left(E_k^0-E_l^0\right)}} &&....(b)\end{aligned}\right\} \qquad (13.5.9)$$

$$\Psi_k=\Psi_k^0+\lambda\Psi_k'$$

$$\Psi_k=\Psi_k^0+\lambda\sum_{l=0}^{\infty}{}'\frac{\langle l|H'|k\rangle\Psi_l^0}{\left(E_k^0-E_l^0\right)}$$

The arbitrary λ can be put equal to 1 and it may be included in symbols, i.e.

$\lambda H'\longrightarrow H'$; then eigen values and eigen functions of the system upto first order perturbation correction terms are expressible as above.

Where the prime over the summation indicates that we have omitted the term *l*=*k*.

13.6 Second Order Perturbation

The second order perturbation (13.2.11c) is

$$(H^0 - E_k^0)\,\Psi''_k + (H' - E'_k)\,\Psi'_k - E''_k\,\Psi_k^0 = 0 \qquad (13.6.1)$$

Expanding second order wave functions Ψ''_k as a linear combination of unperturbed orthonormal wave function Ψ_m^0 by expansion theorem i.e.

$$\Psi''_k = \sum_m b_m\,\Psi_m^0 \qquad (13.6.2)$$

substituting $'_k = \sum'_l \{<l|\ H'\ |k>\Psi_l^0 /(E_k^0 - E_l^0)\}$; $\Psi''_k = \sum_m b_m\,\Psi_m^0$

and $E'_k = <k|\ H'\ |k>$ in (13.6.1); we get

$$(H^0 - E_k^0)\sum_m b_m\,\Psi_m^0 + (H' - <k|\,H'\,|k>)[\sum'_l \{<l|\,H'\,|k>\Psi_l^0 /(E_k^0 - E_l^0)\}]$$
$$- E''_k\,\Psi_k^0 = 0$$

Using unperturbed Schrodinger equation

$H^0\Psi_m^0 = E_m^0\,\Psi_m^0$, we get,

$$\sum_m b_m E_m^0\,\Psi_m^0 - E_k^0\sum_m b_m\,\Psi_m^0$$
$$+(H' - <k|\ H'\ |k>)[\sum'_l \{<l|\ H'\ |k>\Psi_l^0 /(E_k^0 - E_l^0)\}] - E''_k\,\Psi_k^0 = 0$$

or $$\sum_m b_m(E_m^0 - E_k^0)\Psi_m^0 + [(H' - <k|\,H'|k>)\sum'_l\{<l|\,H'\,|k>\Psi_l^0/(E_k^0 - E_l^0)\}]$$
$$- E''_k\,\Psi_k^0 = 0$$

Multiplying by Ψ_n^{0*} and integrating over all space , we get

$$\sum_m b_m\ (E_m^0 - E_k^0)\int \Psi_n^{0*}\,\Psi_m^0\,d\tau +$$
$$\int[\Psi_n^{0*}(H' - <k|\,H'|k>)\sum'_l\{<l|\,H'|\,k>\Psi_l^0/(E_k^0 - E_l^0)\}]d\tau - E''_k\int\Psi_n^{0*}\,\Psi_k^0$$
$$d\tau = 0$$

Using orthonormal property of unperturbed wave functions Ψ^0's ,we get

$$\sum_m b_m(E_m^0 - E_k^0)\delta_{nm} + \sum'_l \{<n|\,H'|\,l><l|\,H'\,|k>/(E_k^0 - E_l^0)\}$$
$$-\sum'_l\{<k|\,H'\,|k><l|\,H'\,|k>\delta_{nl}/(E_k^0 - E_l^0)\} - E''_k\delta_{nk} = 0 \qquad (13.6.3)$$

13.7 Calculation of Second order Energy Correction

Setting n=k in(13.6.3), we get

$$\sum_m b_m(E_m^0 - E_k^0)\delta_{km} + {\sum}'_l \{<l\,|\,H'|\,k><k\,|\,H'\,|\,l>/(E_k^0 - E_l^0)\}$$
$$-{\sum}'_l\{<k\,|\,H'\,|\,k><l\,|\,H'\,|\,k>\delta_{kl}/(E_k^0 - E_l^0)\} - E''_k\delta_{kk} = 0 \qquad (13.7.1)$$

As $\delta_{kk}=1$ and $\sum_m b_m(E_m^0 - E_k^0)\delta_{km}=0$ for all values of m,

Equation (13.7.1) gives

$$E''_k = {\sum}'_l \{<l\,|\,H'|\,k><k\,|\,H'\,|\,l>/(E_k^0 - E_l^0)\}$$
$$-{\sum}'_l\{<k\,|\,H'\,|\,k><l\,|\,H'\,|\,k>\delta_{kl}/(E_k^0 - E_l^0)\}$$
$$(13.7.2)$$

Considering the second term in equation (13.7.2), we note that this term is zero since $\delta_{kl}=0$ for all values of *l* except for *l*=k and this term is not included in the summation. Then equation (13.7.2) gives

$$E''_k = {\sum}'_l \{<l\,|\,H'|\,k><k\,|\,H'\,|\,l>/(E_k^0 - E_l^0)\}$$

If we assume that H' is *Hermitian Operator*, we may write

$$\boxed{E''_k = \sum_{\substack{l=0\\ l\neq k}}^{\infty} \frac{\left|\langle l|H'|k\rangle\right|^2}{\left(E_k^0 - E_l^0\right)}} \qquad (13.7.3)$$

$$E''_k = {\sum_{l=0}^{\infty}}' \frac{\left|\langle l|H'|k\rangle\right|^2}{\left(E_k^0 - E_l^0\right)}$$

$$E = E_k^0 + \lambda E'_k + \lambda^2 E''_k$$

This equation gives second order energy correction term E''_k. The prime on summation reminds the omission of the term *l*=k in the summation.

13.8 Calculation of second order correction to wave function

For m=n, equation (13.6.3) gives

$$b_n(E_n^0 - E_k^0) + {\sum}'_l \{<l\,|\,H'|\,k><n\,|\,H'\,|\,l>/(E_k^0 - E_l^0)\}$$

$$-{\sum}'_{l}\{\langle k|H'|k\rangle\langle l|H'|k\rangle\delta_{nl}/(E_k^0-E_l^0)\}=0$$

or
$$b_n(E_n^0-E_k^0)+{\sum}'_{l}\{\langle l|H'|k\rangle\langle n|H'|l\rangle/(E_k^0-E_l^0)\}$$
$$-\{\langle k|H'|k\rangle\langle n|H'|k\rangle/(E_k^0-E_n^0)\}=0$$

This gives

$$b_n={\sum}'_{l}\langle l|H'|k\rangle\langle n|H'|l\rangle/(E_k^0-E_l^0)(E_k^0-E_n^0)$$
$$-\langle k|H'|k\rangle\langle n|H'|k\rangle/(E_k^0-E_n^0)^2=0$$

Setting n=m, we get

$$b_m={\sum}'_{l}\{\langle l|H'|k\rangle\langle m|H'|l\rangle/(E_k^0-E_l^0)(E_k^0-E_m^0)\}$$
$$-\{\langle k|H'|k\rangle\langle m|H'|k\rangle/(E_k^0-E_m^0)^2\}=0 \tag{13.8.1}$$

This equation determines all coefficients b_m's but not b_k. The coefficient b_k is determined by the normalisation condition for Ψ_k retaining only terms up to second order in λ.

$$\Psi_k=\Psi_k^0+\lambda\Psi'_k+\lambda^2\Psi''_k=\Psi_k^0+\lambda\Psi'_k+\lambda^2\sum_m b_m\Psi_m^0$$
$$=\Psi_k^0+\lambda\Psi'_k+\lambda^2 b_k\Psi_k^0+\lambda^2\sum_m\Big[{\sum}'_{l}\{\langle l|H'|k\rangle\langle m|H'|l\rangle/(E_k^0-E_l^0)(E_k^0-E_m^0)\}-\{\langle k|H'|k\rangle\langle m|H'|k\rangle/(E_k^0-E_m^0)^2\}\Big]\Psi_m^0 \tag{13.8.2}$$

The normalisation condition for Ψ_k gives

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

Substituting $_k$ from (13.8.2); we get

$$\int\Psi_k^{0*}\Psi_k^0\,d\tau+\lambda\int\Psi_k^{0*}\Psi'_k\,d\tau+\lambda^2 b_k\int\Psi_k^{0*}\Psi_k^0\,d\tau+$$
$$\lambda^2\Big[\sum_m\{{\sum}'_{l}\langle l|H'|k\rangle\langle m|H'|l\rangle/(E_k^0-E_l^0)(E_k^0-E_m^0)$$
$$-\langle k|H'|k\rangle\langle m|H'|k\rangle/(E_k^0-E_m^0)^2\}\int\Psi_k^{0*}\Psi_m^0\,d\tau\Big]$$
$$+\lambda\int\Psi'^*_k\Psi_k^0\,d\tau+\lambda^2 b_k^*\int\Psi_k^{0*}\Psi_k^0\,d\tau$$
$$+\lambda^2{\sum}'_{m}{\sum}'_{l}\langle l|H'|k\rangle^*\langle k|H'|l\rangle^*/(E_k^0-E_l^0)(E_k^0-E_m^0)$$
$$-\langle k|H'|k\rangle^*\langle m|H'|k\rangle^*/(E_k^0-E_m^0)^2\}\int\Psi_m^{0*}\Psi_k^0\,d\tau$$
$$+\lambda^2\int\Psi'^*_k\Psi'_k\,d\tau=1$$

or $1+0+\lambda^2 b_k+\lambda^2\sum'_m \{\sum_l <l \mid H' \mid k><k \mid H' \mid l>/(E_k^0-E_l^0)(E_k^0- E_m^0) -<k \mid H' \mid$

$$k><m \mid H' \mid k>/(E_k^0-E_m^0)^2\}\delta_{km}+0+ \lambda^2 b_k^*$$

$$+ \lambda^2\sum'_m\{\sum'_l<l \mid H' \mid k>^*<k \mid H' \mid l>^*/(E_k^0-E_l^0)(E_k^0- E_m^0)$$

$$-<k \mid H' \mid k>^*<m \mid H' \mid k>^*/(E_k^0-E_m^0)^2\}\delta_{mk}$$

$$+\lambda^2\sum'_l\sum'_m<l \mid H' \mid k>^*<m \mid H' \mid k>/ (E_k^0-E_l^0)(E_k^0- E_m^0)$$

$$\int\Psi_l^0{}^*\Psi_m^0\, d\tau=1$$

Using equation 13.6.1b)

Or $\lambda^2 b_k+\lambda^2 b_k^*$

$$+\lambda^2\sum'_l\sum'_m<l \mid H' \mid k>^*<m \mid H' \mid k>/(E_k^0-E_l^0)(E_k^0- E_m^0)\delta_{lm}=0$$

Or $\lambda^2[b_k+ b_k^*+\sum'_l<l \mid H' \mid k>^*<l \mid H' \mid k>/(E_k^0-E_l^0)(E_k^0- E_m^0)]=0$

As $\lambda^2\neq 0$, therefore, we have

$$b_k+ b_k^*=-\sum'_l |<l \mid H' \mid k>|^2/(E_k^0-E_l^0)^2 \qquad (13.8.3)$$

The real part of b_k is fixed by this equation but the imaginary part is arbitrary. The choice of imaginary part simply affects the phase of the unperturbed wave function and it does not affect the energy of the system. Hence the imaginary part of b_k may be equal to zero. Thus, we have

$$b_k= -\sum'_l |<l \mid H' \mid k>|^2/2(E_k^0-E_l^0)^2 \qquad (13.8.4)$$

Then $\Psi''_k=\sum_m b_m\Psi_m^0$

$$=b_k \Psi_k^0 + \sum'_m b_m\Psi_m^0$$

$$= -\sum'_l |<l \mid H' \mid k>|^2\, \Psi_k^0/2(E_k^0-E_l^0)^2$$

$$+\sum'_m\{\sum'_l<l \mid H' \mid k><k \mid H' \mid l>/(E_k^0-E_l^0)(E_k^0- E_m^0)$$

$$-<k \mid H' \mid k><m \mid H' \mid k>/(E_k^0-E_m^0)^2\}\, \Psi_m^0 \qquad (13.8.5)$$

Thus the complete eigenvalues and eigen function corrected upto second order perturbation terms are given by

$$E_k=E_k^0+\lambda\, E'_k+\lambda^2E''_k$$

$$E_k=E_k^0+\lambda<k \mid H' \mid k>+\lambda^2\sum'_l |<k \mid H' \mid l>|^2/(E_k^0-E_l^0) \qquad (13.8.6)$$

and $\Psi_k = \Psi_k^0 + \lambda \Psi'_k + \lambda^2 \Psi''_k$

$$= \Psi_k^0 + \lambda <l \mid H' \mid k> / (E_k^0 - E_l^0) \Psi_l^0$$

$$+ \lambda^2 [- {\sum}'_l \mid <l \mid H' \mid k> \mid^2 \Psi_k^0 / 2(E_k^0 - E_l^0)$$

$$+ {\sum}'_m \{ {\sum}'_l <l \mid H' \mid k><k \mid H' \mid l> / (E_k^0 - E_l^0)(E_k^0 - E_m^0)$$

$$- <k \mid H' \mid k><m \mid H' \mid k> / (E_k^0 - E_m^0)^2 \} \Psi_m^0] \qquad (13.8.7)$$

If we chose arbitrary $\lambda = 1$ or included λ in symbols, i.e. $\lambda H' \longrightarrow H'$; the above equations take the conventional form

$$E_k = E_k^0 + <k \mid H \mid k> + {\sum}'_l \mid <k \mid H' \mid l> \mid^2 / (E_k^0 - E_l^0) \qquad (13.8.8)$$

$$\Psi_k = \Psi_k^0 + <l \mid H' \mid k> / (E_k^0 - E_l^0) \Psi_l^0$$

$$- [{\sum}'_l \mid <l \mid H' \mid k> \mid^2 \Psi_k^0 / 2(E_k^0 - E_l^0)$$

$$+ {\sum}'_m \{ {\sum}'_l <l \mid H' \mid k><k \mid H' \mid l> / (E_k^0 - E_l^0)(E_k^0 - E_m^0)$$

$$- <k \mid H' \mid k><m \mid H' \mid k> / (E_k^0 - E_m^0)^2 \} \Psi_m^0] \qquad (13.8.9)$$

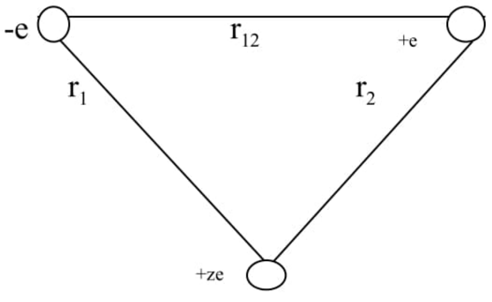
13.9 Physical applications of perturbation theory

(a) Normal helium atom

In this case we considered normal Helium atom without spin as an application of first order perturbation theory for a non-degenerate system.

A normal helium atom consists of a nucleus of charge Ze (Z=2) and two electrons circulating about the nucleus.

The potential energy for a system of two electrons 1 and 2 in Fig. and a nucleus of charge +ze is



NUCLEUS

$$V=-ze^2/r_1-ze^2/r_2+e^2/r_{12} \qquad (13.10.A.1)$$

Where r_1 and r_2 are the distances of electrons 1 and 2 and r_{12} is the separation of the electrons. Then the Hamiltonian of the system

$$H=-\hbar^2(\nabla_1^2+\nabla_2^2)/2m_0-ze^2/r_1-ze^2/r_2+e^2/r_{12} \qquad (13.10.A.2)$$

The wave equation for unperturbed Hamiltonian

i.e. $$H^0\Psi^0=E^0\Psi^0 \qquad (13.10.A.3)$$

can be solved easily, taking as sum of two hydrogen atoms.

The wave equation for two electrons in helium atom is

$$H\Psi=\{-\hbar^2(\nabla_1^2+\nabla_2^2)/2m_0-ze^2/r_1-ze^2/r_2+e^2/r_{12}\}\,\Psi=E\Psi \qquad (13.10.A.4)$$

This equation is applicable for He, Li^+, Be^{++}etc.withZ=2,3,4,etc respectively.

Equation (13.10.A.4) can be written as

$$H\Psi=\{-\hbar^2(\nabla_1^2+\nabla_2^2)/2m_0-(ze^2/r_1+ze^2/r_2)\}\Psi+e^2\,\Psi/r_{12}=E\Psi$$

If we write the Hamiltonian in the form $H=H_0+H'$, we note that unperturbed Hamiltonian

$$H_0=\{-\hbar^2(\nabla_1^2+\nabla_2^2)/2m_0-(ze^2/r_1+ze^2/r_2)\}$$

And perturbation correction term

$$H'=e^2/r_{12}$$

The wave equation for unperturbed state would then be

$$\{-\hbar^2(\nabla_1^2+\nabla_2^2)/2m_0-(ze^2/r_1-ze^2/r_2)\}\Psi^0=E^0\Psi^0 \qquad (13.10.A.5)$$

If we substitute $\Psi_0=\Psi_1^0\Psi_2^0$ and energy $E^0=E_1^0+E_2^0$,then equation(5) may be split into two component equations one for each hydrogen like atom, viz.

The equation for Ψ_1^0 is

$$\nabla_1^2\Psi_1^0+2m/\hbar^2\,(E_1^0+ze^2/r_1)\,\Psi_1^0=0 \qquad (13.10.A.6)$$

And equation for Ψ_2^0 is

$$\nabla_2^2\Psi_2^0+2m/\hbar^2\,(E_2^0+ze^2/r_2)\,\Psi_2^0=0 \qquad (13.10.A.7)$$

These two equations are hydrogen-like wave equations and their solutions for eigen values and eigen functions are

$$E_1^{\,0} = E_2^{\,0} = -z^2 m_0 e^4/2\hbar^2 n^2 = -z^2 W_H/n^2 \qquad (13.10.A.8)$$

where $W_H = m_0 e^4/2\hbar^2 = e^2/2a_0$ (13.10.A.9)

And $$\Psi_1^{\,0} = \sqrt{\left(\frac{z^2}{\pi a_0^{\,3}}\right)}\, e^{\frac{-zr_1}{a_0}} \;{}_{,2}^{\,0} = \sqrt{\left(\frac{z^2}{\pi a^{03}}\right)}\, e^{\frac{-zr_2}{a_0}} \qquad (13.10.A.10)$$

where $a_0 = \hbar^2/m_0 e^2$ (13.10.A.11)

So total unperturbed energy is

$$E^0 = E_1^{\,0} + E_2^{\,0} = -2z^2 W_H \qquad \text{for } n=1 \text{(ground state).}$$

The first order perturbation energy E' is the average value of the perturbation function $H' = e^2/r_{12}$ over the unperturbed state of the system,

$$E' = \int \Psi_0^* H' \Psi_0 \, d\tau = \int (e^2/r_{12})\, |\Psi_0|^2 d\tau,$$

Where $$\Psi_0 = \Psi_1^{\,0}\Psi_2^{\,0} = \sqrt{\left(\frac{z^2}{\pi a^{03}}\right)}\, e^{\frac{-zr_1}{a_0}} \,.\, \sqrt{\left(\frac{z^2}{\pi a^{03}}\right)}\, e^{\frac{-zr_2}{a_0}}$$

$$= \left(\frac{Z^2}{\pi a_0^{\,3}}\right) e^{\frac{-\rho_1}{2}} . e^{\frac{-\rho_2}{2}}$$

Where $\rho_1 = 2zr_1/a_0$, $\rho_2 = 2zr_2/a_0$

i.e. $$\Psi_0 = \left(\frac{Z^2}{\pi a_0^{\,3}}\right) \exp(-\rho_1 - \rho_2)$$

volume element for two electrons in spherical polar coordinates (r,θ,ϕ) is

$$d\tau = r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 \sin\theta_2 d\theta_2 d\phi_2$$

so that

$$E' = \frac{ze^2}{32\pi^2 a_0} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{e^{-\rho_1}.e^{-\rho_2}}{\rho_{12}} \rho_1^2 d\rho_1 \sin\theta_1 d\theta_1 d\phi_1 \;.\; \rho_2^2 d\rho_2 \sin\theta_2 d\theta_2 d\phi_2$$

Where $$\rho_{12} = \frac{2z\, r_{12}}{a_0}$$

This may be expressed as

$$E' = \frac{ze^2}{32\pi^2 a_0} \int\int \frac{e^{-\rho_1}.e^{\rho_2}}{\rho_{12}}\, dV_1\, dV_2 \qquad (13.10.A.10)$$

Where $dV_1 = \rho_1^2 d\rho_1 \sin\theta_1 d\theta_1 d\phi_1$

$dV_2 = \rho_2^2 d\rho_2 \sin\theta_2 d\theta_2 d\phi_2$

The integral (neglect from the factor $\frac{ze^2}{32\pi^2 a_0}$)represents the mutual electrostatic energy for two spherically symmetrically distribution of electricity with density functions $e^{-\rho_1}$and $e^{-\rho_2}$ respectively.

The integral may be evaluated by calculating to potential due to first of these by integrating over dV_1 and then finding the energy of second charge distribution in that potential field.

The potential at a point r due to a spherical shell of radius ρ_1 and thickness $d\rho_1$,i.e. of total charge $4\pi\rho_1^2 e^{-\rho_1} d\rho_1$ falls off with distance outside the shell as if the total charge were concentrated at the centre, so that for $r > \rho_1$, the potential

$$\Phi(r>\rho_1) = q_1/r$$

$$= \frac{4\pi\rho_1^2 e^{-\rho_1} d\rho_1}{r}$$

Within the shell the potential is constant and has value equal to that at shell's surface

i.e. $$\phi(r<\rho_1) = q_1/r = \frac{4\pi\rho_1^2 e^{-\rho_1} d\rho_1}{\rho_1}$$

$$= 4\pi\rho_1 e^{-\rho_1} d\rho_1$$

The potential due to the whole charge is given by

$$\phi(r) = \frac{4\pi}{r}\int_0^r e^{-\rho_1}\rho_1^2 d\rho_1 + 4\pi\int_r^\infty e^{-\rho_1}\rho_1 d\rho_1$$

$$= \frac{4\pi}{r}[(-r^2-2r-2)e^{-r}+2] + 4\pi[r+1]\, e^{-r}$$

$$= \frac{4\pi}{r}[2-e^{-r}(r+2)]$$

The energy of second charge distribution in this potential is,

$$\int(\rho_2)e^{-\rho_2}\, dV_2 = \int\frac{4\pi}{\rho_2}[2-E^{-\rho_2}(\rho_2+2)]e^{-\rho_2} dV_2$$

$$= \int_0^\infty \frac{4\pi}{\rho_2}[2 - E^{-\rho_2}(\rho_2+2)]e^{-\rho_2} 4\pi\rho_2^2 d\rho_2$$

$$=16\pi^2\int_0^\infty [2 - E^{-\rho_2}(\rho_2+2)]e^{-\rho_2}\rho_2 d\rho_2$$

$$=16\pi^2.5/4$$

$$=20\pi^2 \qquad (13.10.A.11)$$

The value of the integral in equation (13.10.A.10) is $20\pi^2$.

Hence $E' = \frac{ze^2.20\pi^2}{32\pi^2 a_0}$

$$=5/8\ ze^2/\hbar^2/m_0e^2$$

$$=5/8\ zm_0e^4/\hbar^2$$

$$=5/4\ zW_H$$

The total energy $E=E_0+E'$

$$=-2z^2W_H+5/4\ zW_H \qquad (13.10.A.12)$$

For helium atom $z=2$

$$E=-(2.4.\ -2.\ 5/4)W_H$$

$$=-11/2\ W_H$$

$$E=-11/2\ m_0e^2/2\hbar^2$$

$$= -2.75\ e^2/a_0$$

The energy of helium atom in ground state without perturbation is

$-2z^2W_H=-8\ W_H=-4e^2/a_0$, which is less than the corrected energy by means of perturbation theory.

(b) Perturbed harmonic oscillator

Case 1:The Perturbation Energy term is proportional to x

Let the Hamiltonian of harmonic oscillator is given as

$$H= -\hbar^2/2m\ \partial^2/\partial x^2 + \tfrac{1}{2}\ kx^2 + \tfrac{1}{2}\ bx \qquad (13.10.B.1)$$

$$H= H_0 + H'$$

where H_0 is unperturbed Hamiltonian and H' is the first order perturbation.

$$H_0= -\hbar^2/2m\ \partial^2/\partial x^2 + \tfrac{1}{2}\ kx^2 \qquad (13.10.B.2)$$

$H' = \frac{1}{2} bx$ (13.10.B.3)

Equation (13.10.B.2) can be easily solve by Schrödinger method

$H_0 = -\hbar^2/2m\, \partial^2/\partial x^2 + \frac{1}{2} kx^2$

But $H_0 \Psi_n = E_n \Psi_n$

$(-\hbar^2/2m)\, \partial^2 \Psi n/\partial x^2 + \frac{1}{2} kx^2 \Psi_n = E_n \Psi_n$

$\partial^2 \Psi n/\partial x^2 + 2m/\hbar^2 (E_n - \frac{1}{2} kx^2)\Psi_n = 0$

This is a simple harmonic oscillator equation having the energy values

$E_n = (n+1/2)\, \hbar\, (k/m)^{\frac{1}{2}}$

$= (n+1/2)\, \hbar\omega,$ $n = 0,1,2,........$

Where ω is angular frequency of oscillations given by

$\omega = (k/m)^{\frac{1}{2}}$

$E_0 = 1/2\, \hbar\omega$ (for n=0) (13.10.B.4)

Similarly $E_n = (n+1/2)\, \hbar\omega$

Ist Order Perturbation Energy:

$E' = <m \mid H' \mid m>$

$E' = < \Psi_0(x) \mid H' \mid \Psi_0(x)>$

Where $\Psi_0(x) = N_0 e^{-\alpha^2 x^2/2}$ (13.10.B.5)

$N_0 = \sqrt{(\frac{\alpha}{\sqrt{\pi}})}$ and $\alpha^4 = mk/\hbar^2$ (13.10.B.6)

But from (13.10.B.3), $H' = \frac{1}{2} bx$

$E' = < \Psi_0 \mid H' \mid \Psi_0>$

$=< \Psi_0 \mid \frac{1}{2} bx \mid {}_0>$

$= \int N_0 e^{-\alpha^2 x^2/2}\, \frac{1}{2} bx\, N_0 e^{-\alpha^2 x^2/2}\, dx$

$= 0$

Since $\int x e^{-x^2} dx = 0$

We should remember that if function H' in E' is odd like $x, x^3, x^5, \ldots\ldots$, Then E' will be zero definitely. Hence 1st order energy E' is zero.

