Chapter 1

General Introduction

PREAMBLE

In 1959, the great physicist of our time Professor Richard Feynman gave the first illuminating talk on nano technology, which was entitles as : **There's Plenty of Room at the Bottom.** He consciously explored the possibility of "direct manipulation" of the individual atoms to be effective as a more powerful form of 'synthetic chemistry'.

Feynman talked about a number of interesting ramifications of a 'general ability' to manipulate matter on an atomic scale. He was particularly interested in the possibility of denser computer circuitry and microscopes that could see things much smaller than is possible with 'scanning electron microscope'. The IBM research scientists created today's 'atomic force microscope' and 'scanning tunneling microscope', and there are other important examples.

Feynman proposed that it could be possible to develop a 'general ability' to manipulate things on an atomic scale with a 'top $\rightarrow$ down' approach. He advocated using ordinary machine shop tools to develop and operate a set of one-fourth-scale machine shop tools, and then further down to one-sixteenth-scale machine tools, including miniaturized *hands* to operate them. We can continue with this particular trend of down-scaling until the tools are able to directly manipulate atoms, which will require redesign of the tools periodically, as different forces and effects come into play. Thus, the effect of gravity will decrease, and the effects of surface tension and Van der Waals attraction will be enhanced. He concluded his talk with challenges to build a tiny motor and to write the information from a book page on a surface 1/25,000 smaller in linear scale.

Although Feynman's talk did not explain the full concept of nano technology, it was K. E. Drexler who envisioned self-replicating 'nanobots', *i.e.,* self-replicating robots at the molecular scale, in **Engines of Creation: The Coming Era of Nano Technology in 1986,** which was a seminal 'molecular nano technology' book.

That brings us to the end of the brief history on how the concept of nano technology emerged.

1.1. INTRODUCTION

In the usual and standard language, when we talk about 'materials science' and 'materials technology', we normally mean ceramics or crystalline materials, glasses or non-crystalline materials, polymers or heavy chain molecular materials and metals or cohesively-bonded materials. All these materials have a wide variety of applications in the diverse fields towards the service for the betterment of human life.

The world of materials is rapidly progressing with new and trendiest technologies, and obviously novel applications. Nano technology is among these modern and sophisticated technologies $\rightarrow$ which is

creating waves in the modern times. Actually, nano technology includes the concept of physics and chemistry of materials. It beckons a new field coming to the limelight. So, nano technology is an interesting but emerging field of study, which is under constant evolution offering a very wide scope of research activity.

1.1.1. What is Nano Technology ?

Nano technology is an advanced technology, which deals with the synthesis of nano-particles, processing of the nano materials and their applications. Normally, if the particle sizes are in the **1-100 nm** ranges, they are generally called nano particles or materials. In order to give an idea on this size range, let us look at some dimensions : **1 nm** = 10 Å = 10^{-9} meter and 1 μm (*i.e.,* 1 micron) = 10^{-4} cm = **1000 nm.** For oxide materials, the diameter of one oxygen ion is about 1.4 Å. So, seven oxygen ions will make about 10 Å or **1 nm**, *i.e.,* the 'lower' side of the nano range. On the higher side, about 700 oxygen ions in a spatial dimension will make the so-called 'limit' of the nano range of materials.

1.1.2. Why Nano Technology ?

In the materials world, particularly in ceramics, the trend is always to prepare finer powder for the ultimate processing and better sintering to achieve dense materials with dense fine-grained microstructure of the particulates with better and useful properties for various applications. The fineness can reach up to a molecular level **(1 nm – 100 nm),** by special processing techniques. More is the fineness, more is the surface area, which increases the 'reactivity' of the material. So, the densification or consolidation occurs very well at lower temperature than that of conventional ceramic systems, which is finally 'cost-effective' and also improves the properties of materials like abrasion resistance, corrosion resistance, mechanical properties, electrical properties, optical properties, magnetic properties, and a host of other properties for various useful applications in diverse fields.

1.1.3. Scope of Applications

The deviations from the bulk phase diagram may be exploited to form certain compositions of alloys that are otherwise unstable in the bulk form. In addition, the thermal stability of interfacial regions is typically less than that of the bulk material : thus the nano phase materials are often sintered or undergo phase transformation at temperatures below those of the bulk material. This is a characteristic which has numerous applications to material processing.

By improving material properties, we are able to find the applications as varied as semiconductor electronics, sensors, special polymers, magnetics, advanced ceramics, and membranes. We need to improve our current understanding of particle size control and methodologies for several classes of nano-phase materials and address the issues of their characterization. We should also explore the fields in which there are foreseeable application of nano-phase materials to long standing materials problems, since these 'issues' have to be tackled by us.

As said earlier, there is a scope of wider applications in different fields such as : (*a*) Electronics in terms of Thin Films, Electronic Devices like MOSFET, JFET and in Electrical Ceramics, (*b*) Bionics, (*c*) Photonics, (*d*) Bioceramics, (*e*) Biotechnology, (*f*) Medical Instrumentation, etc.

1.2. BASICS OF QUANTUM MECHANICS

It was mentioned above that about 7 oxygen ions make the lowest side of nano particles. Below this level or even at this level, the concept of 'quantum mechanics' is useful. If we do not understand the

atoms themselves, then how we can aspire to know more about the behaviour of the "nano particles", which are either embedded within a particular matrix or just remain as a mixture in a 'particulate assembly'.

In order to talk about quantum mechanics, we must clarify different aspects of mechanics—which is a pillar in science since the era of 'Newtonian Mechanics'. Actually, there are four realms of mechanics, which will put quantum mechanics in proper perspectives. The following diagram simply illustrates this point :

Speed ↑

QUANTUM FIELD THEORY **(Pauli, Dirac, Schwinger,** **Feynman, et al.)**	**RELATIVISTIC MECHANICS** **(Einstein)**
QUANTUM MECHANICS **(Planck, Bohr, Schrödinger,** **de Broglie, Heisenberg, et al)**	**CLASSICAL MECHANICS** **(Newton)**

Distance→

Some people say that the subject of quantum mechanics is all about 'waves' and that's why sometimes we call it 'wave mechanics' in common parlance, yet many textbooks on this subject do not explicitly clarify how the 'waves' are created through the mathematical route. When this part is made clear, it has been observed that many readers find quantum mechanics quite interesting. Hence, a simple attempt is made here towards this objective.