2nd Order Perturbation Energy:

We know that

$$E'' = {\sum}'_m \{ |\langle n | H' | m \rangle|^2 / (E_m - E_n) \} \qquad (13.10.B.7)$$

The prime on summation shows that m=n term is omitted.

We have $\langle n | H' | m \rangle = \langle \Psi_n |x| \Psi_m \rangle$

From the knowledge of eigenfunctions of harmonic oscillator, we know that

$$\langle \Psi_n |x| \Psi_m \rangle = \begin{cases} 1/\alpha\ (n+1/2)^{1/2} & \text{for } m=n+1 \\ 1/\alpha\ (n/2)^{1/2} & \text{for } m=n-1 \\ 0 & \text{otherwise} \end{cases} \qquad (13.10.B.8)$$

$$\langle \Psi_n |x| \Psi_m \rangle = (1/\alpha)\ (m/2)^{1/2} \qquad \text{for } m=n+1$$

If n=0, m=1, then

$$\langle \Psi_0 |x| \Psi_1 \rangle = (1/\alpha)(1/2)^{1/2}$$

So $$\langle \Psi_0 | H' | \Psi_1 \rangle = \tfrac{1}{2}\, b.\ (1/\ )(1/2)^{1/2}$$

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

$$|\langle \Psi_0 | H' | \Psi_1 \rangle|^2 = b^2/(8\alpha^2)$$

On substituting (13.10.B.8), in (13.10.B.7) we get E'' for zero state

$$E''^0 = \frac{b^2/8\alpha^2}{\frac{3}{2}\hbar\omega - \frac{1\hbar\omega}{2}}$$

$$= b^2/(8\alpha^2\hbar\omega) \qquad (13.10.B.9)$$

Hence total correction for ground state up to second order is given by

$$E = E_0 + E'^0 + E''^0$$

$$= 1/2\ \hbar\omega + b^2/(8\alpha^2\hbar\omega)$$

But in general

$$E = E_n + E'_n + E''_n$$

Where $E''_n = {\sum}'_m \langle n \mid H' \mid m\rangle|^2 / (E_m - E_n)$

$$= {\sum}'_m |b/2 \langle n \mid H' \mid m\rangle|^2 / (E_m - E_n)$$

Substituting (13.10.B.8) in above expression, we get

$$E''_n = \left\{ \begin{array}{ll} {\sum}'_m (b^2/4) .(1/\alpha^2)(m/2)/ (E_m - E_n) & \text{for } m=n+1 \\ {\sum}'_m (b^2/4).(1/\alpha^2) (n/2)/ (E_m - E_n) & \text{for } m=n-1 \\ 0 & \text{otherwise} \end{array} \right\} \qquad (13.10.B.10)$$

For m=n+1, $(E_m - E_n) = (n+1+1/2)\hbar\omega - (n+1/2)\hbar\omega$

$$= \hbar\omega$$

And for m=n−1, $(E_m - E_n) = -\hbar\omega$

$$E''_n = \left\{ \begin{array}{ll} {\sum}'_m [b^2/(4\alpha^2)] \{(n+1)/2\}.(1/ \hbar\omega) & \text{for } m=n+1 \\ {\sum}'_m [b^2/(4\alpha^2)] (n/2).(1/ \hbar\omega\ ) & \text{for } m=n-1 \\ 0 & \text{otherwise} \end{array} \right\} \qquad (13.10.B.11)$$

So total corrected energy for nth state E_n is

$E_n = (n+1/2)\hbar\omega + E''$, where E''_n is given by (13.10.B.11).

Case 2: When Perturbation energy term is proportional to x^2:

Let the Hamiltonian be given by

$$H = p^2/2m + \tfrac{1}{2} kx^2 + \tfrac{1}{2} bx^2 \qquad (13.10.B.12)$$

$$= H_0 + H' \qquad (13.10.B.12a)$$

Where unperturbed Hamiltonian $H' = p^2/2m + \tfrac{1}{2} kx^2$

And perturbation correction term $H' = 1/2\ bx^2$

Angular frequency

$$\omega = \sqrt{\frac{k+b}{m}} = \sqrt{\left\{\frac{k}{m}\left(1+\frac{b}{k}\right)\right\}}$$

$$=\sqrt{\frac{k}{m}}\left(1+\frac{1}{2}\frac{b}{k}-\frac{1}{8}\frac{b^2}{k^2}+\ldots\ldots\right)$$

$$=\omega_0\left(1+\frac{1}{2}\frac{b}{k}-\frac{1}{8}\frac{b^2}{k^2}+\ldots\ldots\right)$$

Where $\omega_0=\sqrt{\frac{k}{m}}$=angular frequency of free vibrations.

So we shall get corrected energy E_n,

$$E_n=(n+1/2)\,\hbar\omega_0\left(1+\frac{1}{2}\frac{b}{k}-\frac{1}{8}\frac{b^2}{k^2}+\ldots\ldots\right)$$

$$E_n=(n+1/2)\,\hbar\sqrt{\frac{k}{m}}\left(1+\frac{1}{2}\frac{b}{k}-\frac{1}{8}\frac{b^2}{k^2}.\right)$$

As $H'=(1/2)\,bx^2$; so first order energy

$$E'=\langle n\,|\,H'\,|\,n\rangle=(b/2)\langle n\,|\,x^2\,|\,n\rangle$$

We have $|\,n\rangle=\Psi_n=N_nH_n(\alpha x)\,e^{-\alpha^2x^2/2}$

$$N_n=[\alpha/(\sqrt{\pi}\,2^n\,n!)^{1/2}]$$

$$\langle n\,|\,x^2\,|\,n\rangle=\int\Psi_n^*\,x^2\,\Psi_n\,dx$$

$$=N_n^*N_n\int H_n\,e^{-\alpha^2x^2/2}\,x^2\,H_ne^{-\alpha^2x^2/2}dx$$

$$=|\,N_n\,|^2\int H_n^2\,x^2\,e^{-\alpha^2x^2}dx$$

Solving integral by the help of generating function, we get

$$\langle n\,|\,x^2\,|\,n\rangle=(2n+1)/(2\alpha^2)$$

So $E'_n=b/2\langle n\,|\,x^2\,|\,n\rangle=(b/2)\,(2n+1)/(2\alpha^2)$

$$=(2n+1)(b/4\alpha^2)$$

and we know $\alpha=(mk/\hbar^2)^{1/4}$

$$E'_n=(b/4)\,(\hbar^2/mk)^{1/2}\,(2n+1) \qquad (13.10.B.13)$$

Hence $E_n=E_n^0+E'_n$

$$E_n=(n+1/2)\,\hbar\sqrt{\frac{k}{m}}+(b/4)\,(\hbar^2/mk)^{1/2}\,(2n+1)$$

$$= (n+1/2)\,\hbar\sqrt{\frac{k}{m}}\,[1+\frac{b}{2}\sqrt{\frac{m}{k}}\;\sqrt{\frac{1}{mk}}\;]$$

$$E_n = (n+1/2)\,\hbar\sqrt{\frac{k}{m}}\;[1+\frac{b}{2k}] \qquad (13.10.B.14)$$

By adding the value of E''_n, we get correction up to second order for nth state.

So

$$E_n = (n+1/2)\,\hbar\sqrt{\frac{k}{m}}\;\{1+\frac{b}{2k}-\frac{1}{2}\frac{b^2}{k^2}\} \qquad (13.10.B.15)$$

13.10 Self Learning Exercise

Q.1 Calculate the ground state energy up to first order of the anharmonic oscillator having a potential energy

$V=1/2\, m\omega^2x^2+ax^3;\ ax^3<<1/2\, m\omega^2x^2,$

where *a* is independent of *x*.

Q.2 Evaluate the first and second order correction to the energy of the ***n=1*** state of an oscillator of mass ***m*** and angular frequency ***w*** subjected to a potential

$V(x) = 1/2\, m\omega^2x^2+ bx,\ bx<<1/2\, m\omega^2x^2.$

Q.3 A particle of mass m_0 and charge ***e*** oscillates along the x-axis in a one dimensional harmonic potential with an angular frequency ω. If an electric field ϵ is applied along x-axis, evaluate the first and second order corrections to the energy of the nth state.

Q.4 A simple harmonic oscillator of mass m_0 and angular frequency ω perturbed by an additional potential bx^3. Evaluate the second order correction to the ground state energy of the oscillator.

13.11 Summary

In this unit we have detailed study of stationary perturbation theory non degenerate case and physical application of non degenerate perturbation theory using the Schrodinger wave equation

13.12 Glossary

Kronecker Delta: It is given as: $\int \Psi_i^0 \Psi_j^0 d\tau = \delta_{ij}$

Here δ_{ij} is known as Kronecker Delta.

Hamiltonian Operator: The expression for the classical Hamiltonian function of a particle of mass m, moving with a momentum p in a potential field $V(r)$ is

$$H = \frac{p^2}{2m} + V(r)$$

Orthonormal Functions: These are the functions which hold good for both conditions of orthogonality and normalisation.

13.13 Answer to Self Learning Exercise

Ans.1: $E'_0 = \langle 0|ax^3|0\rangle$. The integrand of this integral is an odd function of x and, therefore, the first order correction to the ground state energy is zero.

Ans.2: The first order correction to energy for the n=1 state is given by

$$E'_1 = \langle 1 \mid bx \mid 1\rangle = b(\hbar/2m\omega)^{\frac{1}{2}} \langle 1 \,|a+a'|\, 1\rangle$$

$$= b(\hbar/2m\omega)^{\frac{1}{2}} [\langle 1|a|1\rangle + \langle 1|a'|1\rangle] = 0$$

Since $a|n\rangle = \sqrt{n}\, |n-1|\rangle$ and $a'|n\rangle = \sqrt{n(n+1)}\, |n+1|\rangle$

$$E_1^{2} = b^2\, (\hbar/2m\omega) \sum{}' \, |\langle 1 \,|a+a'|\, k\rangle|^2 / E_1^0 - E_k^0$$

$$= b^2\, (\hbar/2m\omega)\, [1/E_1^0 - E_0^0 + 2/E_1^0 - E_2^0]$$

$$= b^2\, (\hbar/2m\omega)\, (1/\hbar\omega - 2/\hbar\omega)$$

$$= \frac{-b^2}{2m\omega^2}$$

Ans.3: The potential energy due to the field $\epsilon = -e\boldsymbol{\epsilon}x$

The perturbation $H' = -e\boldsymbol{\epsilon}x$

First order correction $E_n^{'} = -e\boldsymbol{\epsilon}\langle n\, |x|\, n\rangle$

In terms of ***a*** and ***a***′, $x = (\hbar/2m_0\omega)^{\frac{1}{2}}\, (a+a')$

$$E_n^1 = -e\epsilon(\hbar/2m_0\omega)^{\frac{1}{2}} \langle n \,|\, a+a' \,|\, n\rangle = 0$$

$$E_n^2 = {\sum}'_m |\langle n \,|\, H' \,|\, m\rangle|^2 / E_n^0 - E_m^0$$

$$\langle n \,|\, H' \,|\, m\rangle = -e\epsilon(\hbar/2m_0\omega)^{\frac{1}{2}} \langle n \,|\, a+a' \,|\, m\rangle$$

Here, m can take all integral values except n. The non-vanishing elements correspond to m=(n+1) to (n−1). Hence

$$E_n^2 = e^2\epsilon^2(\hbar/2m_0\omega)\left[\frac{(\sqrt{n}+1)^2}{-\hbar\omega} + \frac{(\sqrt{n})^2}{\hbar\omega}\right]$$

$$= -\, e^2\epsilon^2/2m_0\omega^2$$

Ans.4: The second order correction to the ground state energy is given by

$$E_0^2 = {\sum}'_m \; |\langle 0 \,|\, H' \,|\, m\rangle|^2 / E_0^0 - E_m^0 \;, \; H' = bx^3$$

In terms of ***a*** and ***a'***

$$x = (\hbar/2m_0\omega)^{\frac{1}{2}} (a+a')$$

$$\langle 0 \,|x^3|\, m\rangle = (\hbar/2m_0\omega)^{\frac{3}{2}} \langle 0|(a+a')(a+a')(a+a')|m\rangle, \quad m=1,2,3,\ldots$$

$$= (\hbar/2m_0\omega)^{\frac{3}{2}} [\langle 0 \,|aaa|\, 3\rangle + \langle |aaa'+aa'a|\, 1\rangle]$$

The other contributions vanish. For the non-vanishing contributions, we have

$$\langle 0|aaa|3\rangle = \sqrt{6}, \qquad \langle 0|aaa'+aa'a|\, 1\rangle = 2+1 = 3$$

$$E_0^2 = b^2(\hbar/2m_0\omega)^3 \left(\frac{6}{-3\hbar\omega} + \frac{9}{-\hbar\omega}\right) \qquad = -11\, b^2\hbar^2/8m_0^3\omega^4$$

13.14 Exercise

Q.1 What do you mean by perturbation theory ? discuss the perturbation theory for non-degenerate levels in first and second orders.

Q.2 Apply the perturbation theory to derive the energy of helium atom in its normal state.

Q.3 Discuss the first order perturbation theory for a non-degenerate level.

Q.4 A Harmonic oscillator of natural frequency ω is placed in a small external potential $\frac{1}{2}\lambda x^4$. By how much is the energy of the ground state changed?

Q.5 A particle moves in a potential field given by

$\Psi(x)=1/2\ kx^2+ax^4$. Treating the term ax^4 as a perturbation, calculate ground state energy for the particle.

Q.6 A one dimensional harmonic oscillator of charge e is perturbed by an electric field of strength E in the positive x-direction. Calculate the change in each energy level to second order in the perturbation for three dimensional isotropic oscillator. Define also polarizibility.

Q.7 By using first order time-independent perturbation theory obtain the correct eigenfunctions and eigenvalues.

Q.8 Consider the infinite square well defined by

$V(x) = 0 \quad \text{for } 0 \leq x < a$

$V(x) = \infty$ otherwise

Using the first order perturbation theory, calculate the energy of the first two states of the potential well if a portion defined by

$V(x)=V_0x/a$, where V_0 is a small constant, with $0 \leq x \leq a$ being sliced off.

Q.9 Calculate the first order correction to the ground state energy of an anharmonic of mass ***m*** and angular frequency ω subjected to a potential

$$V(x)= 1/2\ m\omega^2x^2+ bx^4,$$

where ***b*** is a parameter independent of ***x***. The ground state wave function is

$$\Psi_0{}^0=\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} exp\left(\frac{-m\ \omega x^2}{2\hbar}\right)$$

Q.10 Describe the behaviour of the wave function near origin if the field becomes infinite as $\frac{\alpha}{r^s}$,with s>2, where $r \longrightarrow 0$.

Q.11 (A) The nucleus of an atom in the normal state receives an impulse which gives it ***a*** velocity. Assuming the duration τ of the impulse as very short in comparison both with the electron periods and with a/v (where a is atomic dimension), determine the probability of extinction of the atom under the influence of such a jolt.

(B) determine the total probability of excitation and ionisation of an atom of hydrogen which receives a sudden jolt.

Q.12 A Hydrogen atom in the ground state is placed in an electric field ϵ along the z-axis. Evaluate the first order correction to the energy.

13.15 Answers to Exercise

Ans.9: The first order correction to the ground state energy

$$E_0^{'} = <\Psi_0^0|H|\Psi_0^0> = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} b\int_{-\infty}^{\infty} x^4 \exp\left(\frac{-m\omega x^2}{\hbar}\right)dx$$

Using the result given in the appendix, we get,

$$E_0^{'} = b\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} 2.\frac{3\pi}{8}\left(\frac{\hbar}{m\omega}\right)^{\frac{5}{2}}$$

$$= \frac{3b\hbar^2}{4m^2\omega^2}$$

Ans.10: For small r the approximate wave length is given by

$$\lambda \approx \frac{2\pi\hbar}{\sqrt{2m|V|}} \approx \frac{2\pi\hbar\, r^{\frac{s}{2}}}{\sqrt{2m\alpha}}$$

which gives $\frac{d\lambda}{dr} \approx \frac{\pi s\hbar}{\sqrt{2m\alpha}} r^{\frac{s-2}{2}} << 1$

which satisfies the condition (6.10) for quasi-classical case. For attractive field $V_1 \approx -\infty$, as $r \longrightarrow 0$ and the region near the origin is classically accessible and the radial wave function is

$$u \approx \frac{1}{\sqrt{p}}$$

giving $\Psi \approx r^{\frac{s-4}{4}}$ (6.10)

In a repulsive field, the region of small r is classically inaccessible and the wave function tends to zero exponentially as $r \longrightarrow 0$. Thus we have

$$\Psi \approx \exp \frac{-1}{\hbar}\int_{\alpha}^{r} p\, dr$$

or $$\Psi \approx \exp\left[\frac{2\sqrt{2m\alpha}}{(s-2)\hbar}\, r^{-\frac{(s-2)}{2}}\right] \qquad (6.11)$$

Ans.11: (A) Since the duration of impact τ<<a/v, the nucleus may be regarded as practically stationary during the impact and hence the coordinates of the nucleus in the frame K'(moving with nucleus after impact) are the same as in the original frame K, the initial wave function in K' is

$$\Psi'_{\mathrm{I}} = \Psi_0 \exp(i\mathbf{q} \sum_j r_j$$

where q=mv/ħ and Ψ_0 is the wave function of the normal state with the nucleus at rest. The summation over j for all electrons in the atom. The required probability of transition to the nth excited state is

$$P_n\mathrm{I} = |\langle n\, |\exp(-iq. \sum_J r_j)\,|\, \mathrm{I} \rangle|^2$$

(B) In hydrogen atom the atomic number is unity and hence the required probability is

$$1-P_{\mathrm{II}} = 1-|\int \Psi_{\mathrm{I}}^2 e^{-iq.r} dr\,|^2$$

Where P_{II} is the probability that atom will remain in the ground state

$\Psi_{\mathrm{I}} = ((\pi a^3)^{\frac{-1}{2}} e^{\frac{-r}{a}}$.

Thus we have

$$P_{\mathrm{II}} = \frac{1}{(1+\frac{1}{4}q^2a^2)^4}$$

Now the required probability is $1-\frac{1}{(1+\frac{1}{4}q^2a^2)^4}$.

Ans.12: Consider an atom situated at the origin. If r is the position vector of the electron, the dipole moment

$$\mu = -er$$

The additional potential energy in the electric field ϵ is $-\mu.\epsilon$, where θ is the angle between vectors r and ϵ. This energy can be treated as the perturbation

$$H' = er\,\epsilon\,\cos\theta$$

The unperturbed Hamiltonian

$$H^0 = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

The unperturbed wave function

$$\Psi_{100} = \frac{1}{\pi^{\frac{1}{2}} a_0^{\frac{3}{2}}} e^{\frac{-r}{a_0}}$$

The first order correction to the energy

$$E'_1 = <100\,|er\epsilon\cos\theta|\,100>$$

The angular part of this equation is

$$\int_0^{\pi} \cos\theta\,\sin\theta\,d\theta = 0$$

i.e. the first order correction to the energy is zero.

References and Suggested Readings

1. Lectures on Quantum Mechanics by Steven Weinberg.
2. Quantum Mechanics and Quantum Information by Moses Fayngold and Vadim Fayngold.
3. Quantum Mechanics by David Mcintyre.
4. Concepts of Quantum Mechanics by Vishnu Swarup Mathur and Surendra Singh

UNIT-14

Perturbation Theory for Degenerate Systems

Structure of the Unit

14.0 Objectives

In this unit, we study about the degenerate case of the stationary perturbation theory. When in a system in which a number of orthogonal eigenfunctions correspond to the same eigenvalue, then this system is known as degenerate system. So the main objective of this unit is to study the characteristics of degenerate case of the stationary perturbation theory.

14.1 Introduction

When a degeneracy exists, a linear combination of the degenerate wave functions can be taken as the unperturbed wave function. As an example, consider the case in which E_n^0 is two-fold degenerate.

Let Ψ^0_1 and Ψ^0_2 be eigenfunctions corresponding to the eigenvalues $E_n^0=E_l^0$ and let the linear combination be

$$\phi=\alpha_1\Psi_1^0+\alpha_2\Psi_2^0$$

α_1 and α_2 be constants.

14.2 Stationary perturbation theory: degenerate case

We have assumed that there is one Eigen function for one eign value and have found for the first order correction to wave function as

$$\Psi\acute{k}=\sum a_i\Psi_i^0$$

Where, $a_l = < l\,|H'|m > / (E_m^0 - E_l^0)$

This causes difficulty if the two states $m=l$ correspond to same energy

$E_m^0 = E_l^0$ unless $< l\,|H'|m >= 0.$ As $< l|H'|m >\neq 0,$

In this case, there are systems in which a number of orthogonal eigen functions correspond to the same eigenvalue . Then the system is called degenerate system ; ***the order of degeneracy being equal to the number of eigen-states corresponding to same eigen value***. In such case the perturbation method is as follows :

Suppose two eigen states $\psi_1{}^0$ and $\psi_2{}^0$ having same eigenvalue in unperturbed system i.e. $E_1{}^0=E_2{}^0=E^0$ (say);so that

$$H^0\Psi_1{}^0=E^0\Psi_1{}^0 \text{ and } H^0\Psi_2{}^0=E^0\Psi_2{}^0 \qquad (14.2.1)$$

Eigen function is linear combination of these two will also be an eigenfunction corresponding to this energy . Thus

$$\Psi^0=\alpha_1\Psi_1{}^0+\alpha_2\Psi_2{}^0 \qquad (14.2.2)$$

and $\quad H^0\Psi^0=H^0(\alpha_1\Psi_1{}^0+\alpha_2\Psi_2{}^0)$

$$= \alpha_1 H^0 \Psi_1{}^0 + \alpha_2 H^0 \Psi_2{}^0 = \alpha_1 E^0 \Psi_1{}^0 + \alpha_2 E^0 \Psi_2{}^0$$

$$= E^0 (\alpha_1 \Psi_1{}^0 + \alpha_2 \Psi_2{}^0)$$

i.e. $H^0\Psi^0 = E^0\ \Psi^0$ (14.2.3)

Applying orthonormal properties of $\Psi_1{}^0$ and $\Psi_2{}^0$, we have

$$\alpha_1{}^*\alpha_1 + \alpha_2{}^*\alpha_2 = 1 \qquad (14.2.4)$$

There may be an infinite number of eigenfunctions which may be built out of these two eigenfunctions corresponding to same eigenvalue E^0 . Then a set of n-functions is linearly independent if there exists no relation of the form

$$\alpha_1\Psi_1{}^0 + \alpha_2\Psi_2{}^0 + \alpha_3\Psi_3 + \ldots\ldots.. + \alpha_n\Psi_n{}^0 = 0 \qquad (14.2.5)$$

If there are linearly independent eigen functions corresponding to the same eigen value , the state is said to be n-fold degenerate and any other function possessing the same energy can be expressed as

$$\Psi^0 = \alpha_1\Psi_1{}^0 + \alpha_2\Psi_2{}^0 + \ldots\ldots.. + \alpha_n\Psi_n{}^0 \qquad (14.2.6)$$

Applying the normalisation condition of ψ's, we get

$$\alpha_1{}^*\alpha_1 + \alpha_2{}^*\alpha_2 + \ldots\ldots.. + \alpha_n\alpha_n{}^* = 1 \qquad (14.2.7)$$

Let us we take the perturbed system for which the Schrodinger wave equation is

$$H\Psi = E\Psi$$

Where $H = H^0 + \lambda H'$

So that $(H^0 + \lambda H')\ \Psi = E\Psi$ (14.2.8)

For $\lambda \rightarrow 0$ the system tends to the unperturbed state and let for this case the system be s-fold degenerate.Then the unperturbed schroedinger equation

$$H^0\Psi^0 = E^0\Psi^0 \qquad (14.2.9a)$$

Has the solutions

$$\Psi^0{}_{11}, \Psi^0{}_{12}, \Psi^0{}_{13} \ldots. \Psi^0{}_{1s},\ \Psi^0{}_{21}, \Psi^0{}_{22}, \Psi^0{}_{23} \ldots. \Psi^0{}_{2s} \ldots..$$

$$\Psi^0{}_{k1},\ \Psi^0{}_{k2},\ \Psi^0{}_{k3}, \ldots \Psi^0{}_{ks}, \ldots.. \qquad (14.2.9b)$$

Coresponding to eigen values

$$E_1{}^0, E_2{}^0, \ldots, E^0{}_k \ldots \text{respectively.} \qquad (14.2.9c)$$

Let $\Psi^0{}_{k1}, \Psi^0{}_{k2}, \Psi^0{}_{k3}, \ldots \Psi^0{}_{ks}$ represent some arbitrary chosen orthonormal set of eigen functions . The problem in degenerate system is to find the set of unperturbed wavefunctions to which the perturbed functions reduce when the perturbation vanishes i.e. the evaluation of the coefficients in the linear combination converting the initially chosen wavefunctions into the *correct zeroth order wavefunctions* .

Let the correct eigenfunction in zero approximations be represented by the linear combination

$$\Psi_k{}^0=\sum^{s}{}_{l=1}\;{}_{kl}\Psi_{kl}{}^0 \qquad (14.2.10)$$

The eigenvalue and eigenfunction of perturbed system may be expressed as

$$E_k = E_k{}^0+\lambda\, E_k{}'+\lambda^2\, E_k{}''+\ldots\ldots \qquad (14.2.11)$$

$$\Psi_k = \Psi_k{}^0+\lambda\, \Psi_k{}'+\lambda^2\, \Psi_k{}''+\ldots\ldots$$

$$= \sum^{s}{}_{l=1}\alpha_{kl}\Psi_{kl}{}^0+\lambda\, \Psi_k{}'+\lambda^2\, \Psi_k{}''+\ldots\ldots \qquad (14.2.12)$$

Using (14.2.10)

Substituting theses values in (8), we get

$$(H^0+\lambda H')\left(\sum^{s}{}_{l=1}\alpha_{kl}\Psi_{kl}{}^0+\lambda\, \Psi_k{}'+\lambda^2\, \Psi_k{}''+\ldots\ldots\right)$$

$$=(E_k{}^0+\lambda E_k{}'+\lambda^2 E_k{}''+\ldots\ldots)\left(\sum^{s}{}_{l=1}\alpha_{kl}\Psi^0{}_{kl}+\lambda\Psi_k{}'+\lambda^2\, \Psi_k{}''+\ldots\ldots\right)$$

$$(14.2.13)$$

Comparing coefficients of like powers of λ, we get

$$H^0\sum^{s}{}_{l=1}\alpha_{kl}\Psi^0{}_{kl}= E_k{}^0\sum^{s}{}_{l=1}\alpha_{kl}\Psi^0{}_{kl} \qquad (14.2.14a)$$

or $$(H^0-E_k{}^0)\,\Psi'{}_k=\sum^{s}{}_{l=1}\alpha_{kl}(E_k{}'-H')\,\Psi^0{}_{kl} \qquad (14.2.14b)$$

And so on.

The perturbed wavefunctions may be expressed in terms of unperturbed wave functions like

$$\Psi'{}_{k}=\sum C_{mj}\Psi^0{}_{mj} \qquad (14.2.15)$$

where C_{mj} are constants and $\Psi^0{}_{mj}$ correspond to state.

Then

$$H^0 \Psi'_k = H^0 \sum C_{mj} \Psi^0_{mj}$$

$$= \sum C_{mj} H^0 \Psi^0_{mj} = \sum C_{mj} E^0 \Psi^0_{mj} \qquad (14.2.16)$$

Substituting these values in (14b), we get

$$(H^0 - E_k^0) \sum C_{mj} \Psi^0_{mj} = \alpha_{kl}(E_k' - H')\Psi^0_{kl}$$

i.e. $$\sum C_{mj}(E_m^0 - E_k^0)\Psi^0_{mj} = \sum \alpha_{kl} E_k' \Psi^0_{kl} - \sum \alpha_{kl} H' \Psi^0_{kl}$$

(14.2.17)

Multiplying both sides by $\Psi^0_{np}*$ and integrating over all configuration space, we get

$$\sum C_{mj}(E_m^0 - E_k^0) \int \Psi^0_{np}* \ \Psi^0_{mj} \, d\tau$$

$$= \sum \alpha_{kl} E_k' \int \Psi^0 np * \Psi^0_{kl} \, d\tau - \sum \alpha_{kl} \int \Psi^0_{np}* H' \Psi^0_{kl} \, d\tau$$

or $$\sum C_{mj}(E_m^0 - E_k^0)_{nm} \delta_{pj} = \sum \alpha_{kl} E_k' \delta_{nk} \delta_{pl} - \sum \alpha_{kl} \int \Psi^0_{np} * H' \Psi^0_{kl} \, d\tau$$

(14.2.18)

14.3 Energy Correction and Secular Equation

Let us chose $n=k$, then

$$\sum C_{mj}(E_m^0 - E_k^0)_{km} \delta_{pj} = \sum \alpha_{kl} E_k' \delta_{pl} - \sum \alpha_{kl} \int \Psi^0_{kp} * H' \Psi^0_{kl} \, d\tau \qquad (14.3.1)$$

In above equation L.H.S. is always zero since when $k=m$, it is zero due to $(E_m^0 - E_k^0)$ and when $k \neq m$ it is zero due to $\delta_{km,}$ So, equation (19) gives

$$\sum \alpha_{kl} \int \Psi^0_{kp} * H' \Psi^0_{kl} \, d\tau - \sum \alpha_{kl} E_k' \delta_{pl} = 0$$

By using notations

$$\int \Psi^0_{kp} * H' \Psi^0_{kl} \, d\tau = < p|H'|l > = H'_{pl},$$

We get $\sum (H'_{pl} - E_k' \delta_{pl}) \alpha_{kl} = 0$ (14.3.2)

These simultaneous equations can be written as

$$(H_{11} - E_k')\alpha_{k1} + H'_{12}\alpha_{k2} + H'_{13\ k3} + \dots\dots + H'_{1S}\alpha_{ks} = 0$$

$$H'_{21}\alpha_{k1} + (H_{22} - E_k')\alpha_{k2} + H'_{23}\alpha_{k3} + \dots\dots + H'_{2S}\alpha_{ks} = 0$$

....

....

$$H'_{s1}\alpha_{k1}+H'_{s2}\alpha_{k2}+H'_{s3}\alpha_{k3}+\dots\dots+(H_{ss}-E_k')\alpha_{ks}=0 \tag{14.3.3}$$

If neither of coefficients α_{kl} is zero , the determinant of coefficients of α_{kl} (l=1,2.....s)must vanish i.e.

$$\begin{vmatrix} (H_{11}-E_k') & H'_{12} & H'_{13} & \cdots & H'_{1S} \\ H'_{21} & (H_{22}-E_k') & H'_{23} & \cdots & H'_{2S} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ H'_{s1} & H'_{s2} & H'_{s3} & \cdots & (H_{ss}-E_k') \end{vmatrix} = 0$$

Since H'_{pl} are known , it is an equation of sth degree in E_k' and has s-solutions of E_k'given by E_{k1}',E_{k2}',E_{k3}',.......... E_{ks}'. Such an equation is called ***secular equation*** and the perturbation of this type is called **secular perturbation .**

If this equation gives all the roots E_k' *different , the solutions have completely , removed degeneraey : but it may happen that not all the roots* E_k' *are distinct in which case perturbation has not completely removed degeneracy.*

It is remarkable that in case the secular equation has the form

$$\begin{vmatrix} (H_{11}-E_k') & 0 & 0 & \cdots & 0 \\ 0 & (H_{22}-E_k') & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & (H_{ss}-E_k') \end{vmatrix} = 0 \tag{14.3.5}$$

Initially we chosen functions Ψ_k^0 are correct zeroth order functions for the perturbation H′ . For such an equation the roots of E_k' can be given by following equations

$$(H_{11}-E_k')(H_{22}-E_k')\dots\dots\dots(H_{ss}-E_k')=0 \tag{14.3.6}$$

So that $H'_{11}=E_{k1}'$, $H'_{12}=E_{k2}'$ ....and $H'_{ss}=E_{ks}'$

For solving the eigenfunctions corresponding to roots E_{k1}' , E_{k2}' , ... E_{ks}', a particular root is substituted in (14.2.20) and solved for the ratios

$$\frac{\alpha}{\alpha} = \frac{\sum_{l=1}^{s} H'}{E'} \qquad (14.3.7)$$

From the normalisation condition, we get

$$\alpha^*_{k1}\alpha_{k1} + \alpha^*_{k2}\alpha_{k2} + \ldots\ldots + \alpha^*_{ks}\alpha_{ks} = 1$$

It helps in determining α_{kp}.

For p >s, $\alpha_{kp}=0$, so that we get from (14.2.18)

$$C_{np}(E_n{}^0 - E_k{}^0) = \sum_{l=1}^{s} \alpha_{kl}\, H'_{pl}$$

$$\text{i.e.} \quad C_{np} = \frac{\sum_{l=1}^{s} \alpha_{kl}\, H'_{pl}}{(E_n^0 - E_k^0)} \quad \text{i.e.} \quad C_{mj} = \frac{\sum_{l=1}^{s} \alpha_{kl}\, H'_{jl}}{(E_k^0 - E_m^0)} \qquad (14.3.8)$$

Normalisation of $\Psi_{k,}$ $C_{np}=0$ for $p \leq s$ and we can write the first order perturbation eigen function and eigen value as

$$\Psi_k = \sum_{l=1}^{s} \alpha_{kl} \Psi_{kl}^0 \quad + \lambda$$

$$\text{and} \qquad E_k = E_k{}^0 + \lambda\, E_k' \qquad (14.3.9)$$

14.4 Application of stationary degenrate perturbation theory (first order stark effect in hydrogen atom)

This phenomenon was discovered by Stark in 1413 , while observing Balmer lines of hydrogen with an electric fields of strength 10^5 volt/cm. It states that ***"The splitting of energy levels of an atom caused by a uniform external electric field E is called*** **Stark-Effect."** In this, we shall discuss the energy shifts of Stark effects by perturbation theory . As in Zeeman effect let us choose the unperturbed initial states with a direction of the perturbing electric field along the Z-axis and use the eigen states of L_z.

The force apply on electron of charge $q=-e$, *(e* being positive quantity) in an electric field of strength E is

$$F_e = qE = -eE$$

Field is along Z-axis , therefore extra-energy of electron in electric field $=F_E z= -eEz$

The Schrodinger wave equation for this case is

$$\nabla^2\Psi + \frac{2\mu(W+\frac{Ze^2}{r}+eEZ)\Psi}{\hbar^2} =0 \qquad (14.4.1)$$

where W is the total energy and $\frac{-Ze^2}{r}$, $-eEz$ is the potential energy ofelectron in atom.

Equation (1) may also be written as

$$(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} - eEz)\Psi = W\Psi$$

i.e. $(H^0+H')\Psi=W\Psi$ (14.4.2)

where the unperturbed Hamiltonian;

$$H_0= \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} \qquad (14.4.3)$$

and the first order perturbed Hamiltonian term

$H' = -eEz$

If we use polar co-ordinates (r,θ), $then\ z = r\cos\theta$

and so $H' = -eEz = -eEr\cos\theta$ (14.4.4)

e being again a +ve quantity.

The potential energy is spherically symmetric. We know that the wave functions for any spherically symmetric potential energy . When expressed in spherical harmonics , have even or odd parity according as the azimuthal quantum number is even or odd.

14.4.1 First order stark effect in ground state of hydrogen atom:

The ***ground state of Hydrogen atom is*** specified by

n=1, l=0, m=0

The ground state (n=1, l=0, m=0) of hydrogen atom is non-degenerate state and the corresponding spherically symmetric wave function is given by

$$\Psi_{100}=R_{10}(r)\quad Y_{100}(\theta,\phi) = \frac{1}{\sqrt{\pi a_0{}^3}}e^{\frac{-r}{a_0}}$$

where $a_0 = \frac{\hbar^2}{\mu e^2}$ $is\ the\ radius\ of\ Bohr's\ first\ orbit.$

The first order perturbation energy correction is given by

$$W = \int \Psi^*_{100} H\, \Psi_{100} d\tau$$

$$= \iiint \frac{1}{\sqrt{\pi a_0{}^3}} e^{\frac{-r}{a_0}} (-eEr\cos\theta) \frac{1}{\sqrt{\pi a_0{}^3}} e^{\frac{-r}{a_0}} r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= \frac{-eE}{\pi a_0{}^3} \int_0^\infty r^3 e^{\frac{-2r}{a_0}} dr \int_0^\pi sin\theta cos\theta d\theta \int_0^{2\pi} d\phi = 0$$

Since $\int_0^\pi sin\theta cos\theta d\theta = 0$

Hence for ground state of hydrogen there is no first order Stark effect. Thus we may say that only the non-zero matrix elements of H' are those that have odd parity since the perturbation term H' is odd with respect to inversion (odd parity).

14.4.2 First order stark effect in excited state of hydrogen atom:

Let us know consider the first excited state n=2 for hydrogen atom , Since n=2, therefore l=o,1 and m=1, 0, −1 and hence the quantum number (l,m) can have the following combinations.

(0,0),(1,0),(1,1) and(1,−1)

Thus the wave-function Ψ_{lmn} is four-fold degenerate , i.e., the wave – functions Ψ_{200},Ψ_{210},$\Psi_{211}$and Ψ_{21-1} all have same energy .

The secular equations refer eqn. (14.3.4) for the first order stark effect in the form of determinant is

$$\begin{vmatrix} (<0,0|H'|0,0>-W_1) & (<1,0|H'|0,0>) & (<1,1|H'|0,0>) & (<1,-1|H'|0,0>) \\ (<0,0|H'|1,0>) & (<1,0|H'|1,0>-W_1) & (<1,0|H'|1,1>) & (<1,-1|H'|1,0>) \\ (<0,0|H'|1,1>) & (<1,0|H'|1,1>) & (<1,1|H'|1,1>-W_1) & (<1,-1|H'|1,1>) \\ (<0,0|H'|1,-1>) & (<0,0|H'|1,-1>) & (<1,1|H'|1,-1>) & (<1,-1|H'|1,-1>-W_1) \end{vmatrix} = 0 \quad (14.4.2.1)$$

Now we shall calculate the elements of the secular determinant , we have

$$\Psi_{200} = \frac{1}{\sqrt{32\pi a^{03}}}(2 - \frac{r}{a^0})e^{\frac{-r}{2a^0}}$$

$$\Psi_{210} = \frac{1}{\sqrt{32\pi a_0{}^3}}(\frac{r}{a^0} cos\theta)e^{\frac{-r}{2a_0}}$$

$$\Psi_{211} = \frac{1}{\sqrt{32\pi a_0{}^3}}(\frac{r}{a^0\sqrt{2}} sin\theta e^{-i\phi})e^{\frac{-r}{2a_0}}$$

$$\Psi_{21\ -1} = \frac{1}{\sqrt{32\pi a^{03}}}(\frac{r}{a^0\sqrt{2}} sin\theta e^{-i\phi})e^{\frac{-r}{2a^0}} \qquad (14.4.2.2)$$

$$\therefore |< 0,0|H'|0,0> = \int \Psi^*{}_{200} H' \Psi_{200}\, d\tau = 0 \qquad (14.4.2.3)$$

[Since ($\Psi^*{}_{200}$, Ψ_{200}) have even parity.]

On similar grounds all the elements except $< 1,0|H'|0,0>$ and $< 0,0|H'|1,0>$ * of the secular determinant are zero.

The Non-vanishing element of H' are

$$< 1,0|H'|0,0> = < 0,0|H'|1,0>^*$$

$$= \int \Psi_{210}{}^*(-eEr\cos\theta)\,\Psi_{200}\, d\tau$$

$$= -\iiint \frac{1}{\sqrt{32\pi a_0{}^3}}(\frac{r}{a^0} cos\theta)e^{\frac{-r}{2a_0}}(eEr\cos\theta)\frac{1}{\sqrt{32\pi a^{03}}}(2 - \frac{r}{a^0})e^{\frac{-r}{2a^0}} r^2 dr\, sin\theta dr d\theta d\phi$$

$$[\text{since } d\tau = dr\, rd\theta\, rsin\theta\, d\phi = r^2 sin\theta dr d\theta d\phi]$$

$$= \frac{-eE}{32\pi a_0{}^4}\int_0^\infty (2 - \frac{r}{a_0}) r^4 e^{\frac{-r}{a_0}} dr \int_0^\pi sin\theta cos\theta d\theta \int_0^{2\pi} d\phi \qquad (14.4.2.4)$$

We have

$$\int_0^\pi sin\theta cos^2\theta d\theta = \frac{-1}{3}[\cos^3\theta]_0 = 2/3 \qquad (14.4.2.5)$$

$$\int_0^{2\pi} d\phi = 2\pi \qquad (14.4.2.6)$$

$$\int_0^\infty (2 - \frac{r}{a_0}) r^4 e^{\frac{-r}{a_0}} dr = \int_0^\infty (2-\eta)(\eta a_0)^4 e^{-\eta}(a_0 d\eta) \quad where \frac{r}{a^0} = \eta$$

$$= a_0{}^5[2\int_0^\infty \eta^4 e^{-\eta} d\eta - \int_0^\infty \eta^5 e^{-\eta} d\eta]$$

$$= a_0{}^5[48-120] = -72\, a_0{}^5$$

Using equation (14.4.2.5),(14.4.2.6),(14.4.2.7) equation (14.4.2.4) yields

$$< 1,0|H'|0,0> = < 0,0|H'|1,0>^*$$

$$= \frac{-eE}{32\pi a_0^4}(-72a_0^5).\tfrac{2}{3}.2\pi$$

$$=3eEa_0 \qquad (14.4.2.7)$$

So the secular equation to

$$\begin{vmatrix} -W_1 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & -W_1 & 0 & 0 \\ 0 & 0 & -W_1 & 0 \\ 0 & 0 & 0 & -W_1 \end{vmatrix} =0 \qquad (14.4.2.8)$$

i.e. $(-W_1^2)[W_1^2 - (3eEa_0)^2]=0$

this gives $W_1=0,0$ and $W_1= \pm 3eEa_0$.

This splitting of energy levels is shown in fig. 14.1. the electric potential energy of a dipole of moment p is –p.E.

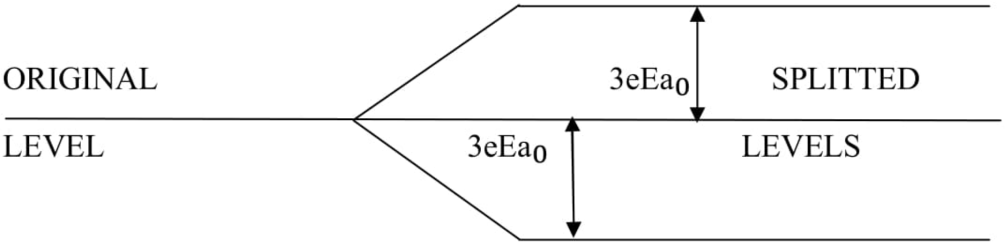


Fig14.1:first order splitting of energy level.

The energy of splitted levels is $\pm 3eEa_0$. Thus *the behaviour of hydrogen atom in first excited state (n=2) is like a permanent electric dipole moment of magnitude* $3ea_0$;which can be oriented in three different ways :

(1) One state parallel to the external electric field.

(2) One state antiparallel to the external electric field and

(3) Two states perpendicular to external electric field.

14.5 Correct Eigen Functions

To find the correct unperturbed eigen functions corresponding to $W_1 = 0,0,$ $3eEa_0$ and $-3eEa_0$. we use secular equation and proceed as follows :

1. When W_1=0,the secular equation (14.4.2.7),gives,

$$\begin{bmatrix} 0 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \alpha_1\Psi_{200} \\ \alpha_2\Psi_{210} \\ \alpha_3\Psi_{211} \\ \alpha_4\Psi_{2,\,1,\,-1} \end{matrix} =0$$

This is equivalent to

$$3eEa_0\alpha_2\Psi_{210}=0 \text{ and } 3eEa_0\alpha_2\Psi_{200} = 0$$

$It\ results\ \alpha_2 = \alpha_1=0$

But there is no restriction on the values of α_3 and α_4.The corresponding linear combination is written as

$$\Psi= \alpha_3\Psi_{2,\,1,\,1}+\alpha_4\ \alpha_4\Psi_{2,\,1,\,-1}$$

From the normalisation condition $\int\Psi*\Psi\ d\tau=1$ gives

$$\alpha_3{}^2+\alpha_4{}^2=1$$

We get $\alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4=\frac{1}{\sqrt{2}}$ in first case

and $\alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4=-\frac{1}{\sqrt{2}}$ in second case.

Hence the correct linear combinations for W_1=0 are

$$\frac{1}{\sqrt{2}}(\Psi_{211} + \Psi_{2,\,1,\,-1}) \quad \text{and} \quad \frac{1}{\sqrt{2}}(\Psi_{211} - \Psi_{21-1}) .$$

2. When $W_1=3eEa_0$, the secular equation gives

$$\begin{bmatrix} -3eEa_0 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & -3eEa_0 & 0 & 0 \\ 0 & 0 & -3eEa_0 & 0 \\ 0 & 0 & 0 & -3eEa_0 \end{bmatrix} \begin{matrix} \alpha_1\Psi_{200} \\ \alpha_2\Psi_{210} \\ \alpha_3\Psi_{211} \\ \alpha_4\Psi_{21-1} \end{matrix} =0$$

This is equivalent to

$$-3eEa_0\alpha_1\,\Psi_{200} +3eEa_0\,\alpha_2\Psi_{210}=0 \text{ or } \alpha_1\Psi_{200} - \alpha_2\Psi_{210}=0$$

$$3eEa_0\alpha_1\Psi_{200} - 3eEa_0\,\alpha_2\Psi_{210} = 0 \text{ or } \alpha_1\Psi_{200} - \alpha_2\Psi_{210} = 0$$

$$-3eEa_0\alpha_3\Psi_{211} = 0 \text{ or } \alpha_3 = 0$$

and $$-3eEa_0\,\alpha_4\Psi_{21-1} = 0 \text{ or } \alpha_4 = 0.$$

Thus we get required linear combination is

$$\Psi = \alpha_1\Psi_{200} - \alpha_2\Psi_{210}$$

From the Normilisation condition gives $\alpha_1^2+\alpha_2^2=1$

Thus $\alpha_1=\alpha_2=\frac{1}{\sqrt{2}}$

Thus the correct linear combination for $W_1=+3eEa_0$ is

$$\frac{1}{\sqrt{2}}(\Psi_{200}-\Psi_{210})$$

3. Similarly when $W_1=-3ea_0$ the correct normalised linear combination is

$$\frac{1}{\sqrt{2}}(\Psi_{200}+\Psi_{210}).$$

14.6 Self Learning Exercise

Q.1 A rigid rotator in a plane is acted on by a perturbation represented by

$$H'=V_0/2\,(3\cos^2\phi-1), \qquad V_0=\text{constant}.$$

Calculate the ground state energy up to the second order in the perturbation.

Q.2 A plane rigid rotator in the first excited state is subjected to the interaction

$$H'=V_0/2\,(3\cos^2\phi-1), \qquad V_0=\text{constant}.$$

Calculate the energies to first order in H'.

Q.3 The energy levels of the one-electron atoms are doublets, except the s-states because of spin-orbit interaction. the spin-orbit Hamiltonian

$$H_{so}=\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\,L.S$$

Treating H_{so} as a perturbation, evaluate the spin-orbit interaction energy. For hydrogenic atoms, assume that the expectation value is

$$\langle\frac{1}{r_3}\rangle=\frac{2z^3}{n^3a_0{}^3l(l+1)(2l+1)}$$

where a_0 is the bohr radius.

Q.4 A rotator having a moment of inertia I and an an electric dipole moment μ executes rotational motion in a plane. Estimate the first and second order corrections to the energy levels when the rotator is acted on by an electric field ϵ in the plane of rotation.

14.7 Summary

In this unit we study about the degenerate case of stationary perturbation theory and its application. This unit includes some important topic as Energy correction , Secular equation, correct Eigen function and Stark effect on hydrogen atom.

14.8 Glossary

Degenerate System: When in a system in which a number of orthogonal eigen functions correspond to the same eigen value, then this system is known as degenerate system.When a degeneracyexists, a linear combination of the degenerate wave functions can be taken as the unperturbed wave function.

The problem in degenerate system is to find the set of unperturbed wavefunctions to which the perturbed functions reduce when the perturbation vanishes.

Secular Perturbation: The perturbation theory of the Secular equation is known as Secular Perturbation.

Stark Effect: The splitting of energy levels of an atom caused by a uniform external electric field E is called Stark-Effect**.**The behaviour of hydrogen atom in first excited state (n=2) is like a permanent electric dipole moment of magnitude $3ea_0$

14.9 Answer of Self Learning Exercise

Ans.1: The energy eigen values and eigen function of a plane rotator are given by

$$E_m = \frac{m^2\hbar^2}{2I} \qquad m=0,1,2,...............$$

and m=0,−1,−2,............