1.2.1 Differential Equations of Wave Mechanics

There are so many problems in wave mechanics, which can be described as the 'solutions' of a differential equation of the following type :

$$\frac{d^2 y}{dx^2} + f(x)\, y \ = \ 0 \qquad\qquad ...(1.1)$$

The readers studying this subject must thoroughly understand this equation. Here, $f(x)$ is a function of the independent variable x. With this equation, we can plot y $vs.$ x, when the values of y and $\frac{d^2 y}{dx^2}$ are provided for an arbitrary value of x.

We can also make an equivalent statement : Two independent solutions of y_1 and y_2 exist and that $(A y_1 + B y_2)$ is the 'general solution'; this is also possible to be shown graphically.

The simplest case of equation (1.1) is that where $f(x)$ is constant. Two cases are possible for this situation as

1. If $f(x)$ is a positive constant, *i.e.* $f(x) = k^2$, we can write the solution as:

$$y = \text{A} \cos kx + \text{B} \sin kx$$

or, $$y = a \cos (kx + \varepsilon)$$

where, A, B, a and ε are all arbitrary constants. This particular solution is clearly shown in **Fig. 1.1(*a*).**

2. If $f(x)$ is constant, but negative, *i.e.,* by setting $f(x) = -\gamma^2$, we get the solutions as $e^{-\gamma x}$ and $e^{\gamma x}$, with the general solution as :

$$y = \text{A} \, e^{-\gamma x} + \text{B} \, e^{\gamma x}$$

These solutions are depicted in **Fig. 1.1(*b*).**

In the general case, where $f(x)$ is not a constant, it is easy to show that if $f(x)$ is positive $\rightarrow y$ is an oscillating function. If $f(x)$ is negative, y is of exponential form.
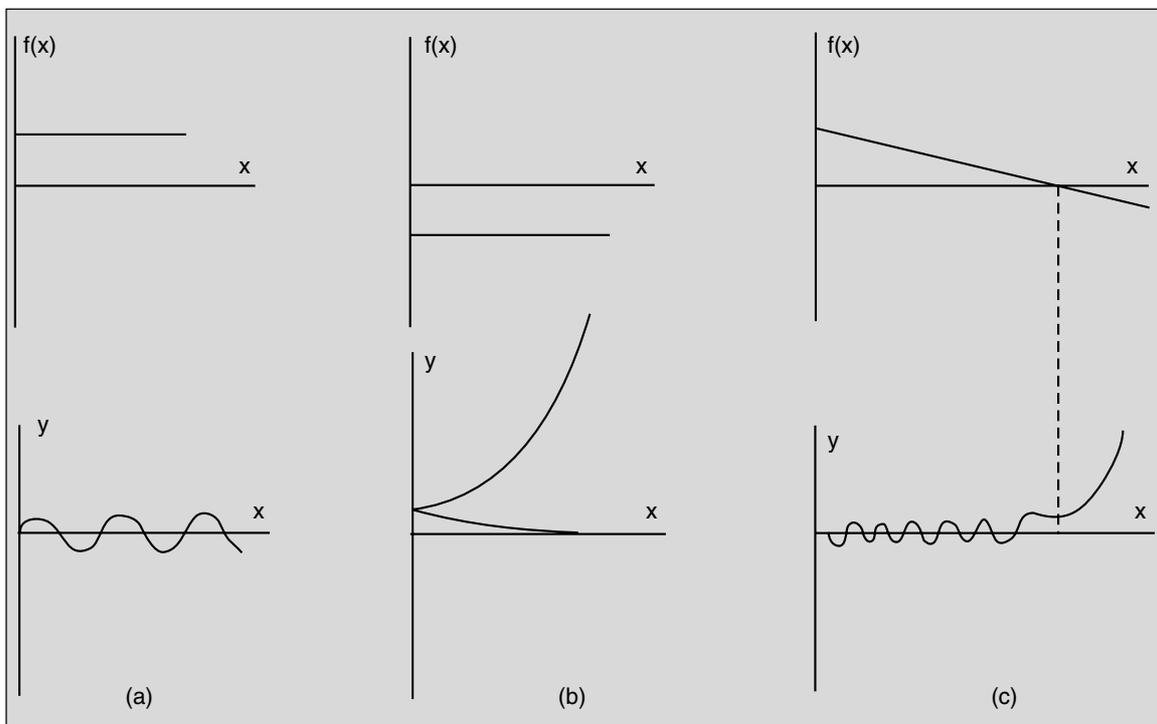

Figure 1.1 : Solutions of the differential equations $y'' + f(x)y = 0$. (*a*) for $f(x) = k^2$,
(*b*) for $f(x) = -\gamma^2$, (*c*) for an arbitrary form of $f(x)$ that changes sign.