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

Except the ground state, all levels are doubly degenerate. The first order correction to the ground state energy is

$$E_0^1 = <\Psi\, |H'|\, \Psi> = \langle \Psi \mid V_0/2\ (3\cos^2\phi - 1) \mid \Psi \rangle$$

$$= \langle \Psi \mid 3\, V_0 \cos^2\phi/2 \mid \Psi \rangle - \langle \Psi \mid V_0/2 \mid \Psi \rangle$$

$$= 3\, V_0/4 - V_0/2$$

$$= V_0/4$$

The second order energy correction

$$E_0^2 = {\sum_m}' |<0 \mid H' \mid m>|^2 / (\, E_0^0 - E_m^0)$$

$$<0 \mid H' \mid m> = V_0/2 \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} (3\cos^2\phi - 1) \frac{1}{\sqrt{2\pi}} e^{im\phi} d\phi$$

$$= 3V_0/4\pi \int_0^{2\pi} \cos^2\phi\, e^{im\phi} d\phi - V_0/4\pi \int_0^{2\pi} e^{im\phi} d\phi$$

We can write $\cos^2\phi = (1+\cos 2\phi)/2$. Also, the second integral vanishes. Hence,

$$<0 \mid H' \mid m> = 3\, V_0/8\pi \int_0^{2\pi} (1 + \cos 2\phi) e^{im\phi}\, d\phi$$

$$= 3\, V_0/8\pi \int_0^{2\pi} \cos 2\phi\, e^{im\phi}\, d\phi$$

Since the other integral vanishes. Putting $\cos 2\phi$ in the exponential, we get

$$<0\, |H'|\, m> = 3V_0/16\pi \int_0^{2\pi} e^{i(m+2)\phi}\, d\phi + 3V_0/16\pi \int_0^{2\pi} e^{i(m-2)\phi}\, d\phi$$

The first integral is finite when m= -2, the second integral is finite when m=+2 and their values are equal to $3\, V_0/8$.

$E_2 = 2\hbar^2/I$, $E_0 = 0$. Hence

$E_0^0 - E_2^0 = -2\hbar^2/I$

Thus

$$E_0^2 = \frac{(\frac{3V^0}{8})^2}{-2\hbar^2/I} + \frac{(\frac{3V^0}{8})^2}{-2\hbar^2/I}$$

$$= \frac{-9}{64} \frac{V_0^2 I}{\hbar^2}$$

Ans.2: For a plane rotator,

$$E_m = \frac{m^2\hbar^2}{2I} \qquad m=0,1,2,..............$$

and m=0,−1,−2,...........

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

Except the ground state, all levels are doubly degenerate.the energy and wave function of the first excited state are

$$E_{\pm 1} = \hbar^2/2I,$$

$$\Psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$$

The first order energy corrections are given by the roots of equation (8.6):

$$\begin{vmatrix} H'_{11} - E'_1 & H'_{12} \\ H'_{21} & H'_{22} - E'_1 \end{vmatrix} = 0$$

$$H'_{11} = H'_{22} = \frac{1}{2\pi}\int_0^{2\pi} V_0/2(3\cos^2\phi - 1)d\phi$$

$$= V_0/4\pi\ (3\pi - 2\pi)$$

$$= V_0/4$$

$$H'_{12} = H'_{21} = \frac{1}{2\pi}\int_0^{2\pi} e^{-i\phi}V_0/2(3\cos^2\phi - 1)e^{-i\phi}d\phi$$

$$= 3V_0/8$$

The secular determinant takes the form

$$\begin{vmatrix} V_0/4 - E'_1 & 3V_0/8 \\ 3V_0/8 & V_0/4 - E'_1 \end{vmatrix} = 0$$

$$(E'_1)^2 - V_0/2\ E'_1 - 5V_0^2/64 = 0$$

The roots of this equation are $-V_0/8$ and $-5V_0/8$. The corrected energies are

$$E = \frac{\hbar^2}{2I} + 5V_0/8 \text{ and } \frac{\hbar^2}{2I} - V_0/8.$$

Ans.3: for the valence electron in a hydrogen- like atom, the potential

$$V(r) = \frac{-ze^2}{4\pi\epsilon_0 r}$$

or $$\frac{dV}{dr} = \frac{ze^2}{4\pi\epsilon_0 r^2} \qquad (1)$$

Substituting the value of $\frac{dV}{dr}$, we get

$$H_{so} = \frac{ze^2}{8\pi\epsilon_0 m^2c^2} \frac{L.S.}{r^3} \tag{2}$$

Since J = L+S

$$J^2=L^2+S^2+2L.S \text{ or } L.S = \frac{J^2-L^2-S^2}{2} \tag{3}$$

Using the basis |*lsjm*>, the expectation value of $J^2 - L^2 - S^2$ is given by

$$<(J^2 - L^2 - S^2)>=[j(j+1)-l(l+1)-s(s+1)]\hbar^2 \tag{4}$$

Since the first order correction to the energy constitutes the diagonal matrix, substituting the values of $<1/r^3>$ and $<(J^2 - L^2 - S^2)>$, we get

$$E_{so} = \frac{z^4e^2\hbar^2}{8\pi\epsilon_0 m^2c^2a_0^3} \frac{[j(j+1)-l(l+1)-s(s+1)]}{n^3l(l+1)(2l+1)} \tag{5}$$

The Bohr radius a_0 and the fine structure constant α are defined as

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}, \quad \alpha = \frac{e^2}{4\pi\epsilon_0 c\hbar} \tag{6}$$

By equation (6), we get

$$E_{so} = \frac{z^4e^2\hbar^2}{8\pi\epsilon_0 m^2c^2a_0^3} \frac{[j(j+1)-l(l+1)-s(s+1)]}{n^3l(l+1)(2l+1)} \tag{7}$$

This make the state $j=l-(1/2)$ to have a lower energy than that with $j=l+(1/2)$

Ans.4: the energy Eigen values and Eigen functions of aplane rotator are

$$E_m = \hbar^2m^2/2I \quad , (\phi) = 1/\sqrt{2\pi}\exp(im\phi) \quad m=0,\pm1,\pm2.......$$

The perturbation $H' = -\mu\epsilon\cos\phi = -\mu\epsilon/2\,(e^{i\phi} + e^{-i\phi})$

$$E_n^{(1)} = <n\,|H'|\,n> = -\mu\epsilon/2\pi \int_0^{2\pi} cos\phi d\phi = 0$$

$$E_n^{(2)} = \sum_m{}' \,|<n\,|H'|\,m>|^2/E_n^0 - E_m^0$$

$$<n\,|H'|\,m> = -\mu\epsilon/4\pi \int_0^{2\pi} e^{-in\phi}\,(e^{i\phi} + e^{-i\phi})e^{im\phi}d\phi$$

$$= -\mu\epsilon/4\pi\ [\int_0^{2\pi} e^{i(m-n+1)\phi}d\phi + \int_0^{2\pi} e^{i(m-1-n)\phi}d\phi$$

The integrals are finite when m=n−1 (first one) and m=n+1 (second one). Therefore,

$$E_n^{(2)} = (-\mu\epsilon/4\pi)^2[4\pi^2/ E_n^0 - E_{n-1}^0 \quad +4\pi^2/ E_n^0 - E_{n+1}^0]$$

$$=(-\mu\epsilon/4\pi)^2 \, 4\pi^2 2I/\hbar^2 \, (1/2n-1 +1/2n+1)$$

$$=\mu^2\epsilon^2 I/\hbar^2(4n^2-1)$$

14.10 Exercise

Q.1 Give the theory of first order stark effect on the basis of quantum mechanics and discuss the splitting of the energy levels.

Q.2 Discuss the effect of a weak external magnetic field on the energy states of an atom using perturbation theory. How is this effect modified when the magnetic field is strong?

Q.3 Give the stationary perturbation theory for the degenerate case and use it to explain the first order stark effect in hydrogen.

Q.4 Explain the stark splitting of n=2 level of hydrogen atom in the presence of an electric field using first order time independent perturbation theory.

Q.5 Calculate the first order stark effect for the first excited state (n=2) of hydrogen atom. Show that you result would imply that a hydrogen atom in its n=2 state behaves as though it has a permanent electric dipole moment of magnitude $3ea_0$. Sketch the arrangement of the energy levels and indicate the wave functions associated with each.

Q.6 The matrices for the unperturbed (H^0) and perturbation (H') Hamiltonians in the orthonormal basis $|\phi_1>$ and $|\phi_2>$ are

$$H^0 = \begin{pmatrix} E^0+\epsilon & 0 \\ 0 & E^0-\epsilon \end{pmatrix} \qquad H' = \begin{pmatrix} 0 & A \\ A & 0 \end{pmatrix}$$

Determine (a) the first order correction to energy, (b) second order correction to energy, and (c) the wave function corrected to first order.

Q.7 A particle in a central has an orbital angular momentum quantum number *l*=3. If its spin s=1, find the energy levels and degeneracies associated with the spin-orbit intraction.

14.11 Answers to Exercise

Ans.6:

(a) The first order correction to the energy is zero since the perturbation matrix has no diagonal element.

(b) $$E_n^2 = \sum_m |\langle n | H' | m \rangle|^2 / (E_n^0 - E_m^0)$$

$$E_1^2 = |\langle 1 | H' | 2 \rangle|^2 / (E_1^0 - E_2^0)$$

$$= |A|^2/2\epsilon$$

$$= A^2/2\epsilon$$

$$E_2^2 = |\langle 2 | H' | 1 \rangle|^2 / (E_2^0 - E_1^0)$$

$$= -A^2/2\epsilon$$

$$E_1 = E_0 + \epsilon + A^2/2\epsilon$$

$$E_2 = E_0 - \epsilon - A^2/2\epsilon$$

(c) The wave function corrected to first order is given by

$$\Psi_n = \Psi_n^0 + \sum_m \langle m | H' | n \rangle |\Psi_m^0\rangle / (E_n^0 - E_m^0)$$

$$\Psi_1 = |\phi_1\rangle + A|\phi_2\rangle / (E_1^0 - E_2^0)$$

$$\Psi_1 = |\phi_1\rangle + (A/2\epsilon)|\phi_2\rangle$$

$$\Psi_2 = |\phi_2\rangle + (A/2\epsilon)|\phi_1\rangle$$

Ans.7: The spin orbit interaction $H_{so} = \xi(r)\,\mathbf{L.S}$

Where $\xi(r)$ is a constant. The total angular momentum

$$J = L + S \text{ Or } \mathbf{L.S} = \tfrac{1}{2}(J^2 - L^2 - S^2)$$

Hence $H_{so} = \tfrac{1}{2}\xi(r)(J^2 - L^2 - S^2)$

In the $|jm_j l_s\rangle$ basis, the first order correction

$$E_{so} = \langle jm_j l_s | \tfrac{1}{2}\xi(r)(J^2 - L^2 - S^2) | jm_j l_s \rangle$$

$$= \tfrac{1}{2}\xi(r)[j(j+1) - l(l+1) - s(s+1)]\hbar^2$$

Since $l=3$ and $s=1$, the possible values of j are 4 , 3, 2,. Hence

$$E_{so} = \begin{cases} 3\,\xi(r)\hbar^2, & j=4 \\ -\xi(r)\hbar^2, & j=3 \\ \xi(r)\hbar^2, & j=2 \end{cases}$$

The degeneracy d is given by the (2j+1) value

$$d = \begin{cases} 9, & j=4 \\ 7, & j=3 \\ 5, & j=2 \end{cases}$$

Reference and Suggested Readings

1. Fundamental of Quantum Mechanics by Springer.
2. Lectures on Quantum Mechanics by Steven Weinberg.
3. Quantum Mechanics and Quantum Information by Moses Fayngold and Vadim Fayngold.
4. Quantum Mechanics by David Mcintyre.
5. Concepts of Quantum Mechanics by Vishnu Swarup Mathur and Surendra Singh

UNIT-15

Time Dependent Perturbation Theory

Structure of the Unit

15.0 Objectives

In this unit, we shall study about those systems whose Hamiltonian contains the time dependent part and energy Eigen states depend upon the time and modified Eigen function. For the study of such type of cases we use the theory of time dependent perturbation. This unit includes some important topics as time dependent perturbation theory, adiabatic approximation and sudden approximation.

15.1 Introduction

Here the Hamiltonian of a system depends on the time, So there are no stationary state solutions of Schrodinger wave equation. Hence the identification of a bound state with discrete energy level and stationary Eigen function must be modified. In this unit we shall discuss three ways in which this modification can be made, given below:

1. Time dependent perturbation theory or method of variation of constants :

In this method Hamiltonian is divided into two parts as given

$$H_0 + H'$$

where H_0 = simple unperturbed Hamiltonian

H' = small time dependent perturbations term

Both has the effect of causing transitions between Eigen-states of H_0 that would be stationary in the absence of H'.

2. Adiabatic Approximation :

In this method we assumes that the Hamiltonian of the system (H) contains the parameter that change very slowly with time. So the system is expected to be described approximately by means of stationary Eigen functions of the instantaneous Hamiltonian.

3. Sudden Approximation :

In this method we assumes that the Hamiltonian of the system (H) is constant for the time except for a very short time interval in which it changes from one form to another form.

15.2 Time-Dependent Perturbation Theory

It is generally impossible to obtain exact solution of the Schrodinger equation when the Hamiltonian depends upon time. Therefore such an equations solved by

Time-Dependent Perturbation Theory. This theory is also known as the *method of variation of constants.*

The total Hamiltonian is expressed as

$$H= H_0 + H' \qquad (15.2.1)$$

where the unperturbed Hamiltonian H_0 can be solved for it's normalized Eigen function ϕ_n and its Eigen value E_n i.e., we have

$$H_0\, \phi_n = E_n\, \phi_n \qquad (15.2.2)$$

Time dependent perturbation term H' is small. Since H' depends upon time, the stationary solution of the actual Schrodinger equation does not exist. The time dependent Schrodinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \qquad (15.2.3)$$

The energy Eigen-states of such a system are stationary; the time enters only in the phases according to

$$\Psi\,(t)=\sum a_n(t)\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} \qquad (15.2.4)$$

Where a_n's are time-dependent constants and ϕ(r) is time dependent.

This equation represents solution of (15.2.3), therefore substituting value of Ψ and H from (15.2.1) and (15.2.4) , we get

$$i\hbar\frac{\partial}{\partial t}[\sum a_n(t)\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)}] = (H_0 + H')\ [\sum a_n(t)\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)}\ ]$$

$$\text{or}\quad [\sum i\hbar\, a_n(t)\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} + \sum\ a_n\, \phi_n(r)\ e^{\left(\frac{-iE_n t}{\hbar}\right)}]$$

$$= \sum a_n\, H_0\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} + \sum a_n\, H'\, \phi_n(r)\ e^{\left(\frac{-iE_n t}{\hbar}\right)}$$

Where $d\, a_n(t)/dt = a_n$

From equation (2), we have $H_0\, \phi_n = E_n\, \phi_n$,

$$\sum i\hbar\, a_n(t)\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} + \sum a_n\, E_n\, \phi_n(r)\ e^{\left(\frac{-iE_n t}{\hbar}\right)}$$

$$= \sum a_n\, E_n\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} + \sum a_n\, H'\, \phi_n(r)\ e^{\left(\frac{-iE_n t}{\hbar}\right)}$$

$$\sum i\hbar\, a_n\, \phi_n(r) e^{\left(\frac{-iE_n t}{\hbar}\right)} = \sum a_n\, H'\, \phi_n(r)\, e^{\left(\frac{-iE_n t}{\hbar}\right)} \qquad (15.2.5)$$

By multiplying both sides by $\phi_k{}^*$ and integrating over configuration space, we get

$$\sum i\hbar\, a_n\, e^{\left(\frac{-iE_n t}{\hbar}\right)} \int \phi_k{}^*\, \phi_n\, d\tau = \sum a_n\, e^{\left(\frac{-iE_n t}{\hbar}\right)} \int \phi_k{}^*\, H' \phi_n d\tau$$

Now by applying orthonormality condition of ϕ's , i.e.

$$\int \phi_k{}^*\, \phi_n\, d\tau = \delta_{kn} \qquad \begin{cases} =0 \text{ for } n \neq k \\ =1 \text{ for } n=k \end{cases}$$

We get $\sum i\hbar\, a_n\, e^{\left(\frac{-iE_n t}{\hbar}\right)}{}_{kn} = = \sum a_n\, e^{\left(\frac{-iE_n t}{\hbar}\right)} \int \phi_k{}^*\, H' \phi_n d\tau$

Because in L.H.S. all terms will be zero except kth term From the properties of Kronecker delta δ_{kn}, we have

$$i\hbar\, a_k\, e^{\left(\frac{-iE_k t}{\hbar}\right)} \delta_{kn} = \sum a_n\, e^{\left(\frac{-iE_n t}{\hbar}\right)} \int \phi_k{}^*\, H' \phi_n d\tau$$

(15.2.6)

The integral $\int \phi_k{}^*\, H' \phi_n d\tau$ at right hand side is a matrix

$<k \mid H' \mid k> = H'_{kn}$

So $$i\hbar\, a_k = \sum a_n\, e^{\left(-i\frac{E_k - E_n}{\hbar} t\right))} H'_{kn}$$

(15.2.7)

But $E_k - E_n/k = \omega_{kn}$ (15.2.8)

Here ω_{kn} Bohr's angular frequency. ω_{kn}

So time dependent constants a_n's are given by

$$\left.\begin{aligned} a_k &= (i\hbar)^{-1} \sum a_n\, e^{\left(\frac{i\omega_{kn}}{\hbar}\right)t}\, H'_{kn} \\ a_k &= (i\hbar)^{-1} \sum a_n <k \mid H' \mid n>\, e^{\left(\frac{i\omega_{kn}}{\hbar}\right)t} \end{aligned}\right\} \qquad (15.2.9)$$

If we replace in equation (15.2.1) H' by $\lambda H'$, where λ is a parameter, then coefficient a's can be expressed in parameter λ as follows :

$$a_n = a_n^0 + \lambda\, a_n^1 + \lambda^2\, a_n^2 + \ldots\ldots\ldots\ldots. \qquad (15.2.10)$$

Substituting the value of a_n in equation (15.2.4) and equating the coefficients of λ on both sides,

$$\left.\begin{array}{l} \text{Equating coefficient of } \lambda_0,\ i\hbar a_k^0 = 0 \\[2ex] \text{Equating coefficient of } \lambda,\ i\hbar a_k^1 = \sum a_n^0\, e^{(\frac{i\omega_{kn}}{\hbar})t}\, H'_{kn} \\[2ex] \text{In general} \quad i\hbar a_k^{S+1} = \sum a_k^s\, e^{(\frac{i\omega_{kn}}{\hbar})t}\, H'_{kn} \\ \text{where } s = 0, 1, 2, \ldots\ldots\ldots\ldots \end{array}\right\} \begin{array}{r} (a) \\[2ex] (b) \\[2ex] (c) \\ (15.2.11) \end{array}$$

so we can get desired order in the perturbation.

15.3 Zeroth Order Calculation

From (15.2.11), we have

$$i\hbar a_k^0 = 0 \quad \text{or} \quad a_k = 0 \text{ i.e. } \frac{d}{dt} a_k^0 = 0$$

Integrating, we obtain

$$a_k^0 = \text{constant in time.}$$

For convenience without loss of generality, we may put

$$a_k^0 = \langle k \mid m \rangle = \delta_{km}$$

According as the initial state m is one of a discrete or continuous set.

Accordingly $a_k^0 = 1$ for k=m i.e. $a_m^0 = 1$

and $\quad a_k^0 = 0$ for $m \neq k$

Thus in the sum we have only one term and equation (15.2.9) may be expressed as

$$a_k = (i\hbar)^{-1} \langle k \mid H' \mid m \rangle\, e^{i\omega kmt} \tag{15.3.1}$$

15.4 1st Order Calculation

Integration of (15.3.1) gives

$$a_k^1(t) = (i\hbar)^{-1} \int_{-\infty}^{t} < k \mid H' \mid m > e^{i\omega_{km}t} dt \tag{15.4.1}$$

The constant of integration is taken to be zero in order that a_k^1 br zero at $t = -\infty$ (before the perturbation is applied)

15.5 Perturbation Constant in Time

Let us consider a perturbation that is constant in time and that it operates only during the time 0 to t, i.e.

$$< k \mid H' \mid m > = \begin{cases} 0 & \text{for } -\infty < t' < 0 \\ < k \mid H' \mid m > & \text{for } 0 \leq t' \leq t \\ 0 & \text{for } t' > t \end{cases} \qquad (15.5.1)$$

Substituting (15.4.1) in (15.5.1), we get

$$a_k^{1}(t) = (i\hbar)^{-1} \int_0^t < k \mid H' \mid m > e^{i\omega_{km}t'} dt'$$

$$= (i\hbar)^{-1} < k \mid H' \mid m > \left[\frac{e^{i\omega_{km}t'}}{i\omega_{km}}\right]_0^t$$

$$= (i\hbar)^{-1} < k \mid H' \mid m > \left[\frac{e^{i\omega_{km}t} - 1}{i\omega_{km}}\right]$$

$$a_k^{1}(t) = \frac{< k \mid H' \mid m >}{\omega_{km}\hbar} (e^{i\omega_{km}t} - 1) \qquad (15.5.2)$$

Thus, to ***first order, the probability*** of the system from mth state to kth state is given by

$$| a_k^{1}(t) |^2 = \frac{|< k \mid H' \mid m >|^2}{\omega_{km}^2\hbar} | (e^{i\omega_{km}t} - 1)|^2 \qquad (15.5.3)$$

Using the relation

$$\lim_{x\to 0}(e^{ix} - 1) = 2ie^{\frac{ix}{2}} \sin\frac{x}{2}$$

$$= 2i \sin\frac{x}{2}$$

or $(e^{ix} - 1)|^2 = 4\sin^2\frac{x}{2}$

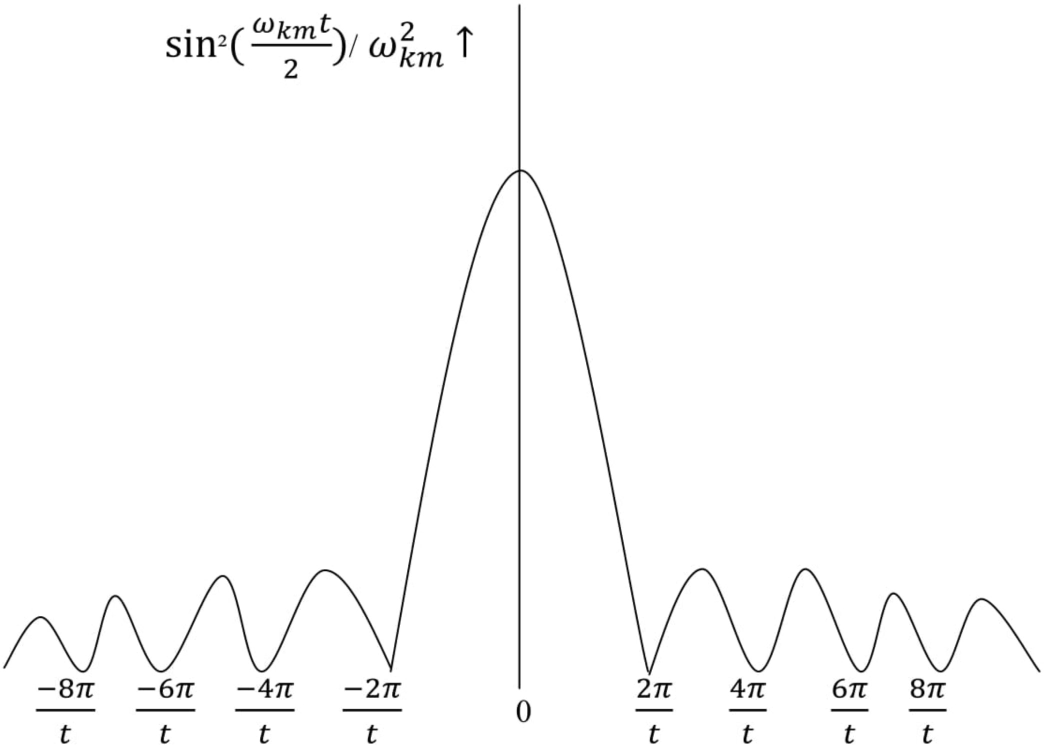
i.e. $(e^{i\omega_{km}t} - 1)|^2 = 4\sin^2(\frac{\omega_{km}t}{2})$

equation (16) takes the form

$$| a_k^{1}(t) |^2 = \frac{|< k \mid H' \mid m >|^2}{\omega_{km}^2\hbar} 4 \sin^2(\frac{\omega_{km}t}{2}) \qquad (15.5.4)$$

15.5.1 Physical Interpretation

In order to interpret equation (15.5.4) physically, we plot $\sin^2(\frac{\omega_{km}t}{2})/\ \omega^2 km$ as a function of ω_{km} and find the curve is as shown in fig. 9.1.



The major maxima of probability curve occurs at $_{km}$=0 i.e.

For $E_k = E_m$. If we substitute ω_{km}=x in $\sin^2(\frac{\omega_{km}t}{2})/\ \omega^2 km$.

We note that

$$\sin^2(\frac{\omega_{km}t}{2})/\ \omega_{km}^2 = \sin^2(\frac{xt}{2})/\ x^2$$

$$=\frac{1}{x^3}[\frac{xt}{2} - \left(\frac{xt}{2}\right)^{3\frac{1}{3}} + \left(\frac{xt}{2}\right)^5 - \cdots \ldots \ldots \ldots.]^2$$

$$=\frac{1}{x^2}(\frac{xt}{2})^2 = t^2/4$$

Thus the height of the main peak is proportional $t^2/4$ and the intensity or probability curve touches the ω_{km} axis at points where $\sin^2(\frac{xt}{2})/x^2 = 0$. This occurs at points where $\frac{xt}{2} = \pm r\pi$ or $x = \pm\frac{2\pi r}{t}$

where r is an integer i.e.(r = 0,1,2,3,..........)