This is due to the fact that if $f(x)$ is positive, both y and $\dfrac{d^2 y}{dx^2}$ have the opposite sign, as shown in **Fig. 1.2(*a*).**
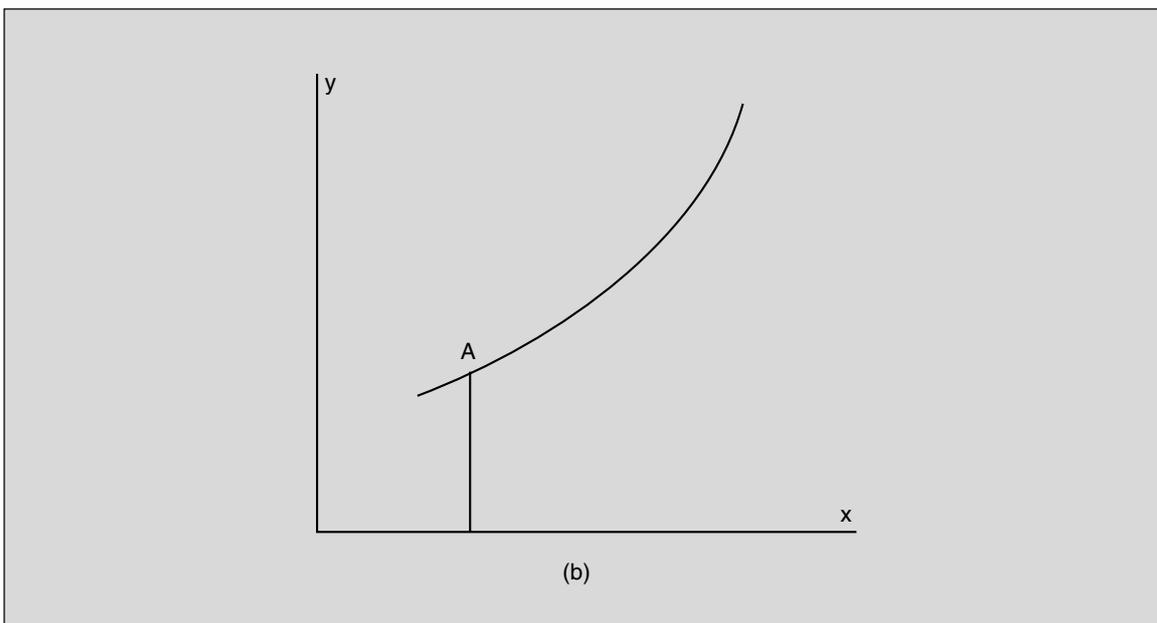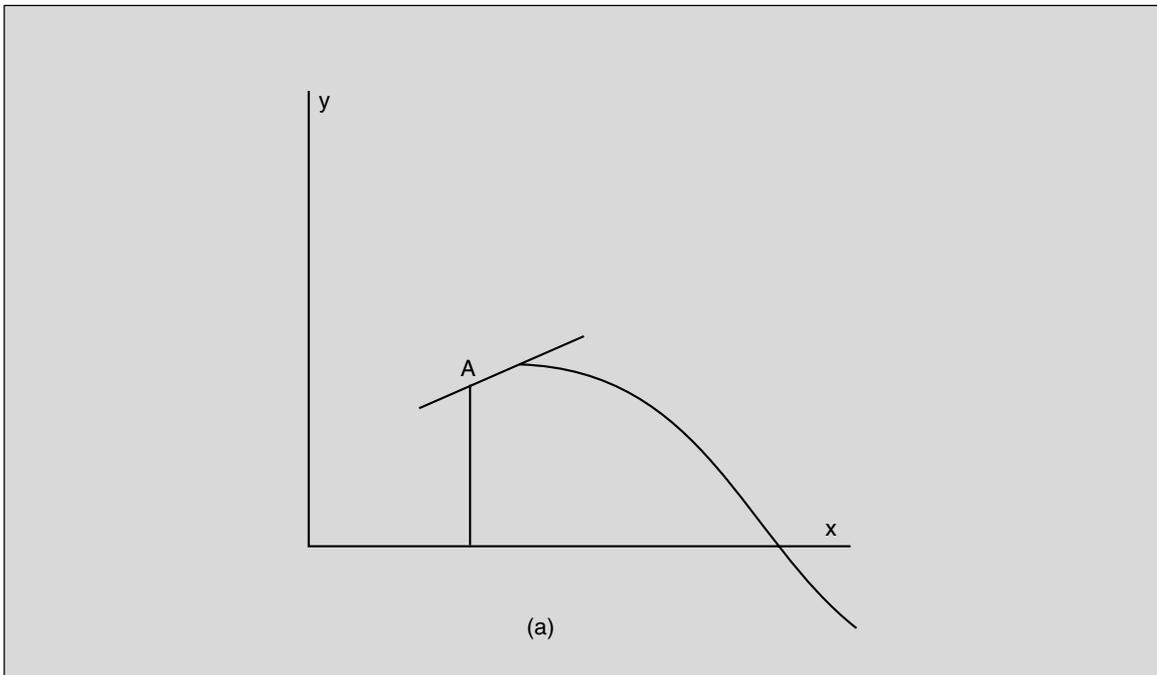
Figure 1.2 : *y vs. x* plot, (*a*) for a decreasing function, (*b*) for an increasing function.

On the other hand, if $f(x)$ is negative, both y and $\dfrac{d^2y}{dx^2}$ are of the same sign, and the slope at any point will increase giving an exponentially increasing curve, as shown in **Fig. 1.2(*b*).** The general form of the solution y for a function $f(x)$ which changes sign is as shown in **Fig. 1.1(*c*).** When $f(x)$ becomes negative, y goes over to the 'exponential' form. Generally speaking, there will always be one solution which decreases exponentially, but the general solution will increase. When we consider that the solution consists of an exponential decrease, this determines the phase of oscillations in the range of x for which the oscillations occur.

A useful method exists for determining approximate solutions of the differential equation (1.1), known as Wentzel-Kramers-Brillouin (WKB) method, which is written as :

$$y = \alpha\, e^{i\beta} \qquad\qquad\qquad ...(1.2)$$

Here, a and b are both functions of x and α represents the amplitude of the oscillations, β the phase. The approximate solution of equation (1.2) is written as :

$$y = \text{Const.}\, f^{-1/4} \exp\left[i \int_{x_0}^{x} f^{1/2}\, dx \right]$$

Immediately, it follows that the 'amplitude' of the oscillations increases, as f becomes smaller and the wavelength increases (as shown in **Fig. 1.1*c***). So that sums up the basics of waves through a simple mathematical route, which should clarify the point mentioned above.

1.2.2. Background of Quantum Mechanics

First of all, it could be stated that a knowledge of quantum mechanics is indispensable to understand many areas of physical sciences. Quantum mechanics is a branch of science, which deals with 'atomic' and 'molecular' properties and behaviour on a microscopic scale, *i.e.,* useful to understand the behaviour of the "nano" particles in the microscopic level. Some salient points can be mentioned as :

It is known that while 'thermodynamics' may be concerned with the heat capacity of a gaseous sample → quantum mechanics is concerned with the specific changes in 'rotational energy states' of the molecules.

While 'chemical kinetics' may deal with the 'rate of change' of one substance to another → quantum mechanics is concerned with the changes in the vibrational states and structure of the reactant molecules as they get transformed.

Quantum mechanics is also concerned with the 'spins' of atomic nuclei and 'population of excited states' of atoms.

Spectroscopy is based on changes of various quantized energy levels. Thus quantum mechanics seem to merge with many other areas of modern science from nuclear physics to organic chemistry to semiconductor electronics.

The modern applications of quantum mechanics have their roots in the development of physics around the turn of the 20th century. Some of the classic experiments date back to 100 years, which provides a solid physical basis for interpretation of quantum mechanics.

The names attached to much of the early times are due to the work of Planck, Einstein, Bohr, de Broglie and Heisenberg, who are legendary in the realm of physics. A brief review of their work is necessary before going to the details of quantum mechanics.

1.2.3 Origin of the Problem : Quantization of Energy

So, a little bit of history needs to be told. Before 1900, with proper statistical considerations, the physicists assumed that the laws governing the 'macroworld' were valid in the 'microworld' → this posed problems in terms of inadequate 'theory of black-body radiation' due to Wien's and Rayleigh-Jeans' radiation laws.

So, the quantum theory was developed, which had its origin in the lapses of 'Classical Mechanics', *i.e.* mechanics, electromagnetism, thermodynamics and optics, to explain experimentally observed energy (E) *vs.* wavelength or frequency (*v*) curves, *i.e.,* distribution, in the 'continuous spectrum' of black-body radiation. Actually, we need to explain the colour of light emitted by an object when heated to a certain temperature. Here, the extraordinary efforts made by Planck needs to be little bit elaborated on how the concept of 'quantization' came into existence.

A correct theory of black-body radiation was developed by Max Planck (1857–1947) in 1900, by assuming that the absorption and emission of radiation still arose from some sort of oscillators, which requires that the radiation be 'quantized'. The fundamental assumption of Planck was that only certain frequencies were possible/permissible for the oscillators instead of the whole range of frequencies, which are normally predicted by classical mechanics. These frequencies were presumed to be some multiple of a fundamental frequency of the oscillators, v.

Furthermore, Planck assumed that the energy needed to be absorbed to make the oscillator move from one allowed frequency to the next higher one, and that the energy was emitted at the frequency lowered by v.

Planck also assumed that the change in energy is proportional to the fundamental frequency, v. By introducing a constant of proportionality, h, *i.e.,* $E = hv$ (h = Planck's Constant = 6.63×10^{-27} erg sec = 6.63×10^{-34} Joule sec). This famous equation predicted the observed relationship between the frequency of radiation emitted by a blackbody and the intensity.

In 1905, Albert Einstein (1879–1955) further developed the 'concept' of energy quantization by assuming that : this phenomenon was a property of the radiation itself and this process applied to both absorption and emission of radiation. By using the above quantization concept, Einstein developed a correct theory of the 'photoelectric' effect.

In 1913, Neils Bohr (1885-1962) combining classical physics and quantization concept postulated theory for the observed spectrum of hydrogen atom as follows :

A. The electron in the hydrogen atom moves around the nucleus, *i.e.* proton, in certain circular orbits (*i.e.,* stationary states) without radiating energy.

B. The allowed 'stationary states' are such that L = *m* V *r* = *n h* (where, L = angular momentum of the electron, *r* = radius of the orbit, *m* = mass of the electron, $\hbar = \dfrac{h}{2\pi}$, V = velocity of the electron with *n* = principal quantum number).

C. When the electron makes a transition from a state of energy E_1 to E_2 ($E_1 > E_2$), electromagnetic radiation (*i.e.,* photon) is emitted from the hydrogen atom. The frequency of this emission process is given by : $v = \dfrac{(E_1 - E_2)}{h}$.

Bohr's theory was applied to other atoms with some success in a generalized form by Wilson and Sommerfeld. By about 1924, it was clear that all we needed is a 'new theory' to interpret the basic properties of atoms and molecules in a proper manner [1-4]

1.2.4 Development of New Quantum Theory

In 1925, Heisenberg (1901) developed a system of mechanics where the knowledge of classical concepts of mechanics was revised. The essence of his theory is : Heisenberg assumed that the atomic theory should talk about the 'observable' quantities' rather than the shapes of electronic orbits (*i.e.,* Bohr's theory), which was later developed into matrix mechanics by matrix algebra. Then came the theory of wave mechanics, which was inspired by de Broglie's (1892-) wave theory of matter :

$$\lambda = \frac{h}{p} \ (p = \text{momentum of a particle and } \lambda = \text{wavelength}).$$

Almost parallel to the advancement of matrix mechanics, in 1926 Schrödinger (1887-1961) introduced an 'equation of motion' based on 'partial differential equation' for matter waves, which proved that wave mechanics was mathematically equivalent to matrix mechanics, although its physical meaning was not very clear at first.

But, Why it is so ?

Schrödinger first considered the 'de Broglie wave' as a physical entity, *i.e.,* the particle, electron, is actually a wave. But this explanation has some difficulty, since a wave may be partially reflected and partially transmitted at a 'boundary' → but an electron cannot be split into two component parts, one for transmission and the other for reflection.

This difficulty was removed by the statistical interpretation of de Broglie wave by Max Born (1882-1970), which is now widely accepted → known as 'Born Interpretation'. The entire subject was very rapidly developed into a cohesive system of mechanics → called Quantum Mechanics. Since it deals with the waves, we may sometimes call it wave mechanics.

Incidentally, it may be mentioned that the famous German Mathematician David Hilbert suggested to Heisenberg to try the route of 'partial differential equations'. If Heisenberg listened to Hilbert, then the famous 'partial differential wave equation' would be to his credit, but Schrödinger got the Nobel Prize for this most important discovery of the past century in 1933 with Paul Dirac. So, this is the short story of quantum mechanics.

How Schrödinger Advanced His Ideas ?

For the 'Wave Equation for Particles', Schrödinger assumed a 'Wave Packet' and used Hamiltonian's 'Principle of Least Action'. During the development of wave mechanics, it was known to Schrödinger that :

A. Hamilton had established an analogy between the Newtonian Mechanics of a particle and geometrical or ray optics called Hamiltonian Mechanics, and

B. Equations of wave optics reduced to those of geometrical optics, if the wavelength in the former is equal to zero.

Hence, Schrödinger postulated that the classical Newtonian Mechanics was the limiting case of a more general 'wave mechanics' and then derived a 2nd order wave equation of particles.

In order to make a complete description of the 'motion of the particle' by the 'motion of a wave', we must do the following:

(*A*) To find a suitable 'wave representation' of a single particle, and

(*B*) To establish the 'kinematical equivalence' of a ray and a particle trajectory

A localized wave whose amplitude is zero everywhere, except in a small region, is called the 'wave packet', which will satisfy the condition (*A*), but we have to also satisfy the condition (*B*).

To Prove the 'Kinematic Equivalence' → How to Start ?