Thus $x = \omega_{km} = \pm\frac{2\pi r}{t} = 0, \pm\frac{2\pi}{t}, \pm\frac{4\pi}{t}, \pm\frac{6\pi}{t}$,...........i.e. width of the peak is proportional to 1/t. As the height of peak is proportional to t^2 and width proportional to 1/t ; the area under the curve is proportional to t i.e. time of application of the perturbation. These results derived under constant perturbation for a definite time are analogous to single slit diffraction experiment and are applicable to problems of excitation and emission of radiation in elementary systems.

Now we seek the physical interpretation from the figure: For sufficiently large t, the area under the central peak is much greater than that under the neighbouring peaks and hence most transitions take place to states under the main peak.

If we have a system with the Hamiltonian H_0 and if this system interacts with an external agency with an interaction Hamiltonian H', then there are transitions in the system and it is observed that there is a definite transition rate from a fixed initial state to a final state.

15.5.2 Transition Probability

Now we suppose that unperturbed Hamiltonian H_0 has a continuous spectrum and the transition are take place to the states in the continuum. This is the situation in most of physical problems e.g. in scattering problem the scattered states belong to the continuum Eigen values of the Hamiltonian.

If the transition takes place to states k energy between E_k and $E_k + dE_k$ and the energy density of states is given by ρ(k) at this stage, then the transition probability per unit time is defined as

$$\omega = \frac{1}{t}\int |a_k^1(t)|^2 (k)\, dE_k \qquad (15.5.5)$$

where (k) dE_k gives the number of final states in the energy interval from $E_k + dE_k$. If t is large enough, the central peak in the probability curve is sharp and then the quantities $<k \mid H' \mid m>$ and (k) may be regarded as sufficiently independent of $dE_{k,}$ so that they may be taken out the integral, therefore

$$\omega = \frac{1}{t}\int_{-\infty}^{+\infty} \frac{4|<k \mid H' \mid m>|^2}{\omega_{km}^2 \hbar^2} \sin^2(\frac{\omega_{km}t}{2}) \text{ (k) } dE_k$$

$$= \frac{|<k \mid H' \mid m>|^2 \rho(k)}{\hbar^2 t}\int_{-\infty}^{+\infty} 4 \sin^2(\frac{\omega_{km}t}{2})\hbar/\omega_{km}^2 \, d\omega_{km}$$

[since $dE_k = E_k - E_m = \hbar \, d\omega_{km]}$

$$\omega = \frac{|<k \mid H' \mid m>|^2 \rho(k)}{\hbar^2 t}\int_{-\infty}^{+\infty} 4 \sin^2(\frac{\omega_{km}t}{2})/(\omega_{km}t/2) \, d\omega_{km} \qquad (15.5.6)$$

We have the standard integral

$$\int_{-\infty}^{+\infty} 4 \sin^2(x)/x^2 dx = \pi$$

Substituting ($\omega_{km}t/2$)=x, i.e. ω_{km}=2x/t , so $d\omega_{km}$=2/t dx

$$\int_{-\infty}^{+\infty} 4 \sin^2(\frac{\omega_{km}t}{2})/(\omega_{km}t/2) \, d\omega_{km} = t\int_{-\infty}^{+\infty} 4 \sin^2(x)/(x/t)^2 \, (\frac{2}{t}dx)$$

$$= 2t \int_{-\infty}^{+\infty} \sin^2(x)/x^2 \, dx = 2\pi t \qquad (15.5.7)$$

Substituting this in (15.5.6), we get

$$\omega = \frac{|<k \mid H' \mid m>|^2 \rho(k)}{\hbar t} . \, 2\pi t = \frac{2\pi}{\hbar} \rho(k) \mid < k \mid H' \mid m > \mid^2 \qquad (15.5.8)$$

This is an important rule of time dependent perturbation theory and is called the ***Fermi Golden Rule.*** This relation has been successfully employed to calculate the transition probabilities between two states and their corresponding life times. In particular in β- decay it has given the results actually observed experimentally.

There may be several different groups of final states k_1, k_2, $k_{3,}$ ....all of which posses nearly the same energy ,

$E_k = E_m + \hbar\omega$ for which the perturbation matrix elements

$<k_j \mid H' \mid m>$ and density of states (k_j) although nearly constant within each group, differ from one group to another. then the transition probability per unit time for jth group (replacing k) by k_j in (21) is given by

$$\omega = \frac{2\pi}{\hbar} \rho(k) \mid < k \mid H' \mid m > \mid^2; \; j=1,2,3,........... \qquad (15.5.9)$$

The spread of energy of final state to which transitions occur is connected with uncertainty relation $\Delta E.\Delta t \approx \hbar$ in the given manner:

According to perturbation H' as a device that measures the final energy of the system by transferring it to one of the states k. The time available for the measurement in ***t*** so that the uncertainty in energy predicted by the relation

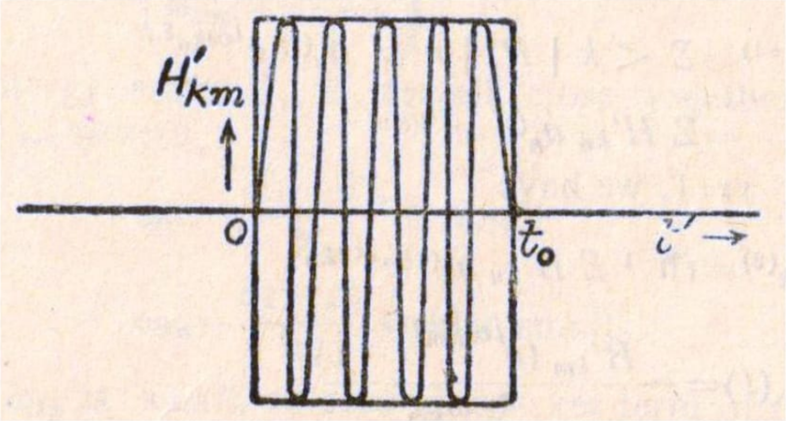
$\Delta E \approx \hbar/t$ and this is in agreement with the width of the main peak. Thus there is no need to insert separate assumption for it.

15.6 Harmonic Perturbation

Here we assume a different but physically important case when the perturbation is harmonic of frequency ω, i.e.

$$|<k\,|\,H'\,|\,m>| > H'_{km}(t') = \begin{cases} 0 \text{ for} \\ 2 \text{ for} \\ 0 \text{ for } t'>t \end{cases} \qquad ....(15.6.1)$$

where $|<k\,|\,H'\,|\,m>|$ is independent of time.



The first order amplitude $a_k^1(t')$ at time t', would then be given as

$$a_k^1(t'\geq t) = (i\hbar)^{-1}\int_0^t <k\,|\,H'\,|\,m>e^{i\omega_{km}t'}dt'$$

$$= (i\hbar)^{-1}\int_0^t 2<k\,|\,H'_0\,|\,m> \sin\omega t' e^{i\omega_{km}t'}dt'$$

$$=2<k\,|\,H'_0\,|\,m>/i\hbar\int_0^t\{e^{i(\omega_{km}+\omega)t'}+e^{i(\omega_{km}-\omega)t'}\}dt'$$

$$= -< k \mid H'_0 \mid m > /\hbar \left[\frac{\{e^{i(\omega_{km}+\omega)t'}}{i(\omega_{km}+\omega)} - \frac{\{e^{i(\omega_{km}-\omega)t'}}{i(\omega_{km}-\omega)} \right]_0^t$$

$$\text{i.e. } a_k^1(t') = -< k \mid H'^0 | m > /i\hbar \left[\frac{\{e^{i(\omega_{km}+\omega)t} - 1}{(\omega_{km}+\omega)} - \frac{\{e^{i(\omega_{km}-\omega)t} - 1}{(\omega_{km}-\omega)} \right] \tag{15.6.2}$$

This equation suggests that

(1) The first order amplitude depends on perturbation duration t and not on time t' .

(2) The amplitude is appreciable only when the denominator of the other terms is practically zero.

The first term is important when $\omega_{km} = -\omega$ or $E_k \approx E_m - \hbar$ and the second term is important when $\omega_{km} = \omega$ or $E_k \approx E_m + \hbar\omega$. Hence the first order harmonic perturbation (i.e. of perturbation that varies sinusoidally with time) with angular frequency ω is to transfer to or receive from the system on which it acts the plank quantum energy $\hbar\omega$.

In the special case in which the initial state m is a discrete bound state and the final state is one of the continuous set of dissociated states. Then $E_k > E_m$ and only the second term in (15.6.2) need be considered. In this case the first order probability of finding the system in kth state after the perturbation is removed is given by

$$| a_k^1(t' \geq t) |^2 = \frac{4|<k \mid H' \mid m>|^2 \sin^2\left(\frac{(\omega_{km}-\omega)}{2}\right)}{\hbar^2(\omega_{km}-\omega)^2} \tag{15.6.3}$$

15.7 Second Order Perturbation

From equation (15.2.11), we have

$$i\hbar\, a_k^{(s+1)} = \sum < k \mid H' \mid n > a_n^s\, e^{i\omega_{kn}t}$$

$$= \sum H'_{kn}\, a_n^s\, e^{(i\omega_{kn})t}$$

By Putting s=1, we have

$$a_k^{(2)} = i\hbar^{-1} \sum H'_{kn}\, a_n^1\, e^{(i\omega_{kn})t}$$

where $a_k^1(t) = -H'_{km}(e^{(i\omega_{km})t} - 1)/\hbar\omega_{km}$

By putting in equation k=n, we get

$$a_n^{\,1}(t) =-H'_{nm}\,(e^{(i\omega_{km})t}-1)/\hbar\omega_{nm}$$

Therefore $a_k^{\,2} = i/\hbar^2 \sum H'_{kn}\,H'_{nm}/\omega_{nm}\,(e^{(i\omega_{km})t} - e^{(i\omega_{kn})t})$

Integrating this equation subject to initial condition $a_k^{(2)}(0)=0=0$

Gives for the second order amplitudes at time t.

$$a_k^{\,2} = i/\hbar^2 \sum H'_{kn}\,H'_{nm}/\omega_{nm}\,\left(\frac{(e^{(i\omega_{km})t}-1}{\omega_{km}} - \frac{e^{(i\omega_{kn})t}-1}{\omega_{kn}}\right) \qquad (15.7.1)$$

this equation shows that transition for which probability increases linearly with the time can be obtained by putting either

$$\omega_{km} \backcong 0 \quad \text{or } \omega_{kn} \backcong 0$$

Suppose that perturbation gives no transition in first order. This means that there is no state n in the first order that conserve energy (i.e. $\omega_{km} \backcong 0$) this means also that

$H'_{nm} = 0$ whenever $_{km} \backcong 0$ So second term in equation (15.7.1) is never appreciable. Therefore second order may be calculated by $a_k^{\,1}$ by replacing H'_{km} by second order matrix element $\sum H_{kn}\,H'_{nm}/E_m - E_n$.

15.8 Effect on First Order Transitions

The second order amplitude at time t is

$$a_k^{\,2} = i/\hbar^2 \sum H'_{kn}\,H'_{nm}/\,E_m - E_n\left(\frac{(e^{(i\omega_{km})t}-1}{\omega_{km}} - \frac{e^{(i\omega_{kn})t}-1}{\omega_{kn}}\right) \qquad (15.8.1)$$

It is still correct that the second term in the bracket of equation (15.4.1) is negligible for states n that have energies appreciably different from E_k (or E_m), since ω_{kn} is large

$$\omega_{mn} = E_k - E_n/\hbar$$

The energy states E_n, E_m are all close together and neither H'_{km} nor H'_{nm} is zero

$$\omega_{mk} = E_k - E_m/\hbar \text{ is small}$$

$$\omega_{kn} = E_k - E_n/\hbar \text{ is small.}$$

Since ω_{kn} is small , so second bracket term of (15.7.1) cannot be neglected without the summation , integration over n would have a singularity, when ω_{mn} is zero .

As $\omega_{mn} = \omega_{mk} - \omega_{kn} = E_k - E_m/\hbar - E_k - E_n/\hbar$

$$= E_n - E_m/\hbar$$

It is easy to see that for any value of ω_{mk}(zero or otherwise). The entire bracket is proportional to ω_{mn}. when ω_{mn} is small; this removes the ω_{mn} in the denominator and makes the summand or integrand finite where $\omega_{mn} = 0$.

We have to evaluate equation (15.8.1) if $\sum$ can be replaced by an integral over ω_{mn} or E_n. We divide the integrals into two parts according as | ω_{mn} | is large or is not large in respect of 1/t. In the first region the second bracket term in equation (15.8.1) can be neglected. Since $|\omega_{kn}| = |\omega_{km} - \omega_{mn}|$ is large in respect of 1/t.

Thus we obtained this part of integral,

$$\frac{(e^{(i\omega_{km})t}-1}{\omega_{km}} \int_0^t \frac{H'_{km} H'_{nm}}{\omega_{nm}} -(n)\, \hbar\, d\omega_{mn} \qquad (15.8.2)$$

Since (n) dE_k the number of states of the particular group n under energy range dE_n , the prime over integration excludes the integration region.

$$-c/t \leq {}_{mn} \leq c/t,$$

Where c is constant number that is large in comparison with unity.

In the second region where $\omega_{mn} \leq c/t$, we assume that t is large enough so that $H'_{kn} H'_{nm} \rho(n)$ can be treated as a constant, taken outside and solved at $\omega_{mn}=0$. We must now take both terms in the bracket of equation (15.8.1) in order that the integrand be finite. This part of the integral is then

$$[\hbar\, H'_{kn} H'_{nm} \rho(n)]\, \omega_{mn} = 0$$

$$\int_{-\frac{c}{t}}^{\frac{c}{t}} [\frac{(e^{(i\omega_{km})t}-1}{\omega_{km}} - \frac{e^{(i\omega_{kn}-\omega_{nm})t}-1}{\omega_{kn}}] d\,\omega_{mn/}\, \omega_{mn} \qquad (15.8.3)$$

This equation (15.8.3) can be solved by considering the contour in complex ω_{mn} plane shown in fig. 9.3 which contains no pole of the integrand.

Thus the integrand over closed contour is zero and the integral in (15.8.2) is equal to integral around the semicircle of radius c/t taken in the counter clockwise direction. The magnitude of ω_{mn} is great enough over this semicircle. Therefore contribution of second term can be ignored in comparison with first. The integrand in (15.8.3) is then easily solved and becomes

$$\pi i(\frac{(e^{(i\omega_{km})t}-1}{\omega_{km}}) \qquad (15.8.4)$$

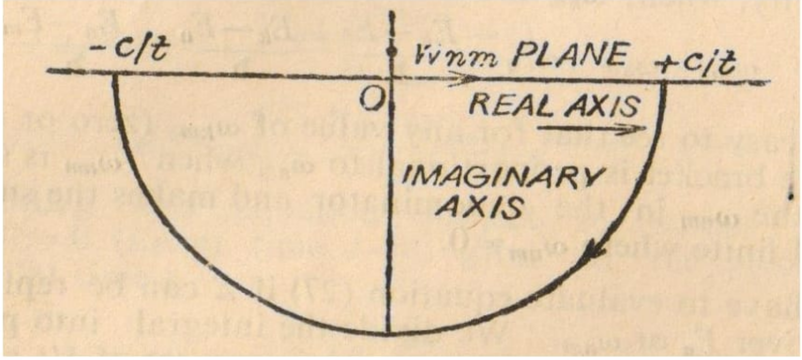


Fig 15.3 : Closed Contour

For large time t, prime on integral (15.8.2) is equivalent to taking its principal value. Therefore if we substitute(15.8.4) in (15.8.3) and add the result to (15.8.2), we get an expression like (15.8.2) except that primed integral is replaced by principal value of the integral plus πi times the residue of integrand at the pole ω_{mn} =0. This is equivalent to evaluating the integral along a counter in the ω_{mn} complex plane. It passes along the real axis $-\infty \; to + \infty$ except for passing beneath the origin. We thus get finally

$$a_k^2(t) = \frac{(e^{(i\omega_{km})t}-1}{\omega_{km}} \int_c H'_{kn}H'_{nm}/E_n\text{-}E_m \, \rho(n) \, \hbar \, dE_k \qquad (15.8.5)$$

where the contour C is over the real axis of E_n except for passing under the pole of the integrand at $E_n = E_{m.}$

Equation (15.8.5) is used to be in place of (15.8.1) whenever $\sum$ can be represented by $\int$(n)dE_n.

15.9 Adiabatic Approximation

In this approximation case, we expect on physical grounds that solutions of the Schrodinger wave equation can be approximated by means of stationary Eigen functions of instantaneous Hamiltonian, so that a particular Eigen function at one time goes over continuously into corresponding Eigen function at a later time.

If the equation

$$H(t)\,\phi_n(t) = E_n(t)\,\phi_n(t)$$

Can be solved at any time. Now we assume that a system that is discrete non-degenerate state $\Psi_m(0)$ with energy $E_m(0)$ at t=0 is likely to be in the state $\phi_n(t)$ with energy $E_m(t)$ at time t, provided that H(t) varies very slowly with time.

The wave function Ψ obeys the time- dependent Schrodinger wave Equation

$$i\hbar\frac{\partial\Psi}{\partial t} = H(t)\,\Psi$$

$$\Psi = \sum_l \quad a_l(t)\phi_l(t)\,\exp\,[1/i\hbar\int_0^t E(t')dt'\,]$$

Then $\quad \sum_l i\hbar\,[a_l{}^*\,\phi_l + a_l\,\phi_l{}^*]\,[\exp\,1/i\hbar\int_0^t E(t')dt'\,] = 0.$

Multiplying by ϕ_n, we have

$$\sum_l\,[a_l{}^*<\phi_n\,|\,\phi_l> + a_l<\phi_n\,|\,\phi_l{}^*>][\exp 1/i\hbar\int_0^t\{E_l(t') - E_n(t')\}dt']=0$$

or $\quad a^*{}_n = -\sum a_l<\phi_n\,|\,\phi_l{}^*>[\,\exp 1/i\hbar\int_0^t\{E_l(t') - E_n(t')\}dt'\,]$

To evaluate $<\phi_n\,|\,\phi_l>$, we have

$$\frac{\partial H}{\partial t}\,\phi_l + H\,\phi_l{}^* = E_l{}^*\,\phi_n + E_n\,\phi_n{}^*$$

or $\quad <\phi_n\,|\frac{\partial H}{\partial t}|\,\phi_l| + E_n<\phi_n\,|\,\phi_l{}^*> = E_l<\phi_n\,|\,\phi_l{}^*>$

or $\quad <\phi_n|\,\phi_l{}^*> = <\phi_n\,|\frac{\partial H}{\partial t}|\,\phi_l|\,/\,E_l - E_n$

To find $<\phi_n|\,\phi_l{}^*>$, on differentiating $<\phi_n|\,\phi_n> =1$ w.r.t. time,

$$<\phi_n{}^*\,|\,\phi_n> +<\phi_n|\,\phi_n{}^*> =0$$

$$<\phi_n{}^*\,|\,\phi_n>= i(t),\ \alpha\rightarrow\text{real}.$$

For new Eigen function $\phi'_n = \phi_n\,e^{i\gamma}$

We have $<\phi'_n | \phi_n> = i(\alpha+\gamma)$.

Choosing γ suitably , we can make this vanish. Hence

$$a_n^* = \sum{}' a_l/\hbar\omega_{nl} \; <\phi_n | \frac{\partial H}{\partial t} | \phi_l > \exp[i \int_0^t \omega_{nl}\, dt' \;]$$

Let the system be initially state , and the time variation be small : thus

$$a_n^* = \sum{}' 1/\hbar\omega_{nn} < \phi_n | \frac{\partial H}{\partial t} | \phi_m > \exp[i\,\omega_{mn} t];\; n \neq m$$

$$\text{or } a_n \approx \sum{}' 1/i\hbar\omega_{nn} < \phi_n | \frac{\partial H}{\partial t} | \phi_m > \exp[i\,\omega_{mn} t] - 1$$

with the above approximation this equation indicates that the probability amplitude for a state over than the initial states oscillates in time and show no steady increase over long periods of time even though H changes by finite amount.

15.10 Sudden Approximation

The sudden approximation consists of the change in Hamiltonian discontinuous on different times.

Suppose that $H = H_0$ for $t<0$

and $H = H_1$ for $t>0$

Then $H_0 u_n = E_n u_n$ for $t<0$

$H_0 v_n = E_n v_n$ for $t>0$

$$\Psi = \sum_\mu a_n\, u_n\, e^{-iEnt/\hbar}$$

and

$$\Psi = \sum_\mu b_\mu\, v_\mu\, e^{-iE\mu t/\hbar}$$

Equating the two solutions at t(0) = 0

$$b_\mu = \sum_\mu a_n <u_\mu | u_n> \qquad (15.10.1)$$

the sudden approximation consist in using above equation (15.10.1) when the change in the Hamiltonian occupies a very short finite interval of time t_0 suppose that

$H = H_0$ for $t<0$

$H = H_1$ for $t>0$

and $H = H_i$ for $0<t<t_0$

The intermediate Hamiltonian H_i, which is taken constant in time, has a complete set of energy Eigen functions :

$$H_k\ W_k = E_k\ W_k$$

The exact solution can be expressed in terms of the u's with constant coefficients

$$\Psi = \sum_k C_k\ W_k \exp(-iE_k t/\hbar)\ ;\ \text{for } 0<t<t_0$$

Using the application of the continuity condition at t=0 gives

$$C_k = \sum_n a_n <W_k \mid W_n> = \sum_n a_n <w \mid n>$$

And at $t= t_0$ gives

$$b_\mu = \sum_\mu C_k <\mu \mid k> \exp\{-i(E_k - E_\mu)t_0/\hbar\}$$

$$= \sum_\mu a_n <\mu \mid k> \exp\{-i(E_k - E_\mu)t_0/\hbar\} <k \mid n>$$

When $t_0=0$, the exponential is equal to unity and b is given by (1).

The sudden approximation will be best only when t_0 is small.

So on expansion exponential term in above equation.

$$a_\beta \approx \sum a_n \sum <\mu \mid k> \{1-i(E_k - E_\mu)t_0/\hbar\} <k \mid n>$$

or $$a_\mu \approx \sum a_n <\mu \mid [it_0(H_i - H_1)/\hbar] \mid n>$$

Hence error in sudden approximation is proportional to $\boldsymbol{t_0}$ for small t_0. If H_i depends upon time, then $\int_0^{t_0} H_i dt$ can be taken in place of $H_i t_0$.

If $H_1 = H_0$, then

$$B_i = \delta_{km}\ it_0/\hbar <k \mid H_i - H_0 \mid m>.$$

This can be used even when $(H_i - H_0)$ is not small as compared to H_0, taking t_0 small.

15.11 A Charged Particle in an Electromagnetic Field

If we apply the time- dependent perturbation theory to the charged particle, Then the effect of electric and magnetic fields on the particle must be calculated.

The electromagnetic force(E.M.F.) on a particle of charge e, and mass 'm' moving with velocity 'v' in an electromagnetic field characterised by electric field '**E**' and magnetic field '**B**' (or scalar potential 'ϕ' and vector potential '**A**') is

$$F = eE + e\frac{v \times B}{C} \qquad (15.11.1)$$

where c= speed of electromagnetic waves.

The electric and magnetic field can be expressed in terms of scalar and vector potentials as

$$E = \frac{-1}{c}\frac{\partial A}{\partial t} - \nabla\phi \text{ and } B = \nabla \times A \qquad (15.11.2)$$

Substituting these values in (15.11.1) and using

$$F = m\frac{d^2r}{dt^2}$$

We get $m\frac{d^2r}{dt^2} = e(\frac{-1}{c}\frac{\partial A}{\partial t} - \nabla\phi) + \frac{e}{C}v \times (\nabla \times A)$

Writing the above equation in terms of Cartesian components

$r = \hat{\imath}x + \hat{\jmath}y + kz,$

$A = \hat{\imath}A_x + \hat{\jmath}A_y + kA_z$, etc.

And comparing coefficients of î, ĵ and k, we get

$$m\frac{d^2x}{dt^2} = (\frac{-e}{c}\frac{\partial Ax}{\partial t} - e\frac{\partial \phi}{\partial x}) + \frac{e}{C}[y^*(\frac{\partial Ay}{\partial x} - \frac{\partial Ax}{\partial y}) - z^*(\frac{\partial Ax}{\partial z} - \frac{\partial Az}{\partial x})]$$

where $y^* = dy/dt \quad z^* = dz/dt$

and similar equations for y and z-components of force.

Writing $m\frac{d^2x}{dt^2} = \frac{d}{dt}(\frac{\partial T}{\partial x^*})$ where T is the kinetic energy, we get

$$\frac{d}{dt}(\frac{\partial T}{\partial x^*}) = \frac{-e}{c}\frac{\partial Ax}{\partial t} - e\frac{\partial \phi}{\partial x} + \frac{e}{C}[(x^*\frac{\partial Ax}{\partial x} + y^*\frac{\partial Ay}{\partial x} + z^*\frac{\partial Az}{\partial x})$$

$$-(x^*\frac{\partial A\infty}{\partial x} + y^*\frac{\partial A\infty}{\partial y} + z^*\frac{\partial A\infty}{\partial z})]$$

$$= -e\frac{\partial \phi}{\partial x} + \frac{e}{C}[\frac{\partial}{\partial x}(v.A) - (\frac{dA\infty}{dt} - \frac{\partial A\infty}{\partial t})]$$

$$= -e\frac{\partial \phi}{\partial x} + \frac{e}{C}\frac{\partial}{\partial x}(v.A) - \frac{e}{C}\frac{dA\infty}{dt}$$

$$\frac{d}{dt}\left(\frac{\partial T}{\partial x*}+\frac{e}{c}A\infty\right)=-e\frac{\partial \Phi}{\partial x}+\frac{e}{C}\frac{\partial}{\partial x}(v.A)$$

$$\frac{d}{dt}\left(\frac{\partial T}{\partial x*}+\frac{e}{c}A\infty\right)-\frac{\partial}{\partial x}\left[-e\phi+\frac{e}{C}(v.A)\right]=0 \qquad (15.11.3)$$

As kinetic energy (K.E.) is velocity dependent and does not depend on position coordinates (x , y, z) and the scalar potential ϕ is position dependent and does not depend on velocity coordinates (x*, y*,z*)

i.e.

$$\frac{\partial \phi}{\partial x*}=\frac{\partial \phi}{\partial y*}=\frac{\partial \phi}{\partial z*}=0 \text{ And } \frac{\partial T}{\partial x}=\frac{\partial T}{\partial y}=\frac{\partial T}{\partial z}=0 \qquad (15.11.4)$$

We may also write

$$A\infty=\frac{\partial}{\partial x*}(x^*A_x+y^*A_y+z^*A_z)=\frac{\partial}{\partial x*}(v.A) \qquad (15.11.5)$$

By using (15.11.4) and (15.11.5) equation (15.11.3) may be expressed as

$$\frac{d}{dt}\left[\frac{\partial}{\partial x*}\{T-e\phi+\frac{e}{c}(v.A)\}-\frac{\partial}{\partial x}\left[T-e\phi+\frac{e}{C}(v.A)\right]\right.=0 \qquad (15.11.6)$$

There are two similar equations for y and z. These equations are in form of Lagrange's equation, with the ***Lagrangian function L*** given by

$$L=\left[T-e\phi+\frac{e}{C}(v.A)\right] \qquad (15.11.7a)$$

$$=\tfrac{1}{2}m(x^{*2}+y^{*2}+z^{*2})-e\phi+\frac{e}{c}[x^*A_x+y^*A_y+z^*A_z] \qquad (15.11.7b)$$

Then canonical momentum associated with x, is

$$\left.\begin{aligned} p_x&=\frac{\partial L}{\partial x*}=mx^*+\frac{e}{c}A_x\\ \text{Similarly } p_y&=\frac{\partial L}{\partial y*}=my^*+\frac{e}{c}A_y\\ p_z&=\frac{\partial L}{\partial z*}=mz^*+\frac{e}{c}A_z \end{aligned}\right\} \qquad (15.11.8)$$

The Hamiltonian function in terms of *Lagrangian function* is

$$H=\sum p_k q_k-L=(x^*p_x+y^*p_y+z^*p_z)-L \qquad (15.11.9)$$

$$=(mx^*+\frac{e}{c}A_x)x^*+(my^*+\frac{e}{c}A_y)y^*+(mz^*+\frac{e}{c}A_z)z^*$$

$$-\{\tfrac{1}{2}m(x^{*2}+y^{*2}+z^{*2})-e\phi+\frac{e}{c}[x^*A_x+y^*A_y+z^*A_z]\}$$

$$=\frac{1}{2} m(x^{*2} + y^{*2} + z^{*2}) + e\phi \qquad (15.11.10)$$

From equation (15.11.8), we have

$$x^* = p_x/m - e A_x/mc, \; y^* = p_y/m - e A_y/mc, \; z^* = p_z/m - e A_z/mc$$

By using these values in equation (15.11.10) gives

$$H = 1/2m\, [(p_x/m - e A_x/mc)^2 + (p_y/m - e A_y/mc)^2$$

$$+ (p_z/m - e A_z/mc)^2] + e\phi \qquad (15.11.11)$$

Replacing $p_x = \hbar/i \, \frac{\partial}{\partial x}$, we note that for a wave function Ψ

$$(p_x - e A_x/c)^2 = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} + 2i\hbar e/c\, A_x \frac{\partial \Psi}{\partial x} + i\hbar\left(\frac{\partial Ax}{\partial x}\right)\Psi + \frac{e^2}{x^2} A^2 \Psi$$

and we get similar expression for $(p_y - e A_y/c)$ and $(p_z - e A_z/c)$

By using these expression equation (11) gives

$$H = \frac{-\hbar^2}{2m} \nabla^2 + e\phi + \frac{ie\hbar}{mc} A.\nabla + \frac{i\hbar e}{2mc} \nabla.A + \frac{e^2}{2mc^2} A^2 \qquad (15.11.12)$$

In electromagnetic field, according to Maxwell's equations

$$\text{div } A = \nabla.A = 0$$

in view of this equation (12) takes the form

$$H = \frac{-\hbar^2}{2m} \nabla^2 + e\phi + \frac{ie\hbar}{mc} A.\nabla + \frac{e^2}{2mc^2} A^2 \qquad (15.11.13)$$

This may be expressed as $H = H^0 + H'$

$$H^0 + H' = \frac{-\hbar^2}{2m} \nabla^2 + e\phi + \frac{ie\hbar}{mc} A.\nabla + \frac{e^2}{2mc^2} A^2 \qquad (15.11.14)$$

Where H^0 is unperturbed Hamiltonian given by

$$H^0 = \frac{-\hbar^2}{2m} \nabla^2 + e\phi = \frac{-\hbar^2}{2m} \nabla^2 + V \qquad (15.11.15)$$

V being potential energy and 'H' is perturbation or interaction term given by

$$H' = \frac{ie\hbar}{mc} A.\nabla + \frac{e^2}{2mc^2} A^2 \qquad (15.11.16)$$

For weak field terms of higher order in A i.e. $\frac{e^2}{2mc^2} A^2$ may be neglected. Therefore for a weak field the interaction part of the Hamiltonian is

$$H' = ie\hbar/mc\, \mathbf{A}.\boldsymbol{\nabla} = -e/mc\, \mathbf{A}.(-i\hbar\boldsymbol{\nabla})$$

i.e. $H' = -e/mc\ \mathbf{A.p}$ **(15.11.17)**

In the case of a number of such particles, the Hamiltonian for the system will be the sum of such Hamiltonians for individual particles. In the case of electron e may be replaced by –e (if e is to be maintained as positive quantity.

15.12 Self Learning Exercise

Q.1 A system in an unperturbed state n is suddenly subjected to a constant perturbation $H'(r)$ which exists during time $0 \rightarrow t$. Find the probability for transition from state n to state k and show that it varies simple harmonically with angular frequency $(E_k - E_n)/2\hbar$ and amplitude $4|H'_{kn}|/(E_k - E_n)^2$.

Q.2 For Hydrogenic atoms, the states are specified by the quantum numbers n, l, m. For a transition to be allowed, show that

$$\Delta n = \text{any value},\ \Delta l = \pm 1,\ \ l = 0, \pm 1$$

Q.3 Obtain the selection rule for electric dipole transitions of a linear harmonic oscillator.

15.13 Summary

In this unit we discussed about the identification of a bound state with discrete energy level and stationary Eigen function with the help of *Method of variation of constants, adiabatic approximation, and sudden approximation.*

15.14 Glossary

Adiabatic Approximation **:**

A method in which the Hamiltonian of the system (H) contains the parameter that change very slowly with time.

Sudden Approximation **:**A method in which the Hamiltonian of the system (H) is constant for the time except for a very short time interval and changes from one form to another form, known as Sudden Approximation.

15.15 Answer to Self Learning Exercise

Ans.1: Equation (10.6) gives the value of $c_k^1(t)$. When the perturbation is constant in time, $H'_{kn}(r)$ can be taken outside the integral. Hence

$c_k^1(t) = H'_{kn}(r)/i\hbar \int_0^t exp\,(i\omega_{kn}t')dt'$

$= -H'_{kn}/\hbar\omega_{kn}\,[\exp(i\omega_{kn}t)-1]$

$=-H'_{kn}/\hbar\omega_{kn}\exp(i\omega_{kn}t/2)[\exp(i\omega_{kn}t/2)-\exp(-i\omega_{kn}t/2)]$

$= -2iH'_{kn}/\hbar\omega_{kn}\exp(i\omega_{kn}t/2)\sin(i\omega_{kn}t/2)$

$|c_k^1(t)|^2 = 4|H'_{kn}|^2/\hbar^2\omega^2_{kn}\sin^2(i\omega_{kn}t/2)$

which is the probability for transition from state n to state k. From the above expression it is obvious that the probability varies simple harmonically with angular frequency $\omega_{kn}/2=(E_k - E_n)/2\hbar$. The amplitude of vibration is

$4|H'_{kn}|^2/\hbar^2\omega^2_{kn} = 4|H'_{kn}|^2/(E_k - E_n)^2$.

Ans.2: the form of the radial wave functions are such that the radial part of the integral $<n'l'm'|er|nlm>$is nonvanishing, whatever be the values of n', l',n and l. Hence Δn = any value is allowed.

By the Laporte selection rule , for a transition to be allowed, it is necessary that

$I_k + I_n = \text{odd}$

Therefore,

$l_k - l_n = \Delta l = \pm 1$

To obtain the selection rule for the quantum number m, the matrix element may be written as

$<n'l'm'|r|nlm> = \hat{i}<n'l'm'|r|nlm>+\hat{j}<n'l'm'|r|nlm>$

$+k<n'l'm'|r|nlm>$

If the radiation is plane polarized with the electric field in the z- direction, the z-component is the only relevant quantity, which is $<n'l'm'|r\cos\theta|nlm>$. The ϕ-part of this integral is

$$\int_0^{2\pi}\exp[i(m-m')\phi]\,d\phi$$

which is finite only when

$m - m' = 0$ or $\Delta m = 0$

if the relation is polarized in the xy- plane, it is convenient to find the matrix elements of x±iy since it is always possible to get the values for x and y by the relations

$$x = \tfrac{1}{2}[(x+iy) + (x-iy)], \qquad y = 1/2i\,[(x+iy) - (x-iy)]$$

in the polar coordinates,

$$x \pm iy = r\sin\theta\cos\phi \pm i\, r\sin\theta\sin\phi = r\sin\theta\ e^{\pm i\phi}$$

The matrix elements of x±iy are

$$\langle n'l'm'|r\sin\theta\ e^{\pm i\phi}\,|nlm\rangle = f(r,)\int_0^{2\pi} \exp[i(m-m'\pm 1)\phi]\,d\phi$$

This integral is non vanishing only when

$$m - m' \pm 1 = 0 \quad \text{or } m' - m = \pm 1 \quad \text{or } \Delta m = \pm 1$$

for arbitrary polarization, the general selection rule is

$$\Delta m = 0, \pm 1$$

Thus, the selection rules for hydrogenic atoms are

$$\Delta n = \text{any value},\ \ l = \pm 1,\ \ \Delta m = 0, \pm 1$$

Ans.3: Consider a charged particle having a charge r executing simple harmonic motion along the x- axis about a point where an opposite charge is situated. At a given instant, the dipole moment is ex, where x is the displacement from the mean position. The harmonic oscillator wave function is

$$\Psi_n(y) = N_n H_n(y) \exp(-y^2/2)\ y = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x$$

The dipole matrix element is given by

$$\langle k\,|\,y\,|\,n\rangle = \text{constant} \int H_k(y)\ y\ H_n(y) \exp(-y^2)dy$$

For Hermite polynomials

$$y\,H_n(y) = nH_{n-1} + \tfrac{1}{2} H_{n+1}(y)$$

substituting this value of y $H_n(y)$, we get

$$\langle k\,|y|\,n\rangle = \text{constant} \int H_k(y)[\,nH_{n-1} + \tfrac{1}{2} H_{n+1}(y)] \exp(-y^2)dy$$

In view of the orthogonality relation, we have

$$\int H_k(y)\,H_n(y) \exp(-y^2)dy = \text{constant}\ \delta_{kn}$$

$<k\ |y|\ n>$ is finite only when $k=n-1$ or $k=n+1$, i.e. the harmonic oscillator selection rule is $K-n=\pm1$ or $\Delta n=\pm1$.

15.16 Exercise

Q.1 Give the time dependent perturbation theory for the case of a perturbation which is constant in time except that it is switched on at t=0 and switched off at time t.

Q.2 Prove that the transition probability per unit time is

$$2\pi/\hbar\ (k)\ |\ H'_{km}|^2$$

where (k) denotes the density of final states and H'_{km} is the matrix element of the perturbation H'_{km}.

Q.3 Show that the transition probability per unit time for a system to make a transition from an initial state to a final state in the continuum is given by

$$\omega_{km} = 2\pi/\hbar\ (k)\ |\ <k\ |H'|\ k>|^2$$

where the symbols have their usual meanings.

Q.4 Give the theory of induced emission and absorption of radiation on the basis of time dependent perturbation theory.

Q.5 A small time dependent perturbation $H_1(t)$ is applied to a system in the state Ψ. Obtain the expansion coefficient $C_j(t)$ for the new state function. When the perturbation is kept on for a small time t. Calculate the transition probability per unit time when

$$H_1(t) = \cos\omega t.$$

Q.6 Prove the following:

(a) If the source temperature is 1000K, in the optical region (λ=5000Å), the emission is predominantly due to spontaneous transitions.

(b) If the source temperature is 300K, in the microwave region (λ=1 cm), the emission is predominantly due to stimulated emission. The Boltzmann constant is 1.38×10^{-23} JK^{-1}.

Q.7 Obtain Einstein's A coefficient for a one-dimensional harmonic oscillator of angular frequency ω in its nth state.

15.17 Answers to Exercise

Ans.6: Spontaneous emission/stimulated emission= $\exp(\hbar v/kT)-1$

(a)In the optical region,

$$v = c/\lambda = \frac{3\times10^{8}}{5000\times10^{-10}}$$

$$=6\times10^{14}\text{ Hz}$$

$$\hbar v/kT = \frac{6.626\times10^{-34}}{1.38\times10^{-23}}$$

$$=28.8$$

$$\exp(28.8)-1 = 3.22\times10^{12}$$

Thus, spontaneous emission is predominant.

(b) In the microwave region,

$$v = c/\lambda = \frac{3\times10^{8}}{10^{-2}} = 3\times10^{10}\text{ Hz}$$

$$\hbar v/kT = \frac{6.626\times10^{-34}\times3\times10^{10}}{1.38\times10^{-23}\times300}$$

$$= 4.8\times10^{-3}$$

$$\exp(4.8\times10^{-3})-1 = 0.0048$$

Therefore, stimulated emission is predominant.

Ans.7: $A_{n\rightarrow k} = 4\omega_{kn}^{3}e^{2}/3\hbar c^{3}\,|<k\,|x|\,n>|^{2}$

For linear harmonic oscillator, $|<k\,|x|\,n>|$ is finite only when k= n-1 or k= n+1

For emission from state n, k must be n-1. Hence

$$|<k\,|x|\,n>| = <n-1\,|x|\,n>$$

$$= <n-1\,|\left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}}(a + a*)|\,n>$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}}[(n-1)|a|n> + <(n-1)|a*|n>$$

$$=\left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}}(\sqrt{n}+0)=\left(\frac{n\hbar}{2m\omega}\right)^{\frac{1}{2}} \qquad k= n-1$$

Substituting this value of |<k |x| n>|

$$\mathbf{A}_{n\rightarrow k} = 4\omega_{kn}{}^{3}e^{2}/3\hbar c^{3}\left(\frac{n\hbar}{2m\omega}\right)^{\frac{2}{2}}$$

$$=2e^{2}\omega^{2}n/3mc^{3}$$

References and Suggested Readings

1. Lectures on Quantum Mechanics by Steven Weinberg.
2. Quantum Mechanics and Quantum Information by Moses Fayngold and Vadim Fayngold.
3. Quantum Mechanics by David Mcintyre.
4. Concepts of Quantum Mechanics by Vishnu Swarup Mathur and Surendra Singh
5. Fundamental of Quantum Mechanics by Springer.

UNIT-16

Quasi Classical Case : Bohr and Sommerfeld's Quantization

Structure of the Unit

16.0 Objectives

The main objective of this topic is to study about W.K.B. approximation in detail. In this chapter we shall study all things which is related to the WKB approximation method. In this topic we use the Schrodinger wave equation and study about its importance.

16.1 Introduction

The WKB approximation is based on the expansion of the wave function in powers of $\hbar$. This method invented by three scientists named as *Wentzel-Kramers–Brillouin*. This method is applicable when the potential V(x) is slowly varying. In this the solution of wave equation is two type

1:exponential, 2: oscillatory.

Therefore we study the connection formula of the solution also.

16.2 The Quasi Classical Condition

It is also known as W.K.B. approximation. W.K.B. stands for *Wentzel-Kramers–Brillouin* approximation. WKB approximation is a final type of time independent approximate calculations. It applies to only situations in which the ***potential energy is slowly varying function of position***. Problems of one dimension and also of three dimensions reducible in one dimension (radial) are solved by this method.

A slowly changing potential means the variation of potential energy V(r) slightly over several wavelengths (De Broglie waves) of the particles shown in fig.16.1.

The De Broglie wavelength associated with a particle moving with energy E in a region of potential V is

$$\lambda = h/p = \frac{h}{[2m(E-V)]^{\frac{1}{2}}} \tag{16.2.1}$$

Since $\frac{1}{2} mv^2 = E-V$

$$m^2v^2 = 2m(E-V)$$

$$\boxed{p = mv = \sqrt{2m(E-V)}}$$

The propagation constant

$$\boxed{k = \frac{2\pi}{\lambda} = \frac{\sqrt{[2m[E-V(x)]}}{\hbar}} \tag{16.2.2}$$

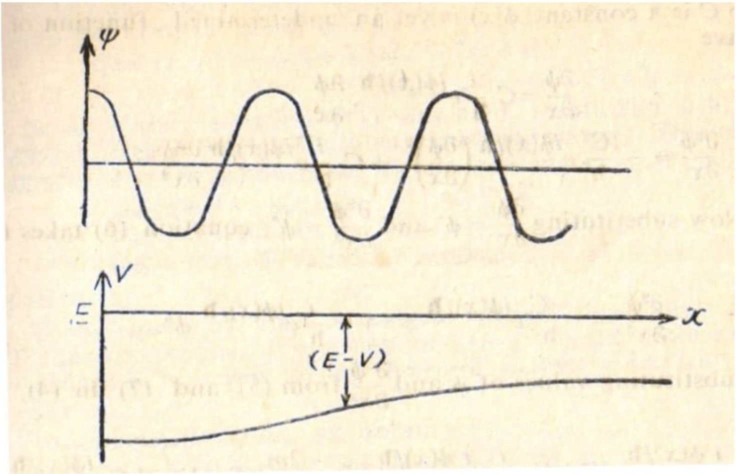


Fig.(16.1)"Slowly changing" one dimensional potential and its associated wave function.

Mathematically slowly varying potential can be expressed by the conditions

$$|1/k^2\, dk/dx| << 1$$

Substituting value of k form (1), we get

$$\frac{\hbar m|\frac{\partial V}{\partial X}|}{[2m(E-V)]^{\frac{3}{2}}} << 1 \text{ or } \lambda\frac{\partial V}{\partial X}/4(E-V) << 1 \qquad (16.2.3)$$

This equation gives the ***validity of W.K.B. approximation.***

16.3 Principle of the W.K.B. Approximation

W.K.B. approximation consists in introducing an expression in the powers of ħ and neglecting the terms in higher order of ħ. Hence Schrodinger wave equation (in some regions of space) is reduced in its classical limit. However, the method has a wider range of applicability than the classical approximation, because this procedure can be carried out even in regions of space where classical interpretation is meaningless (region E<V is inaccessible to classical particle).

Let Ψ(x) be the wave function satisfying Schrodinger wave equation

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{2m}{\hbar}[E-V(x)]=0 \qquad (16.3.1)$$

Let the solution of equation (16.3.1) be of the form

$$\Psi = Ce^{\frac{i\phi(x)}{\hbar}} \qquad (16.3.2)$$

where C is a constant, $\phi(x)$ is yet an undetermined function of x, we have

$$\frac{\partial \Psi}{\partial x} = C\, i/\hbar\ e^{\frac{i\phi(x)}{\hbar}} \frac{\partial \phi}{\partial x}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -C/\hbar^2 e^{\frac{i\phi(x)}{\hbar}} \left(\frac{\partial \phi}{\partial x}\right)^2 + C\, i/\hbar\ e^{\frac{i\phi(x)}{\hbar}}\ \frac{\partial^2 \phi}{\partial x^2} \qquad (16.3.3)$$

Now substituting $\frac{\partial \phi}{\partial x} = \phi'$ and $\frac{\partial^2 \phi}{\partial x^2} = \phi''$,

Equation (16.3.3)takes the form

$$\frac{\partial^2 \Psi}{\partial x^2} = -C/\hbar^2\ e^{\frac{i\phi(x)}{\hbar}} \phi'^2 + C\, i/\hbar\ e^{\frac{i\phi(x)}{\hbar}} \phi'' \qquad (16.3.4)$$

Now substituting the values of Ψ and $\frac{\partial^2 \Psi}{\partial x^2}$ from (16.3.2) and (16.3.4) in (16.3.1), we get

$$-C/\hbar^2\ e^{\frac{i\phi(x)}{\hbar}} \phi'^2 + C\, i/\hbar\ e^{\frac{i\phi(x)}{\hbar}} \phi'' + \frac{2m}{\hbar}[E-V(x)]\, Ce^{\frac{i\phi(x)}{\hbar}} = 0$$

or $$C/\hbar^2\ e^{\frac{i\phi(x)}{\hbar}} [-\phi'^2 + i\hbar\, \phi'' + 2m[E - V(x)]Ce^{\frac{i\phi(x)}{\hbar}}] = 0$$

As $$\Psi = C\, e^{\frac{i\phi(x)}{\hbar}} \neq 0;$$

Therefore above equation yields

$$[i\hbar\, \phi'' - \phi'^2 + 2m[E - V(x)] = 0 \qquad (16.3.5)$$

To get an approximate solution of (16.3.5), we apply W.K.B. method and ***hence expand $\phi(x)$ in powers of $\hbar$ i.e.***

$$\phi(x) = {}_0(x) + \hbar\phi_1(x) + \hbar^2/2\ \phi_2(x) + \ldots\ldots \qquad (16.3.6)$$

where the subscripts ϕ's are independent of $\hbar$. Let us assume that on account of the smallness of $\hbar$, the first two terms in equation (16.3.6) give a sufficiently good approximation to ϕ.

Differentiating equation (16.3.6), we obtain

$$\left.\begin{aligned} \phi'(x) &= \phi'_0(x) + \hbar\phi'_1(x) + \hbar^2/2\ \phi'_2(x) + \ldots\ldots \\ \phi''(x) &= \phi''_0(x) + \hbar\phi''_1(x) + \hbar^2/2\ \phi''_2(x) + \ldots\ldots \end{aligned}\right\} \qquad (16.3.7)$$

Substituting the values of $\phi'(x)$ and $\phi''(x)$ from (16.3.7) in equation (16.3.5), we get

$$i\hbar[\phi''_0(x) + \hbar\phi''_1(x) + \hbar^2/2\, \phi''_2(x)+......]$$

$$-[\, \phi'_0(x) + \hbar\phi'_1(x) + \hbar^2/2\, \phi'_2(x)+......+2m[E - V(x)]=0$$

Comparing the coefficients of various powers of ħ, we see that up to second order in ħ, the result is

$$[2m(E-V) - \phi_0^2 [\hbar\{i\, \phi''_0 - 2\, \phi'_0\, \phi'_1\} + \hbar^2\{i\, \phi''_1 - \phi'^2_1 - \phi'_0\, \phi'_2\}]=0 \tag{16.3.8}$$

In order that equation (16.3.8) may hold identically in ħ, the coefficient of each power ħ must vanish separately. This requirement leads to the following series of equations

$$\left.\begin{array}{ll} 2m(E-V) - \phi'^2_0 = 0 & \text{(a)} \\ i\, \phi''_0 - 2\, \phi'_0 \phi'_1 = 0 & \text{(b)} \\ i\, \phi''_1 - \phi'^2_1 - \phi'_0\, \phi'_2 = 0 & \text{(c)} \end{array}\right\} \tag{16.3.9}$$

and so on.

These equations may be solved successively. That is, the first equation defines ϕ_0 in terms of |(E−V)|, the second equation defines ϕ_1 in terms of ϕ_0, the third defines ϕ_2 in terms of ϕ_1 and ϕ_0 etc.

From equation (16.3.9a), we obtain

$$\phi'_0 = \pm\sqrt{2m(E - V)} \tag{16.3.10}$$

Integrating above equation yields

$$\phi_0 = \int_{x_0}^{x} \sqrt{2m(E - V)}\, dx \tag{16.3.11}$$

where x_0 is an arbitrary fixed value of x.