A monochromatic 'plane wave' in one dimension can be represented by :

$$\varphi_k(x, t) = \varphi(k) \exp[i(kx - \omega t)] \qquad \qquad ...(1.3)$$

where, k is the x-component of the propagation vector, denoted by k or $|k| = \dfrac{2\pi}{\lambda}$, and $\omega = \omega(k) = 2\pi\nu$. It has to be noted that a superposition of a group of plane waves of nearly the same wavelength and frequency that interfere destructively everywhere except in a small region gives rise to a 'wave packet'. In the one-dimensional case, such a 'wave packet' can be represented by 'Fourier Analysis', by taking an 'wave packet' centered at k which extends to $\pm \Delta k$ so that the 'Fourier Integral' can be used between $k - \Delta k/2$ and $k + \Delta k/2$ as :

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) \exp \ [i(kx - wt)] \ dk \qquad \qquad ...(1.4)$$

A maximum, *i.e.,* constructive interference, will occur when $(kx - \omega t) = 0$, since 'the sum' over the 'oscillating exponential function' for different values of k would result on an average in a flat pattern, *i.e.,* a destructive interference.

Let us assume that the form of $\psi(0, 0)$ is

$$\psi(0, 0) = \frac{1}{\sqrt{2\pi}} \int_{k_0 - \Delta k/2}^{k_0 + \Delta k/2} F(k) \, dk \qquad \qquad ...(1.5)$$

At a later time Δt and a further distance Δx, the form of ψ is

$$\psi(\Delta x, \Delta t) = \frac{1}{\sqrt{2\pi}} \int_{k_0 - \Delta k/2}^{k_0 + \Delta k/2} F(k) \ \exp[i(k\Delta x - \omega\Delta t)]dk$$

$$= \frac{1}{\sqrt{2\pi}} \exp[i(k_0\Delta x - \omega_0\Delta t)] \int_{k_0 - \Delta k/2}^{k_0 + \Delta k/2} F(k) \exp\{i[(k - k_0)\Delta x - (\omega - \omega_0)\Delta t]\} dk$$

$$...(1.6)$$

In order to get a 'maximum', we require that

$$i[(k - k_0)\Delta x - (\omega - \omega_0)\Delta t] = 0$$

or,
$$\frac{\Delta x}{\Delta t} = \frac{(\omega - \omega_0)}{(k - k_0)} \qquad \qquad ...(1.7)$$

By expanding $\omega(k)$ in a Taylor series about k_0, we get

$$\omega = \omega_0 + (k - k_0) \left(\frac{d\omega}{dk}\right)_{\omega = \omega_0} + (k - k_0)^2 \left(\frac{d^2\omega}{dk^2}\right)_{\omega = \omega_0} + ... \qquad \qquad ...(1.8)$$

By neglecting the 2nd derivative of ω and the higher order terms in the above expansion, ultimately we find that the equation (1.7) becomes

$$\frac{\Delta x}{\Delta t} = \left(\frac{d\omega}{dk}\right)_{\omega = \omega_0}$$

or, $$V_{group\ velocity} = \lim_{\Delta t \to 0}\left(\frac{\Delta x}{\Delta t}\right) = \frac{d\omega}{dk} \qquad ...(1.9)$$

Now, it is clear how we establish the 'kinematical equivalence' of a 'ray' and a 'particle' trajectory, *i.e.,* the condition (*B*) as explained above, by requiring that the 'group velocity' of the 'wave packet' equals the velocity of the particle $\to$ which means that

$$V_g = V_p \qquad ...(1.10)$$

The velocity of the particle, V_p , is given by

$$V_p = \frac{d\,E}{dp} = \frac{d(E/H)}{d(1/\lambda)} \qquad ...(1.11)$$

Since, the energy is written as

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

and the momentum is written as

$$p^2 = 2m[E - V] = \frac{H}{\lambda}$$

the group velocity of the wave can be written as

$$V_g = \frac{d\omega}{dk} = \frac{d\omega}{d(2\pi/\lambda)} = \frac{d\left(\dfrac{\omega}{2\pi}\right)}{d\left(\dfrac{1}{\lambda}\right)} \qquad ...(1.12)$$

Since we require that $V_g = V_p$, we must have the following relation

$$\frac{E}{H} = \frac{\omega}{2\pi} = \nu$$

or, $$E = H\nu = h\nu = \text{Planck's Constant} \times \nu \qquad ...(1.13)$$

Now, we have finally established the fact that it is reasonable to consider $\to$ describing the motion of a particle by the use of a 'localised wave', *i.e.,* wave packet $\to$ if we require that $E = \text{Constant} \times \nu$. Surprisingly, this is exactly the 'Planck's Quantization of Energy Condition', where $H = h$ (*i.e.* the Planck's Constant), as described earlier.

1.2.5 Quantum Mechanical Way: The Wave Equations

In order to familiarize with procedures and terminology, we can start by stating the 'postulates' of quantum mechanics and showing some of their uses.

The Postulate 1 → **For any possible 'state of a system', there is a function ψ, of the coordinates of the parts of the system and time that completely describe the 'system'.**

For a single particle described by the Cartesian coordinates, we can write it as

$$\psi = \psi(x, y, z, t) \qquad \qquad ...(1.14)$$

For two particles, the coordinates of each particle must be specified so that

$$\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2, t) \qquad \qquad ...(1.15)$$

For a general system, we can use generalized coordinates q_i, and it is written as

$$\psi = \psi(q_i, t) \qquad \qquad ...(1.16)$$

Since the model is that of a wave, the function is called a 'wave function'. The state of the system which is described by this function is called the 'quantum state'.

The meaning of this wave function is that ψ^2 is proportional to the probability. Since ψ may be complex, we are interested in $\psi\psi^*$, where ψ^* is the complex conjugate of ψ. The complex conjugate is the same function with i replaced by $-i$, where $i = \sqrt{-1}$.

For example → If we square the function $(x + ib)$, we obtain : $(x + ib)(x + ib) = x^2 + 2ibx + i^2 b^2 = x^2 + 2ibx - b^2$ and the resulting function is still complex. Now, if we multiply $(x + ib)$ by its complex conjugate $(x - ib)$, we obtain : $(x + ib)(x - ib) = x^2 - i^2 b^2 = x^2 + b^2$, which is real. Hence, for the calculation of probability, it is always done by multiplying a function with its complex conjugate.

The quantity $\psi\psi^* \, dV$ is proportional to the probability of finding the particle of the system in the volume element, $dV = dx \, dy \, dz$. We require that the total probability be unity so that the particle must be somewhere, *i.e.,* it can be expressed as

$$\int_V \psi\psi^* \, dV = 1 \qquad \qquad ...(1.17)$$

If this condition is met, then ψ is normalized. In addition, ψ must be 'Finite', 'Single Valued' and 'Continuous'. These conditions describe a "well behaved" wave function. The reasons for these requirements are as follows:

1. **Finite.** A probability of unity denotes a 'sure thing'. A probability of zero means that a particular event cannot happen. Hence, the probability varies from zero to unity. If ψ were infinite, the probability could be greater than unity.