From equation (16.3.9b), we obtain

$$\phi'_1 = i\, \phi''_0/2\, \phi'_0$$

Integration of above equation yields

$$\phi_1 = i/2 \log \phi'_0 + C_1 \qquad (16.3.12)$$

where C_1 is a constant of integration. This result is convenient is ϕ'_0 is negative. Therefore keeping in mind that the logarithm of a negative function differs only by an imaginary constant from the logarithm of the absolute value of the function, we replace equation (16.3.12) by

$$\phi_1 = i/2 \log |\phi'_0| + C_2 \qquad (16.3.13)$$

where C_2 is an arbitrary constant.

Similarly

$$\phi_2 = ½ \frac{m(\frac{\partial V}{\partial X})}{[2m(E-V)]^{\frac{3}{2}}} - ¼ \int_{x_0}^{x} \frac{m^2(\frac{\partial V}{\partial X})}{[2m(E-V)]^{\frac{5}{2}}} \qquad (16.3.14)$$

From equation (16.3.13) we see that ϕ_1 is represented as a logarithm of $|\phi'_0|$, therefore it i9s not, in general, small compared with ϕ_0. Consequently ϕ_0 and ϕ_1 both must be retained. On the other hand from equation (16.3.14) we see that ϕ_2 will be small whenever $\frac{\partial V}{\partial x}$ is small and (E-V) is not too close to zero. ***Further it can be seen easily that the smallness of the higher approximation(ϕ_3,$\phi_{4,\ldots\ldots}$etc) requires the smallness of all derivatives of V. Hence the W.K.B. approximation will be suitable in cases where V is a sufficiently smooth and slowly varying function of position.***

Now the approximate W.K.B. solution of equation (16.3.5) may be expressed in the form

$$\phi \approx \phi_0(x) + ½ i\hbar \log |\phi'_0| \qquad (16.3.15)$$

Assuming constant C_2 is absorbed in $\phi_0(x)$.

Substituting value of $\phi(x)$ from (16.3.15) in equation (16.3.2) and rearranging the result. We finally get the approximation solution Ψ_{app} of equation (16.3.1) in the form

$$\Psi_{app} = C \{2m|E - V(x)|\}^{\frac{-1}{4}} \exp[\pm i/\hbar \int_{x_0}^{x} \sqrt{2m[E - V(x)]}\, dx] \qquad (16.3.16)$$

where C remains arbitrary. The two solutions contained in (16.3.16) and differing sign of the exponent are linearly and hence the approximate general solution, according to W.K.B. approximation, is

$$\Psi_{\text{app}}=\mathrm{C}\,\{2\mathrm{m}|\mathrm{E}-\mathrm{V(x)}|\}^{\frac{-1}{4}}\,[\mathrm{A}\exp\{\mathrm{i}/\hbar\int_{x_0}^{x}\sqrt{2\mathrm{m}[\mathrm{E}-\mathrm{V(x)}]}\,dx\}$$

$$+\mathrm{B}\exp\{\mathrm{i}/\hbar\int_{x_0}^{x}\sqrt{2\mathrm{m}[\mathrm{E}-\mathrm{V(x)}]}\,dx\}] \qquad (16.3.17)$$

where A and B are arbitrary constants. The positive exponential corresponds to a wave moving in the positive direction and the negative exponential corresponds to a wave moving in the negative direction. For the special case when V(x) is a constant, these reduce respectively to the plane waves

$\exp\{\mathrm{ipx}/\hbar\}$ and $\exp\{-\mathrm{ipx}/\hbar\}$.

The alternative form of equation (16.3.17) may be expressed as

$$\Psi_{\text{app}}=\mathrm{C}\,\{2\mathrm{m}|\mathrm{E}-\mathrm{V(x)}|\}^{\frac{-1}{4}}\cos[1/\hbar\int_{x_0}^{x}\sqrt{2\mathrm{m}[\mathrm{E}-\mathrm{V(x)}]}\,dx+\theta] \qquad (16.3.18)$$

where C and θ are arbitrary constants.

The approximate solutions (16.3.17) and (16.3.18) of the Schrodinger wave equation are usually called W.K.B. Ψ-functions.

16.4 Connection Formulas for Penetration of a Barrier

W.K.B. approximation is applicable so the problems only where the potential function does not change too rapidly; because in the regions approximations considered do not apply. In the problems where the potential function vary slowly in some regions, so that W.K.B. approximation holds and the potential function varies rapidly in other regions, so that W.K.B. approximation is inapplicable; we find the solution in the regions of inapplicability of W.K.B. approximation by some other approximations and carry it to the regions where W.K.B. Approximation is applicable. In order to connect these two solutions: we need for the connection formulas.

To treat the problem of barrier penetration where W.K.B. approximation is valid, we must find how to connect solutions in the region where E<V with those V<E.

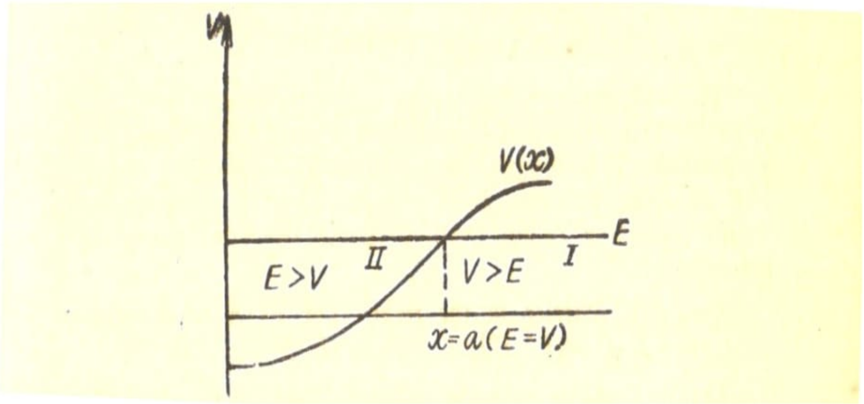


Fig : 16.2 Potential Barrier

Consider the potential barrier shown fig(16.2). Suppose the energy E of particle is such that E = V at point x=a.

Classically, the particle should slow down to zero velocity at this point and turn back. Quantum mechanically we know that the wave penetrates some distance further into the barrier. Obviously we cannot use the W.K.B. approximation in the region near x=a because when E=V, the condition for applicability breaks down.

Hence if we start with a given solution at some distance to the right of x=a (in 1 region)say

$$\Psi \sim 1/\sqrt{p_1}\,\exp\left(\int_a^x p_1 dx/\hbar\right) \qquad (16.4.1)$$

where $p_1 = \sqrt{2m[V-E]}$

From W.K.B. method, we know that a sufficient distance to left of x=a(in 2nd region), the approximate solution will be

$$\Psi \sim A/\sqrt{p_2}\,\exp\left(+i\int_a^x p_2 dx/\hbar\right) + B/\sqrt{p_2}\,\exp\left(-i\int_a^x p_2 dx/\hbar\right) \qquad (16.4.2)$$

where $p_2 = \sqrt{2m[E-V]}$ and A and B are unknown constants.

The values of A and B cannot be found by W.K.B. method alone, because they determined by the nature of the solution in the region of inapplicability of W.K.B. method. To obtain the values of A and B we need an exact solution near x=a; but it is too complex problem to be solved. If the W.K.B. method is applicable at some distance from x=a and inapplicability at small enough region x=a ; then the potential function can be represented approximately by a straight line within the region, with slope equal to that of potential curve at the classical turning point x=a.

As E=V, at x=a, we can write

$$V-E = C(x-a)$$

where C is a constant, equal to $(\frac{\partial V}{\partial x})_{x=a}$. Hence in region x=a the Schrodinger wave equation reduces approximately to

$$\frac{\partial^2 \Psi}{\partial x^2} - \frac{2m}{\hbar^2}C(x-a)= 0 \tag{16.4.3}$$

The difficult equation can be solved by Bessel's function of order 1/3. The solution of equation (16.4.3) is carried far enough from x=a, so that W.K.B. approximation becomes applicable. In this way, we may determine the constants A and B. Here we shall simply write the results without going through the complex procedure.

16.4.1 Case (a). Barrier to the right

Let V>E to the right of x=a

$$p_1 = \sqrt{2m[V-E]} \text{ ; and } p_2=\sqrt{2m[E-V]}$$

Here we consider that far to the right of x=a, the W.K.B. approximate solution, which is exponential, namely

$$\Psi_1 \approx B/\sqrt{p_1}\exp(-\int_x^a p_1 dx/\hbar) \tag{16.4.4}$$

For to the left to x=a, the connection formula states that this solution approaches

$$\Psi_2 \approx B/\sqrt{p_2}\,\mathrm{Cos}(\int_x^a p_2 dx/\hbar - \frac{\pi}{4}) \tag{16.4.5}$$

Hence the connection formula may be expressed as

$$1/\sqrt{p_1}\exp(-\int_a^x p_1 dx/\hbar) \rightleftharpoons 2/\sqrt{p_2}\,\mathrm{Cos}(\int_x^a p_2 dx/\hbar - \frac{\pi}{4}) \tag{16.4.6}$$

Similarly if the approximate solution is an increasing exponential to the right of x=a, the following connections hold

$$1/\sqrt{p_2}\,\mathrm{Sin}(\int_x^a p_2 dx/\hbar - \frac{\pi}{4}) \rightleftharpoons -1/\sqrt{p_1}\exp(\int_a^x p_1 dx/\hbar) \tag{16.4.7}$$

16.4.2 Case (b). Barrier to the left

For the solution which decays exponentially to the left of x=a, the following connections hold

$$1/\sqrt{p_1}\exp(-\int_x^a p_1 dx/\hbar) \rightleftharpoons 2/\sqrt{p_2}\,\mathrm{Cos}(\int_a^x p_2 dx/\hbar - \frac{\pi}{4}) \tag{16.4.8}$$

If the solution increases exponentially to the left, we obtain the following connection formula

$$1/\sqrt{p_2}\, \mathrm{Sin}\left(\int_a^x p_2 dx/\hbar - \frac{\pi}{4}\right) \rightleftharpoons -1/\sqrt{p_1}\, \exp\left(\int_x^a p_1 dx/\hbar\right) \qquad (16.4.9)$$

It may be noted that the connection formulas enable us only to obtain the relation between the solutions in a region at some distance to the right of the turning point x=a, with those in a region some distance to the left. In order to obtain the form of wave-function in the intermediate region, we should consider the exact solution, which involves Bessel functions of order 1/3.

For applying W.K.B. approximation, the following requirements must be satisfied.

1. On either side of the turning point, there exist regions when potential functions changes slowly so that W.K.B. approximation is applicable.

2. In the region near the turning point x=a where W.K.B. method becomes inapplicable, the kinetic energy can be represented approximately by a straight line (E-V) = C (x-a). In other words the potential should not undergo a large fractional change in slope within this region. Inside the barrier W.K.B. approximation begins to hold after

$$\int_a^x \sqrt{2m[V-E]}\,dx/\hbar$$ becomes appreciably greater than unity.

16.5 Application of W.K.B. Probability of Penetration of a Barrier

In order that W.K.B. approximation may be applied within a barrier, it is necessary that the potential function must vary slowly. For the application of connection formulae, it is also necessary that the barrier be thick enough and high enough, so that

$$\int_a^b \frac{\sqrt{2m[V-E]}}{\hbar}\,dx$$ can be considerably greater than unity.

By the application of these conditions we can calculate the probability of penetration of the barrier.

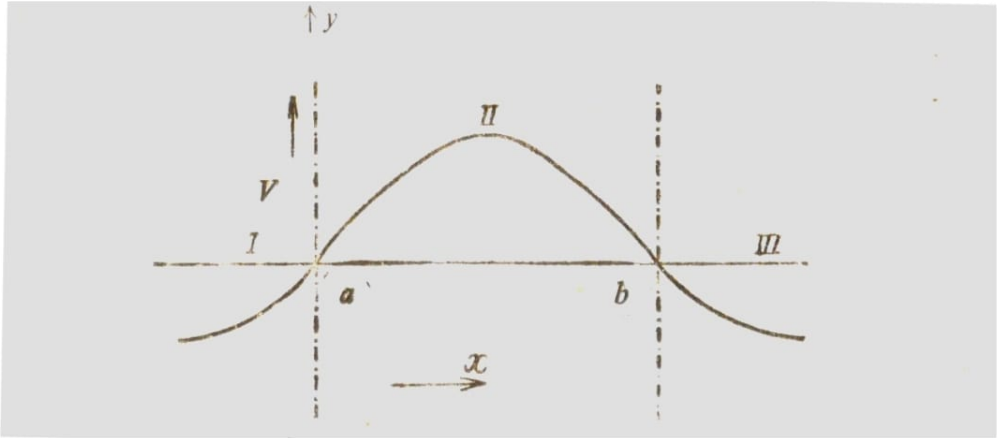


Fig.6.3: Slowly changing potential with boundaries

The barrier is shown in fig. 16.3 and the energy of particles is such that the turning points are at x=a and x=b. Let the beam of particles of energy E be incident from the left side. The beam of particles of energy E be incident from the left side. The beam of particles is partly reflected and partly transmitted at x=a due to wave nature of particles. The beam transmitted at x=b. The beam transmitted in region 3rd continues propagating along positive X-axis and is never reflected back. Therefore in 3rd region, there is only transmitted beam. According to W.K.B. method the solution of Schrodinger wave equation in one dimension

$$\frac{\partial^2\Psi}{\partial x^2} - \frac{2m}{\hbar^2}(E-V)\Psi = 0 \qquad (16.5.1)$$

is written as

$$\Psi_3 \approx A/\sqrt{p_2}\, \exp(i \int_b^x p_2 dx/\hbar - \frac{\pi}{4}) \qquad (16.5.2)$$

where $p_2 = \sqrt{2m[E-V]}$ and the phase factor $(-\pi/4)$ is included in exponential for convenience in applying connection formulae. As the constant A is a complex; such a phase factor may be absorbed in it. To apply the connection formula, we write equation (16.5.2) in the form

$$\Psi_3 \approx A/\sqrt{p_2}[\mathrm{Cos}(\int_b^x p_2 dx/\hbar - \frac{\pi}{4}) + i\mathrm{Sin}(\int_b^x p_2 dx/\hbar - \frac{\pi}{4})] \qquad (16.5.3)$$

On applying the connection formulae of **the barrier to the left** of x=b, the solution in 2nd region is expressed as

$$\Psi_2 \approx A/\sqrt{p_1}\,[1/2 \exp(-\int_x^b p_1 dx/\hbar) - i \exp(\int_x^b p_1 dx/\hbar)] \qquad (16.5.4)$$

where $p_1 = \sqrt{2m[V - E]}$ since in region 2nd, V>E.

The next step is to apply the connection formulae to find the wave-function in 1st region. To do so equation (16.5.4) must be modified accordingly. For this we use the property of definite integrals, viz.

$$\int_a^b \frac{p_1}{\hbar} dx = \int_a^x p_1 dx/\hbar + \int_x^b p_1 dx/\hbar$$

i.e.
$$\int_x^b p_1 dx/\hbar = \int_a^b \frac{p_1}{\hbar} dx - \int_a^x p_1 dx/\hbar \tag{16.5.5}$$

and write equation (16.5.4) as

$$\Psi_2 \approx A/\sqrt{p_1}\,[1/2 \exp(-\int_a^b \frac{p_1}{\hbar} dx + \int_a^x p_1 dx/\hbar)$$
$$- i \exp(\int_a^b \frac{p_1}{\hbar} dx - \int_a^x p_1 dx/\hbar)] \tag{16.5.6}$$
$$\approx A\,[1/2 \exp(-\int_a^b \frac{p_1}{\hbar} dx) \frac{1}{\sqrt{p_1}} exp(\int_a^x p_1 dx/\hbar)$$
$$- i \exp(\int_a^b \frac{p_1}{\hbar} dx). \frac{1}{\sqrt{p_1}} \exp(-\int_a^x p_1 dx/\hbar)]$$

Corresponding to region 1st, the barrier is to right, therefore applying connection formulae for the barrier to the right, we get the wave function in region 1st region as

$$\Psi_1 \approx A\,[-1/2 \exp(-\int_a^b \frac{p_1}{\hbar} dx) \frac{1}{\sqrt{p_2}} sin(\int_x^a p_2 dx/\hbar - \frac{\pi}{4})$$
$$- i \exp(\int_a^b \frac{p_1}{\hbar} dx). \frac{2}{\sqrt{p_2}} \cos(\int_x^a p_2 dx/\hbar - \frac{\pi}{4})]$$

$$\approx -A/\sqrt{p_2}[\,1/2 \exp(-\int_a^b \frac{p_1}{\hbar} dx) \{\frac{\exp[i\int_x^a(\frac{p^2 dx}{\hbar} - \frac{\pi}{4})] - \exp[-i\int_x^a(\frac{p^2 dx}{\hbar} - \frac{\pi}{4})]}{2i}\}$$
$$+2i \exp(\int_a^b \frac{p_1}{\hbar} dx) \{\frac{\exp[i\int_x^a(\frac{p_2 dx}{\hbar} - \frac{\pi}{4})] + \exp[-i\int_x^a(\frac{p_2 dx}{\hbar} - \frac{\pi}{4})]}{2}\}\,]$$

$$\approx -iA/\,[\sqrt{p_2} \exp\{i\int_x^a(\frac{p_2 dx}{\hbar} - \frac{\pi}{4})\}\{exp(\int_a^b \frac{p_1}{\hbar} dx) - \frac{1}{4}\exp\left(-\int_a^b \frac{p_1}{\hbar} dx\right)\}$$
$$+ \exp\left\{-i\int_x^a(\frac{p^2 dx}{\hbar} - \frac{\pi}{4}\right)\{exp(\int_a^b \frac{p_1}{\hbar} dx) + \frac{1}{4}\exp\left(-\int_a^b \frac{p_1}{\hbar} dx\right)\}] \tag{16.5.7}$$

In this expression the term containing positive exponential

i.e. $$-iA/\sqrt{p_2}\,\exp\{i\int_x^a(\frac{p_2dx}{\hbar}-\frac{\pi}{4})\}\{exp(\int_a^b\frac{p_1}{\hbar}dx)-\frac{1}{4}\exp\left(-\int_a^b\frac{p_1}{\hbar}dx\right)\} \tag{16.5.8}$$

is the wave travelling along positive X-axis in 1st region, i.e. incident wave while the second term containing negative exponential i.e.,

$$-iA/\sqrt{p_2}[\exp\left\{-i\int_x^a(\frac{p^2dx}{\hbar}-\frac{\pi}{4}\right)\{exp(\int_a^b\frac{p_1}{\hbar}dx)+\frac{1}{4}\exp\left(-\int_a^b\frac{p_1}{\hbar}dx\right)\}] \tag{16.5.9}$$

is the wave travelling along negative X-axis, i.e. wave reflected at x=a.

The transmission coefficient which is just the ratio of transmitted flux to incident flux is given by

$$T=\frac{transmitted\ flux}{incident\ flux}$$

$$=\frac{(transmitted\ intensity)\times velocity of\ particles}{(incident\ intensity)\times velocity of\ particles}$$

$$=\frac{(transmitted\ intensity)(\frac{p_2}{m})}{(incident\ intensity)(\frac{p_2}{m})}$$

$$=\frac{(transmitted\ intensity)}{(incident\ intensity)} \tag{16.5.10}$$

From (16.5.2), transmitted intensity $=AA^*/\sqrt{p_2}\sqrt{p_2}^*$

$$=\frac{|A|^2}{p_2}$$

From (16.5.8), incident intensity

$$=\frac{|A|^2}{p_2}\{exp(\int_a^b\frac{p_1}{\hbar}dx)-\frac{1}{4}\exp\left(-\int_a^b\frac{p_1}{\hbar}dx\right)\}^2$$

So transmission coefficient

$$T=\frac{\frac{|A|^2}{p_2}}{\frac{|A|^2}{p_2}\{exp(\int_a^b\frac{p_1}{\hbar}dx)-\frac{1}{4}\exp\left(-\int_a^b\frac{p_1}{\hbar}dx\right)\}^2}$$

$$T=\{exp(\int_a^b\frac{p_1}{\hbar}dx)-\frac{1}{4}\exp\left(-\int_a^b\frac{p_1}{\hbar}dx\right)\}^{-2} \tag{16.5.11}$$

If W.K.B. approximation is applicable, then

$$\int_a^b \frac{p_1}{\hbar} dx >> 1$$

So negative exponential may be ignored in comparison with the positive exponential. Hence the transmission coefficient is given by

$$T \simeq exp(-2\int_a^b \frac{p_1}{\hbar} dx)$$

$$= \exp[(-2\int_a^b \frac{\sqrt{2m[V-E]}}{\hbar} dx) \qquad (16.5.12)$$

16.6 Bohr Sommerfeld Quantization rule

Consider, a bound stationary state in a potential well. Let the energy of state be E and assume that the particle is classically allowed in the region a $\leq$ x$\leq$ b. Hence then region of x is divided into three parts namely:

(a) x<a, region 1st

(b) a< x <b, region 2nd and

(c) x>b, region 3rd .

The classical turning points are at x=a and x=b. Therefore the wave function Ψ decays exponentially to the left of x=a and to the right of x=b. In regions 1st and 3rd , V>E and in region 2nd, V<E. Let $p_1 = \sqrt{2m[V-E]}$ and $p_2 = \sqrt{2m[E-V]}$.

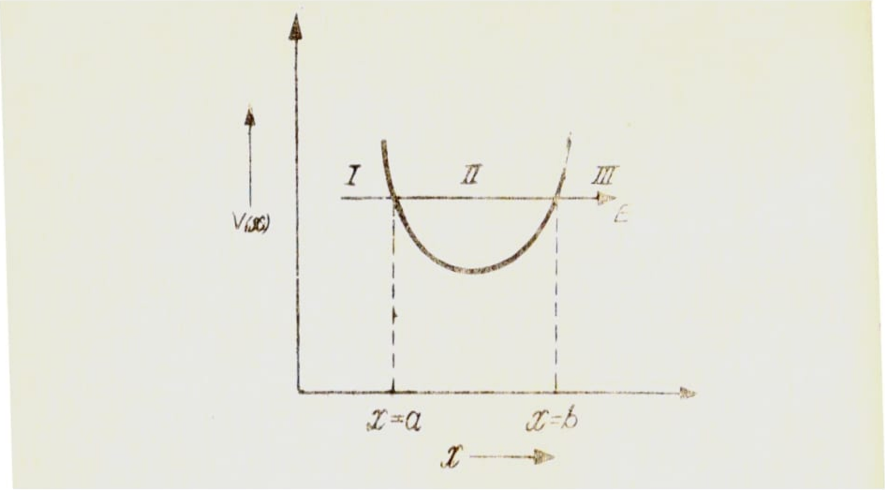


FIG. 16.4 Potential barrier

Obviously in region 1st , the wave function by W.K.B. approximation is

$$\Psi_1 \approx A/\sqrt{p_1}\exp\left(-\int_x^a p_2 dx/\hbar\right) \tag{16.6.1}$$

Applying connection formula of barrier to the left of x=a, we get the solution in region 2nd as

$$\Psi_2 \approx 2A/\sqrt{p_2}\,\mathrm{Cos}\left(\int_a^x p_2 dx/\hbar - \frac{\pi}{4}\right) \tag{16.6.2}$$

This equation may be written in the form

$$\Psi_2 \approx 2A/\sqrt{p_2}\,\mathrm{Cos}\left[\left\{\int_a^b p_2 dx/\hbar + \int_b^x p_2 dx/\hbar\right\} - \frac{\pi}{4}\right]$$

Now by adding and subtracting $\frac{\pi}{4}$

$$\Psi_2 \approx 2A/\sqrt{p_2}\,\mathrm{Cos}\left[\left\{\left(\int_a^b p_2 dx/\hbar - \frac{\pi}{2}\right) - \left(\int_b^x p_2 dx/\hbar - \frac{\pi}{4}\right)\right]$$

$$\Psi_2 \approx 2A/\sqrt{p_2}\left[\mathrm{Cos}\left(\int_a^b p_2 dx/\hbar - \frac{\pi}{2}\right)\mathrm{Cos}\left(\int_x^b p_2 dx/\hbar - \frac{\pi}{4}\right)\right.$$

$$\left. + \mathrm{Sin}\left(\int_a^b p_2 dx/\hbar - \frac{\pi}{2}\right)\mathrm{Sin}\left(\int_x^b p_2 dx/\hbar - \frac{\pi}{4}\right)\right]$$

$$\Psi_2 \approx 2A/\sqrt{p_2}\left[\mathrm{Sin}\left(\int_a^b p_2 dx/\hbar\right)\mathrm{Cos}\left(\int_x^b p_2 dx/\hbar - \frac{\pi}{4}\right)\right.$$

$$\left. + \mathrm{Cos}\left(\int_a^b p_2 dx/\hbar\right)\mathrm{Sin}\left(\int_x^b p_2 dx/\hbar - \frac{\pi}{4}\right)\right] \tag{16.6.3}$$

Applying connection formulae of barrier to the right x=b, we get the solution in 3rd region (x>b) as

$$\Psi_3 = A/\sqrt{p_1}\left[\mathrm{Sin}\left(\int_a^b p_2 dx/\hbar\right)\exp\left(-\int_b^x p_1 dx/\hbar\right)\right.$$

$$\left. + 2\mathrm{Cos}\left(\int_a^b p_1 dx/\hbar\right)\exp\left(\int_b^x p_1 dx/\hbar\right)\right] \tag{16.6.4}$$

In 3rd region (x>b), i.e. boundary condition is that $|\Psi| \to 0$ as $x \to \infty$, therefore in the solution Ψ_3, there must be the term containing decreasing exponential only. Consequently the second term in (4) must vanish in order that Ψ_3 be an acceptable solution for bound state. This gives

$$\mathrm{Sin}\left(\int_a^b p_2 dx/\hbar\right) = 0$$

or

$$\int_a^b p_2 dx/\hbar = (n + 1/2)\pi \tag{16.6.5}$$

where n=0,1,2,3,.......

or $$\int_a^b p_2 dx = (n+1/2)\pi\hbar = (n+1/2)\frac{\pi h}{2\pi}$$

$$= (n+1/2)\frac{h}{2} \tag{16.6.6}$$

In the semi classical approximation the period of the particle is the time taken by the particle to move from a to b and back. Therefore writing p for p_2, we get

$$\boxed{\oint p dx = 2\int_a^b p dx = \left(n+\frac{1}{2}\right)h} \tag{16.6.7}$$

This is known as ***Bohr Sommerfeld Quantization*** **Rule.**

16.7 Self Learning Exercise

Q.1 An anharmonic oscillator is described by the Hamiltonian

$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + Ax^4$$

Determine its ground state energy by selecting

$$\Psi = \frac{\lambda^{\frac{1}{2}}}{\pi^{\frac{1}{4}}}\exp\left(\frac{-\lambda^2 x^2}{2}\right)$$

λ being a variable parameter as the variational trial wave function.

Q.2 Consider a particle having momentum p moving inside the one-dimensional potential well shown in fig . If E<V(x), show by the W.K.B. method, that

$$\int_{x_1}^{x_2} p dx = (n+1/2)h, \quad n = 0, 1, 2, \ldots\ldots$$

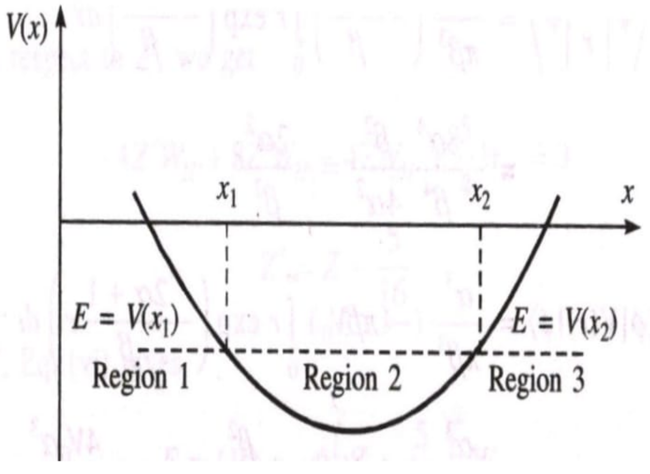


Figure: A potential well with linear turning points at x_1 and x_2.

Q.3 Estimate the ground state energy of helium atom by taking the product of two normalised Hydrogenic ground state wave functions as the trial wave function, the nuclear charge Z'e being the variable parameter. Assume that the expectation value of the interelectronic repulsion term is (5/4) ZW_H, W_H = 13.6eV

Q.4 Obtain the energy values of harmonic oscillator by the W.K.B. method.

Q.5 Solve the following one-dimensional infinite potential well:

$$V(x) = 0 \text{ for } -a< x <a;\ V(x) = \infty \text{ for } |x| >a$$

Using W.K.B. method and compare it with the exact solution.

Q.6 Estimate the energy levels of a particle moving in the potential

$$V(x) = \begin{cases} \infty, & x<0 \\ Ax, & x>0 \end{cases}$$

A being a constant.

16.8 Summary

In this chapter mainly we study about the WKB approximation method. We also study the connection formula of the solution of the wave equation. This chapter contains some important topic named Bohr-Summerfield quantisation rule, Quasi classical condition and application of the WKB approximation method.

16.9 Glossary

WKB approximation: It is based onthe expansion of the wave function in powers of $\hbar$. This method invented by three scientists named as *Wentzel-Kramers–Brillouin*.WKB approximation applies to only situations in which the potential energy is slowly varying function of position.

Bohr-Sommerfeld Quantisation Rule:

$$\oint p\, dx = 2\int_a^b p dx = (n+1/2)\, h$$

Here a and b is the boundaries (limits) of the integration.

$$\mathbf{T} = \frac{transmitted\ flux}{incident\ flux}$$

$$= \frac{(transmitted\ intensity) \times velocity of\ particles}{(incident\ intensity) \times velocity of\ particles}$$

$$= \frac{(transmitted\ intensity)(\frac{p_2}{m})}{(incident\ intensity)(\frac{p_2}{m})} = \frac{(transmitted\ intensity)}{(incident\ intensity)}$$

16.10 Answer of Self Learning Exercise

Ans.1: With the trial function Ψ, the expectation value of H is

$$<H> = \lambda\pi^{\frac{-1}{2}} \int_{-\infty}^{+\infty} e^{\frac{-\lambda^2 x^2}{2}} \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + Ax^4\right) e^{\frac{-\lambda^2 x^2}{2}} dx$$

Using the values of the first three integrals from the appendix, we obtain

$$<H> = \frac{\hbar^2\lambda^2}{4m} + \frac{3A}{4\lambda^4}$$

Minimizing <H> with respect the variable parameter λ, we get

$$0 = \frac{\partial <H>}{\partial\lambda} = \frac{\hbar^2\lambda}{2m} - \frac{3A}{\lambda^5}$$

$$\lambda = \left(\frac{6mA}{\hbar^2}\right)^{\frac{1}{6}}$$

Substituting this value of λ, we obtain

$$<H> = \frac{\hbar^2}{4m}\left(\frac{6mA}{\hbar^2}\right)^{\frac{1}{3}} + \frac{3A}{4}\left(\frac{\hbar^2}{6mA}\right)^{\frac{2}{3}}$$

$$<H> = \frac{3^{\frac{1}{3}}}{2}\left(\frac{\hbar^2}{2m}\right)^{\frac{2}{3}} A^{\frac{1}{3}} + \frac{3^{\frac{1}{3}}}{2}\left(\frac{\hbar^2}{2m}\right)^{\frac{2}{3}} A^{\frac{1}{3}}$$

$$= \frac{3^{\frac{4}{3}}}{2}\left(\frac{\hbar^2}{2m}\right)^{\frac{2}{3}} A^{\frac{1}{3}} = 1.082\left(\frac{\hbar^2}{2m}\right)^{\frac{2}{3}} A^{\frac{1}{3}}$$

It may be noted that numerical integration gives a coefficient of 1.08 , illustrating the usefulness of the variation method. It may be noted that perturbation technique is not possible as there is no way to split H into an unperturbed part and a perturbed part.

Ans.2: Classically, the particle will oscillate back and forth between the turning points x_1 and x_2. Quantum mechanically, the particles can penetrate into regions 1 and 2. The wave functions in regions 1 and 2 are exponentially decreasing. When we move from region 1 to region 2, the barrier is to the left of the turning point and, when we move from region 2 to region 3, the barrier is to the right of the turning point. The wave function in region 1 is

$$\Psi_1 = \frac{1}{\sqrt{r}} \exp\left(-\int_{x_2}^{x_1} \gamma dx\right), \quad \gamma^2 = \frac{2m[V(x)-E]}{\hbar^2} \tag{1}$$

$$\Psi_2 = \frac{2}{\sqrt{k}} \cos\left(\int_{x_2}^{x_1} k dx - \frac{\pi}{4}\right), \; k^2 = \frac{2m[E-V(x)]}{\hbar^2} \tag{2}$$

The wave function that connects region 2 with the decreasing potential of region 3 being of the type

$$\text{Cos}\left(\int_{x_1}^{x_2} k dx - \frac{\pi}{4}\right),$$

Hence, equation (2) should be modified as

$$\Psi_2 = \frac{2}{\sqrt{k}} \cos\left(\int_{x_2}^{x_1} k dx + \int_{x_2}^{x} k dx - \frac{\pi}{4}\right) \tag{3}$$

Since Cos(-ϕ)=Cosϕ and sin(-ϕ) = sinϕ, equation(3) can be written as

$$\Psi_2 = \frac{2}{\sqrt{k}} \cos\left(\int_{x_1}^{x_2} k dx\right) Cos\left(\int_{x}^{x_2} k dx + \frac{\pi}{4}\right)$$

$$+ \frac{2}{\sqrt{k}} \text{Sin}\left(\int_{x_1}^{x_2} k dx\right) Sin\left(\int_{x}^{x_2} k dx + \frac{\pi}{4}\right)$$

$$= \frac{2}{\sqrt{k}} \cos\left(\int_{x_1}^{x_2} k dx\right) Sin\left(\int_{x}^{x_2} k dx - \frac{\pi}{4}\right)$$

$$+ \frac{2}{\sqrt{k}} \text{Sin}\left(\int_{x_1}^{x_2} k dx\right) Cos\left(\int_{x}^{x_2} k dx - \frac{\pi}{4}\right) \tag{4}$$

Here second term of equation (4) is the one that connects with the decreasing exponential of region 3, while the first term connects with the increasing exponential. Since an increasing exponential in region 3 is not acceptable, the first term has to be zero. This is possible if

$$\text{Cos}\left(\int_{x_1}^{x_2} k dx\right) = 0 \text{ or } \int_{x_1}^{x_2} k dx = (n+1/2)\pi, \; n=0,1,2,....... \tag{5}$$

Substituting the value of k, we get

$$\left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \int_{x_1}^{x_2} [E - V(x)]^{\frac{1}{2}} \, dx = (n+1/2)\pi, \; n=0,1,2,....... \tag{6}$$

Which gives the allowed energy value. Classically, since the linear momentum $p = [2m(E - V)]^{\frac{1}{2}}$, equation (6) can be written as

$$2\int_{x_1}^{x_2} p\,dx = \left(n+\frac{1}{2}\right)\pi\hbar \qquad n= 0,1,2\ ,\ldots.. \tag{7}$$

The LHS is the value of the integral over a complete cycle.

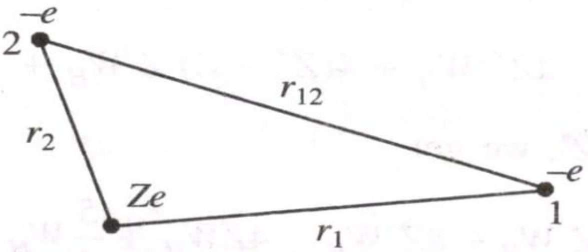
Ans.3: The Hamiltonian of the helium atom having a nuclear charge Ze is given by

$$H = \left(\frac{-\hbar^2}{2m}\nabla_1{}^2 - \frac{kze^2}{r_1}\right)+\left(\frac{-\hbar^2}{2m}\nabla_2{}^2 - \frac{kze^2}{r^2}\right) + \frac{ke^2}{r_{12}} \tag{1}$$

where $k = \dfrac{1}{4\pi\epsilon_0}$

In terms of the variable parameter Z'e, it is convenient to write the Hamiltonian as

$$H=\left(\frac{-\hbar^2}{2m}\nabla_1{}^2 - \frac{kz'e^2}{r_1}\right)+\left(\frac{-\hbar^2}{2m}\nabla_2{}^2 - \frac{kz'e^2}{r^2}\right) + (Z'-Z)ke^2\left(\frac{1}{r^1}+\frac{1}{r^2}\right) + \frac{ke^2}{r_{12}} \tag{2}$$



The product of the two normalized Hydrogenic ground state wave functions is

$$\Psi=\Psi_1(r_1)\Psi_2(r_2) = \frac{Z'^3}{\pi a_0{}^3}\exp\left[\frac{-Z'}{a^0}(r_1+r_2)\right] \tag{3}$$

Where $\Psi_1(r_1)$ and $\Psi_2(r_2)$ are the normalized Hydrogenic ground state wave functions with Z replaced by Z'. The expectation value of H with the trial wave function, as seen from Eq. (3), is

$$\langle H\rangle = \langle \Psi_1|\frac{-\hbar^2}{2m}\nabla_1{}^2 - \frac{kz'e^2}{r_1}|\Psi_1\rangle + \langle \Psi_2|\frac{-\hbar^2}{2m}\nabla_2{}^2 - \frac{kz'e^2}{r_2}|\Psi_2\rangle$$

$$+(Z'-Z)\langle \Psi_1\left|\frac{ke^2}{r^1}\right|\Psi_1\rangle + (Z'-Z)\langle \Psi_2|\frac{ke^2}{r_2}|\Psi_2\rangle$$

$$+\langle \Psi_1\Psi_2|\frac{ke^2}{r_{12}}|\Psi_1\Psi_2\rangle$$

The value of the first and second terms are equal and each is

$-Z'^2W_H$, and $W_H = k^2me^4/2\hbar^2$

$$< \psi^1 \left|\frac{ke^2}{r^1}\right| \Psi^1 > = \frac{Z'^3 ke^2}{\pi {a_0}^3} \int_0^{2\pi} d\phi_1 \int_0^{\pi} sin\theta_1 d\phi_1 \int_0^{\infty} r_1 \exp\left(\frac{-2Z'r_1}{a_0}\right) dr_1$$

$$= \frac{Z'^3 ke^2}{\pi {a_0}^3} 4\pi \frac{1}{(2Z'/a_0)^2}$$

$$= 2Z' W_H \tag{4}$$

where the value of a_0 is substituted. Given

$$<\Psi_1 \Psi_2 | \frac{ke^2}{r_{12}} | \Psi_1 \Psi_2> = 5/4\, Z' W_H \tag{5}$$

Using equation (4) and (5) in equation (3), we have

$$<H> = -Z'^2 W_H + 4(Z' - Z) Z' W_H + 5/4\, Z' W_H \tag{6}$$

Minimizing <H> with respect to Z', we get

$$-4Z' W_H + 8Z' W_H - 4\, Z W_H + 5/4\, W_H = 0$$

$$Z' = Z - \frac{5}{16} \tag{7}$$

With this value of Z', equation (6) gives

$$E = <H> = -2\left(Z - \frac{5}{16}\right)^2 W_H$$

Substitution of W_H = 13.6 eV leads to a ground state energy of −77.46eV.

Ans.4: The classical turning points of the oscillator are those points at which the potential $V(x)=E$, i.e. $1/2 m\omega^2 x^2 = E$ or

$x_1 = -(2E/m\omega^2)^{\frac{1}{2}}$ and $x_2 = (2E/m\omega^2)^{\frac{1}{2}}$. For a particle constrained to move between classical turning points x_1 and x_2 in a potential well, the energies given by

$$E = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \text{ or } p = 2m\left[\left(E - \frac{1}{2} m\omega^2 x^2\right)\right]^{\frac{1}{2}}$$

Substituting this value of p in equation $2\int_{x_1}^{x_2} p\,dx = (n + \frac{1}{2})\pi\hbar$

We get

$$2\int_{x_1}^{x_2} 2m\left[\left(E - \frac{1}{2} m\omega^2 x^2\right)\right]^{\frac{1}{2}} dx = \left(n + \frac{1}{2}\right)\pi\hbar \quad n = 0, 1, 2, \ldots..$$

Writing $\mathrm{Sin}\theta = (m\omega^2/2E)^{\frac{1}{2}}x$, the above integral reduces to

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}(2mE)^{\frac{1}{2}}\,Cos^2\theta(2E/m\omega^2)^{\frac{1}{2}}d\theta = (n+1/2)\pi\hbar$$

$$(2E/\omega)\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} Cos^2\theta d\theta = (n+1/2)\pi\hbar$$

$$\frac{2E}{\omega}\times\frac{\pi}{2} = (n+\frac{1}{2})\pi\hbar \text{ or } E = (n+\frac{1}{2})\hbar\omega$$

Ans.5: $V(x) = 0$ for $-a< x <a$ and $V(x) = \infty$ for $|x|>a$, the turning points are $x_1=-a$ and $x_2 = a$. The allowed energies can be obtained using the relation

$$\int_{-a}^{a} kdx = (n+\frac{1}{2})\pi$$

$$E_n = \frac{[n+\left(\frac{1}{2}\right)^2\pi^2\hbar^2]}{8ma^2} \qquad n=0, 1, 2, \ldots\ldots\ldots\ldots.$$

The exact solution gives

$$E_n = \frac{[n^2\pi^2\hbar^2]}{8ma^2} \qquad n= 1, 2, 3, \ldots\ldots\ldots\ldots.$$

The WKB solution has (n+1/2) in place of n. Another major difference is in the allowed values of n.

Ans.6: The classical turning points are at $x_1=0$ and at $x_2=E/A$. Now

$$\int_{x_1}^{x_2} kdx = (n+\frac{1}{2})\pi, \quad k^2 = \frac{2m}{\hbar^2}(E-V)$$

In the given case,

$$k = (2m/\hbar^2)^{\frac{1}{2}}(E-Ax)^{\frac{1}{2}}$$

$$(2m/\hbar^2)^{\frac{1}{2}}\int_{0}^{\frac{E}{A}}(E-Ax)^{\frac{1}{2}}dx = (n+\frac{1}{2})\pi$$

$$E_n = \left(\frac{\hbar^2}{2m}\right)^{\frac{1}{3}}\left[\frac{3\pi A(2n+1)}{4}\right]^{\frac{2}{3}}, \qquad n= 0, 1, 2, \ldots\ldots..$$

16.11 Exercise

Q.1 Describe W.K.B. method for the solution of Schrodinger wave equation in a potential field and discuss its validity.

Q.2 Define W.K.B. approximation method and give an application of this method.

Q.3 What is the principle of W.K.B. approximation method. Define in detail.

Q.4 Show that the W.K.B. approximation method gives exact energy values for a harmonic oscillator.

Q.5 Outline W.K.B. approximation method for a one-dimensional case and derive the connection formulae.

Q.6 Apply the W.K.B. approximation method to obtain the quantisation condition for a bound state.

Q.7 Prove that the sums of reflection and transmission coefficients are unity for penetration of a barrier.

Q.8 Derive an expression for transmission probability through a potential barrier.

Q.9 Comment on the statement " W.K.B. approximation is a link between quantum and classical mechanics".

Q.10 Use the W.K.B. approximation method to find the transmission coefficient of a particle through a barrier.

Q.11 Find the energy levels of a particle moving in the potential $V(x) = V_0|x|$, V_0 being a positive constant.

Q.12 Consider a particle of mass m moving in a spherically symmetric potential V=kr, k being a positive constant. Estimate the ground state energy using a trial function of the type $\phi = \exp(-\alpha r)$, where α is the variable parameter.

Q.13 Using the W.K.B. method, calculate the transmission coefficient for the potential barrier

$$V(x) = \begin{cases} V_0\left(1 - \frac{|x|}{\lambda}\right), & |x| < \lambda \\ 0, & |x| > \lambda \end{cases}$$

Q.14 Use the W.K.B. method to calculate the transmission coefficient for the potential barrier

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

16.12 Answers to Exercise

Ans.11: The turning points are given by

$$E = V_0(x) \text{ or } |x| = E/V_0 \text{ or } x = \pm E/V_0$$

$$\int_{x_1}^{x_2} k\,dx = (n+\frac{1}{2})\pi, \quad k^2 = \frac{2m}{\hbar^2}[E-V_0(x)]$$

$$(2m/\hbar^2)^{\frac{1}{2}} \int_{-\frac{E}{V_0}}^{\frac{E}{V_0}} [E - V_0(x)]^{\frac{1}{2}} dx = (n+\frac{1}{2})\pi$$

As the integrand is even,

$$(2m/\hbar^2)^{\frac{1}{2}}\, 2 \int_{0}^{\frac{E}{V_0}} [E - V_0(x)]^{\frac{1}{2}} dx = (n+\frac{1}{2})\pi$$

$$E_n = [\frac{3}{4}(n+\frac{1}{2})\pi V_0]^{\frac{2}{3}} (\frac{\hbar^2}{2m})^{\frac{1}{3}} \quad n=0, 1, 2, 3, \ldots\ldots\ldots\ldots$$

Ans.12: The Hamiltonian operator is

$$H = \frac{\hbar^2}{2m}\nabla^2 + kr$$

As the trial wave function is not normalized

$$\langle H\rangle = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}, \quad \phi = e^{-\alpha r}$$

$$\langle\phi|\phi\rangle = \int_0^\infty e^{-2\alpha r} r^2 dr = \frac{2!}{(2\alpha)^3} = \frac{1}{4\alpha^3}$$

Now,

$$< \phi |H| \phi > = \frac{-\hbar^2}{2m}\int_0^\infty e^{-\alpha r}\,\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\,\frac{d}{dr}\right)e^{-\alpha r}\right]r^2 dr$$

$$+k\int_0^\infty r^3 e^{-2\alpha r}\,dr$$

$$= \frac{-\hbar^2\alpha^2}{2m}\int_0^\infty r^2 e^{-2\alpha r}\,dr + \frac{\hbar^2\alpha}{m}\int_0^\infty r e^{-2\alpha r}\,dr + k\int_0^\infty r^3 e^{-2\alpha r}\,dr$$

Using the standard integral in the appendix, we get

$$< \phi |H| \phi > = \frac{-\hbar^2\alpha^2}{2m}\,\frac{1}{4\alpha^3} + \frac{\hbar^2\alpha}{m}\,\frac{1}{(2\alpha)^2} + k\frac{3!}{(2\alpha)^4}$$

$$= \frac{\hbar^2}{8m\alpha} + \frac{3k}{8\alpha^4}$$

$$<H> = \frac{<\phi\, |H|\, \phi>}{<\phi|\phi>} = \frac{\hbar^2\alpha^2}{2m} + \frac{3k}{2\alpha}$$

For <H> to be minimum, it is necessary that

$$\frac{\partial <H>}{\partial \alpha} = 0$$

$$\frac{\hbar^2\alpha}{m} - \frac{3k}{2\alpha^2} = 0 \text{ or } \alpha = \left(\frac{3km}{2\hbar^2}\right)^{\frac{1}{3}}$$

With this value of α, the ground state energy

$$E = \frac{\hbar^2}{2m}\left(\frac{3km}{2\hbar^2}\right)^{\frac{2}{3}} + \frac{3k}{2}\left(\frac{2\hbar^2}{3km}\right)^{\frac{2}{3}} = \frac{3}{2}\left(\frac{9k^2\hbar^2}{4m}\right)^{\frac{1}{3}}$$

Ans.13: The transmission coefficient is

$$T = \exp\left(-2\int_{x_1}^{x_2}\gamma\, dx\right), \qquad \gamma^2 = \frac{2m}{\hbar^2}[V(x) - E]$$

Where x_1 and x_2 are turning points. At the turning points

$$E = V(x) = V_0\left(1 - \frac{|\,x\,|}{\lambda}\right) \text{ or } \frac{E}{V_0} = \left(1 - \frac{|\,x\,|}{\lambda}\right)$$

$$x = \pm\lambda\left(\frac{V_0 - E}{V_0}\right)$$

Here $x_1 = -\left(\frac{V_0 - E}{V_0}\right)$ and $x_2 = +\lambda\left(\frac{V_0 - E}{V_0}\right)$

$$-2\int_{x_1}^{x_2}\gamma\, dx = -2\sqrt{\frac{2m}{\hbar^2}}\int_{x_1}^{x_2}\left(V_0 - \frac{V_0 x}{\lambda} - E\right)^{\frac{1}{2}}dx$$

$$= -2\sqrt{\frac{2m}{\hbar^2}}\left(\frac{2}{3}\right)(-\frac{\lambda}{V_0})(V_0 - E)^{\frac{3}{2}}$$

$$\mathrm{T} = \exp[\frac{-16\sqrt{m}}{3\hbar}\frac{\lambda}{V_0}(V_0 - E)^{\frac{3}{2}}]$$

Ans.14: The transmission coefficient is

$$\mathrm{T} = \exp\left(-2\int_{x_1}^{x_2}\gamma\, dx\right) \qquad \gamma^2 = \frac{2m}{\hbar^2}[\mathrm{V(x)} - \mathrm{E}]$$

From the value of V(x), it is clear that the turning point $x_1=0$. To get the other turning point, it is necessary that

$$\mathrm{E} = \mathrm{V(x)} = \mathrm{V}_0 - \mathrm{ax}_2$$

$$\mathrm{x}_2 = \mathrm{V}_0 - \mathrm{E/a}$$

$$\gamma = \frac{\sqrt{2m}}{\hbar}(V_0 - ax - E)^{\frac{1}{2}}$$

$$-2\int_{x_1}^{x_2}\gamma\, dx = -2\frac{\sqrt{2m}}{\hbar}\int_0^{x_2}(V_0 - ax - E)^{\frac{1}{2}}\, dx$$

$$= -2\frac{\sqrt{2m}}{\hbar}\frac{2}{3}(\frac{-1}{a})\,[(V_0 - ax - E)^{\frac{3}{2}} - (V_0 - E)^{\frac{3}{2}}]$$

$$= \frac{-4\sqrt{2m}}{3\hbar a}[V_0 - E]^{\frac{3}{2}}$$

$$\mathrm{T} = \exp[\frac{-4\sqrt{2m}}{3\hbar a}(V_0 - E)^{\frac{3}{2}}]$$

References and Suggested Readings

1. Fundamental of Quantum Mechanics by Springer.
2. Modern Physics byArthur Beiser.
3. Quantum Mechanics by Schiff.
4. Quantum Mechanics Concepts and applications by Nouredine Zettili.
5. Quantum Mechanics by David Griffiths.