2. **Single valued.** In a given area of space, there is only one probability of finding a particle. For example, there is a single probability of finding an electron at some specified distance from the nucleus in a hydrogen atom. There cannot be two different probabilities of finding the electron at some given distance.

3. **Continuous.** If there is a certain probability of finding an electron at a given distance from the nucleus in a hydrogen atom, there will be a slightly different probability if the distance is changed slightly. The probability function does not have 'discontinuties' so the wave function must be continuous.

If two functions ψ_1 and ψ_2 have the following property

$$\int \psi_1^* \, \psi_2 \, dV = 0$$

or,
$$\int \psi_1 \psi_2 * d\mathrm{V} = 0 \qquad\qquad ...(1.18)$$

They are said to be orthogonal. Whether the integral vanishes or not may depend on the 'limits of integration', and hence we always speak of the "orthogonality" within a certain interval.

Therefore, the 'limits of integration' must be clear. In the above case, the integration is carried out over the possible range of coordinates used in $d\mathrm{V}$. If the coordinates are x, y and z, the limits are from $-\infty$ to $+\infty$ for each variable. If the coordinates are r, θ and ϕ, the limits of integration are 0 to ∞, 0 to π, and 0 to 2π, respectively.

Postulate 2. For every 'dynamical variable' (classical observable), there is a corresponding "operator".

This postulate provides the 'connection' between the quantities which are classical observables and the quantum mechanical techniques for doing things.

But what are the dynamic variables ?

These are such quantities as energy, momentum, angular momentum and position coordinates.

The operators are symbols which indicate that some mathematical operations have to be performed.

Such symbols include $(\ )^2$, $\dfrac{d}{dx}$ and $\int$. The coordinates are the same in operator and classical forms, *e.g.*, the coordinate x is simply used in operator form as x. Some operators can be combined, *e.g.*, since the kinetic energy is $\dfrac{m\mathrm{V}^2}{2}$, it can be written in terms of the momentum p, as $\dfrac{p^2}{2m}$.

The operators that are important in quantum mechanics have two important characteristics :

1. First, the operators are linear, which means that :
$$\alpha(\phi_1 + \phi_2) = \alpha\phi_1 + \alpha\phi_2 \qquad\qquad ...(1.19)$$
where α is the operator and ϕ_1 and ϕ_2 are the 'functions' being operated on. Also, if C is a constant, we get
$$\alpha(C\phi) = C\ (\alpha\ \phi) \qquad\qquad ...(1.20)$$

The linear character of the operator is related to the superposition of 'states' and waves reinforcing each other in the process.

2. Secondly, the operators that we encounter in quantum mechanics are Hermitian. If we consider two functions ϕ_1 and ϕ_2, the operator α is Hermitian if we have the following relation :
$$\int \phi_1 * \alpha\phi_2\ d\mathrm{V} = \int \phi_2\ \alpha * \phi_1^{*}\ d\mathrm{V} \qquad\qquad ...(1.21)$$

This requirement is necessary to ensure that the calculated quantities are real. We will come across these types of behaviour in the operators that we use in quantum mechanics.

The Eigenvalues

Postulate 3. The permissible values that a dynamical variable may have are those given by $\alpha\phi = a\phi$, where ϕ is the eigenfunction of the operator α that corresponds to the observable, whose permissible values are "a".

The postulate can be stated in terms of an equation as

$$\underset{\text{operator}}{\alpha} \quad \underset{\substack{\text{wave} \\ \text{function}}}{\phi} \quad = \quad \underset{\substack{a \\ \text{constant} \\ \text{(eigenvalue)}}}{} \quad \underset{\substack{\text{wave} \\ \text{function}}}{\phi} \qquad \qquad ...(1.22)$$

If we are performing a particular operation on the 'wave function', which yields the 'original function' multiplied by a 'constant', then ϕ is an 'eigenfunction' of the operator α. This can be illustrated by letting the value of $\phi = e^{2x}$ and taking the operator as $\dfrac{d}{dx}$. Then, by operating on this function with the operator, we get

$$\frac{d\phi}{dx} = 2\, e^{2x} = \text{constant} \,.\, e^{2x} \qquad\qquad ...(1.23)$$

Therefore, e^{2x} is an 'eigenfunction' of the operator α with an 'eigenvalue' of 2. For example, if we let $\phi = e^{2x}$ and the operator be $(\ )^2$, we get $(e^{2x})^2 = e^{4x}$, which is not a constant times the original function. Hence, e^{2x} is not an eigenfunction of the operator $(\ )^2$. If we use the operator for the z component of angular momentum,

$$L_z = \left(\frac{\hbar}{i}\right) \frac{\partial}{\partial \phi} \qquad\qquad ...(1.24)$$

Operating on the function $e^{in\phi}$ (where n is a constant), we get

$$\left(\frac{\hbar}{i}\right) \frac{\partial}{\partial \phi}\, (e^{in\phi}) = in \left(\frac{\hbar}{i}\right) e^{in\phi} = n\,\hbar \,.\, e^{in\phi} \qquad\qquad ...(1.25)$$

which is a constant $(n\,\hbar)$ times the original (eigen)function. Hence, the 'eigenvalue' is $n\,\hbar$.

The Expectation Value

For a given system, there may be various possible values of a 'parameter' we wish to calculate. Since most properties (such as the 'distance' from the nucleus to an electron) may vary, we desire to determine an average or 'expectation' value. By using the operator equation $\alpha\phi = a\phi$ where ϕ is some function, we multiply both sides of this equation by ϕ^*

$$\phi^* \, \alpha \, \phi = \phi^* \, a \, \phi \qquad\qquad ...(1.26)$$

However, it has to be noted that $\phi^* a\phi$ is not necessarily the same as $\phi a \phi^*$. In order to obtain the sum of the probability over all space, we write this in the form of the integral equation as

$$\int_V \phi^* \, \alpha \, \phi \, dV \; = \; \int_V \phi^* \, a \, \phi \, dV \qquad\qquad ...(1.27)$$

But 'a' is a constant and is not affected by the order of operations. By removing it from the integral and solving for 'a' yields

$$a = \frac{\displaystyle\int_V \phi^* \, \alpha \, \phi \, dV}{\displaystyle\int_V \phi^* \, \phi \, dV} \qquad\qquad ...(1.28)$$

It has to be remembered that since α is an operator, $\phi * \alpha \phi$ is not necessarily the same as $\alpha\phi*\phi$, so that the order of $\phi*\alpha \phi$ must be preserved and α cannot be removed from the integral.

Now, if ϕ is normalized, then by definition $\int \phi * \alpha \phi \, dV = 1$, and we get

$$\bar{a} = <a> = \int \phi * \alpha \phi \, dV \qquad \qquad ...(1.29)$$

Where, $\bar{a}$ and $<a>$ are the usual ways of expressing the average or expectation value. If the wave function is known, then theoretically an expectation or average value can be calculated for a given parameter by using its operator.

A Concrete Example → The Hydrogen Atom

Let us consider the following simple example, which illustrates the 'application' of these ideas.

Let us suppose that we want to calculate the 'radius' of the hydrogen atom in the **1s** state. The normalized wave function is written as

$$\psi_{1s} = \left(\frac{1}{\sqrt{\pi}}\right) \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} = \psi*_{1s} \qquad \qquad ...(1.30)$$

Where a_0 is the Bohr radius. This equation becomes

$$<r> = \int \psi*_{1s} \, (\text{operator}) \, \psi_{1s} \, dV \qquad \qquad ...(1.31)$$

Here the operator is just r, since the position coordinates have the same form in operator and classical forms. In polar coordinates, the volume element $dV = r^2 \sin \theta \, dr \, d\theta \, d\phi$. Hence, the problem becomes integration in three different coordinates with different limits as

$$<r> = \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} (r) \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \times e^{-r/a_0} r^2 \sin \theta \, dr \, d\theta \, d\phi$$

$$...(1.32)$$

While this may look rather complicated, it simplifies greatly, since the operator r becomes a multiplier and the function r can be multiplied. Then the result is written as

$$<r> = \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\frac{1}{\pi a_0^3}\right) r^3 \, e^{-2r/a_0} \sin \theta \, dr \, d\theta \, d\phi \qquad \qquad ...(1.33)$$

By using the technique from the calculus, which allows us to separate multiple integrals as :
$$\int f(x) \, g(y) \, dx \, dy = \int f(x) \, dx \int g(y) \, dy \qquad \qquad ...(1.34)$$
We can write equation (1.33) as

$$<r> = \left(\frac{1}{\pi a_0^3}\right) \int_0^\infty r^3 \, e^{-2 r/a_0} \, dr \int_0^\pi \int_0^{2\pi} \sin \theta \, d\theta \, d\phi \qquad \qquad ...(1.35)$$
It can be easily verified that

$$\int_0^\pi \int_0^{2\pi} \sin \theta \, d\theta \, d\phi = 4\pi \qquad \qquad ...(1.36)$$

and the exponential integral is a commonly occurring one in quantum mechanics. It can be easily evaluated by using the formula

$$\int_0^\infty x^n \, e^{-bx} \, dx = n! \, / b^{n+1} \qquad \qquad ...(1.37)$$

In this case, $n = 3$ and $b = 2a_0$. Therefore, we get

$$\int_0^\infty r^3 \, e^{-2 \, r/a_0} \, dr = \frac{3!}{(2/a_0)^4} \qquad \qquad ...(1.38)$$

so that we can write the 'expectation value' as

$$< r > = \left(\frac{4\pi}{\pi a_0{}^3} \right) \frac{3!}{(2/a_0)^4} = \left(\frac{3}{2} \right) a_0 \qquad \qquad ...(1.39)$$

Thus, finally, we can get the 'expectation value' for the hydrogen $1s$ state as

$$< r >_{1s} = 1.5 \, a_0 \quad (a_0 = 0.529 \text{ Å}) \qquad \qquad ...(1.40)$$

With a probability curve of the electron in $1s$ state as a function of the distance from the nucleus, this typical value of the 'expectation value' is shown in **Fig. 1.3,** where the meaning of the maximum of probability of finding an electron at certain distance and its expectation value are quite different.
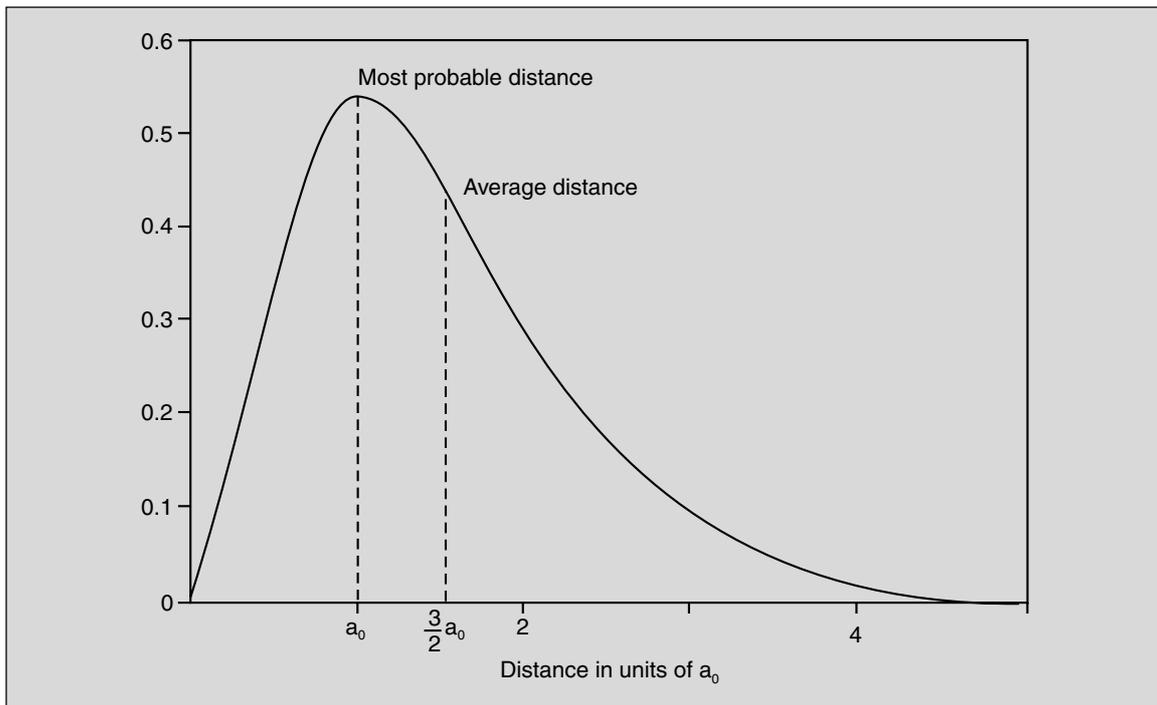

Figure 1.3: Probability of finding a 1s electron as a function of distance from the nucleus.

1.2.6 The Wave Function

Postulate 4. The 'state' function, ψ, is given as a solution of : $H\psi = E\psi$, where, H is the operator for total energy, the Hamiltonian Operator.

This postulate provides a starting point for formulating a problem in quantum mechanical terms, because we usually seek to determine a wave function to describe the system being studied. The Hamiltonian function in classical physics is the total energy, $K + V$, where K is the translational (kinetic) energy and V is the potential energy. In operator form

$$H = K + V \qquad \qquad ...(1.41)$$

Where K is the operator for kinetic energy and V is the operator for potential energy. If we write in the generalized coordinates, q_i, and time, the starting equation becomes

$$H\psi(q_i, t) = -\left(\frac{\hbar}{i}\right) \partial\psi(q_i, t)/\partial t \qquad \qquad ...(1.42)$$

The kinetic energy can be written in terms of the momentum as

$$K = \frac{mV^2}{2} = \frac{p^2}{2m} \qquad \qquad ...(1.43)$$

Now, we can write it in three dimensions as

$$K = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \qquad \qquad ...(1.44)$$

By putting this in operator form, we make use of the momentum operators as

$$K = \left(\frac{1}{2m}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{1}{2m}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{1}{2m}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)^2 \qquad \qquad ...(1.45)$$

However, we can write the square of each momentum operator as

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) = \frac{\hbar^2}{i^2}\frac{\partial^2}{\partial x^2} = -\hbar^2\frac{\partial^2}{\partial x^2} \qquad \qquad ...(1.46)$$

so that we get

$$K = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\left(\frac{\hbar^2}{2m}\right)\nabla^2 \qquad \qquad ...(1.47)$$

where ∇^2 is Laplacian operator or simply Laplacian. The general form of the potential energy can be written as

$$V = V(q_i, t) \qquad \qquad ...(1.48)$$

So that the operator equation becomes

$$\left\{-\left(\frac{\hbar^2}{2m}\right)\nabla^2 + V(q_i, t)\right\}\psi(q_i, t) = -\left(\frac{\hbar}{i}\right)\frac{\partial\psi(q_i, t)}{\partial t} \qquad \qquad ...(1.49)$$

This is the famous Schrödinger time dependent equation or, Schrödinger second equation.

In many problems, the classical observables have values that do not change with time, or at least their average values do not change with time. Therefore, in most cases, it would be advantageous to simplify the problem by the removal of the dependence on the 'time'.

How to do it ?

The well known 'separation of variable technique' can now be applied to see if the time dependence can be separated from the 'joint function'. First of all, it is assumed that $\psi(q_i, t)$ is the product of two functions : one a function which contains only the q_i and another which contains only the 'time' (t). Then, we can easily write it as

$$\Psi(q_i, t) = \psi(q_i)\tau(t) \tag{1.50}$$

It has to be noted that Ψ is used to denote the complete 'state' function and the lower case ψ is used to represent the 'state' function with the time dependence removed. The Hamiltonian can now be written in terms of the two functions ψ and τ as

$$H\Psi(q_i, t) = H\psi(q_i)\tau(t) \tag{1.51}$$

Therefore, the equation (1.49) can be written as

$$H\psi(q_i)\,\tau(t) = -\left(\frac{\hbar}{i}\right)\frac{\partial}{\partial t}\,[\psi(q_i)\,\tau(t)] = -\left(\frac{\hbar}{i}\right)\psi(q_i)\frac{\partial\tau(t)}{\partial t} \tag{1.52}$$

By dividing equation (1.52) by the product $\psi(q_i)\tau(t)$, we get

$$\frac{H\psi(q_i)\,\tau(t)}{\psi(q_i)\,\tau(t)} = -\left(\frac{\hbar}{i}\right)\psi(q_i)\frac{\left[\dfrac{\partial\tau(t)}{\partial t}\right]}{\psi(q_i)\tau(t)} \tag{1.53}$$

Then, we get :

$$\left[\frac{1}{\psi(q_i)}\right]H\psi(q_i) = -\left(\frac{\hbar}{i}\right)\left[\frac{1}{\tau(t)}\right]\frac{\partial\tau(t)}{\partial t} \tag{1.54}$$

It has to be noted that $\psi(q_i)$ does not cancel, since $H\psi(q_i)$ does not represent H times $\psi(q_i)$, but rather H operating on $\psi(q_i)$. The left-hand side is a function of q_i and the right-hand side is a function of 'time' (t), so each can be considered as a constant with respect to changes in the values of the other variable. Both sides can be set equal to some new parameter, X, so that

$$\left[\frac{1}{\psi(q_i)}\right]H\psi(q_i) = X$$

and,

$$-\left(\frac{\hbar}{i}\right)\left[\frac{1}{\tau(t)}\right]\frac{\partial\tau(t)}{\partial t} = X \tag{1.55}$$

From the first of these equations, we get

$$H\psi(q_i) = X\psi(q_i) \tag{1.56}$$

and from the second one, we get

$$\left[\frac{1}{\tau(t)}\right]\frac{d\tau(t)}{dt} = -\left(\frac{i}{\hbar}\right)X\tau(t) \qquad \text{...(1.57)}$$

The differential equation involving the 'time' can be solved readily to give

$$\tau(t) = e^{-(i/\hbar)Xt} \qquad \text{...(1.58)}$$

By substituting this result into equation (1.50), we find that the total 'state' function, Ψ, is

$$\Psi(q_i, t) = \psi(q_i)\, e^{-(i/\hbar)Xt} \qquad \text{...(1.59)}$$

Therefore, the equation (1.52) can be written as :

$$e^{-(i/\hbar)Xt}\, H\psi(q_i) = +\left(\frac{\hbar}{i}\right)\left(\frac{i}{\hbar}\right)X\psi(q_i)\,e^{-(i/\hbar)Xt} \qquad \text{...(1.60)}$$

or,
$$e^{-(i/\hbar)Xt}\, H\psi(q_i) = X\psi(q_i)\, e^{-(i/\hbar)Wt} \qquad \text{...(1.61)}$$

The factor $e^{-(i/\hbar)Xt}$ can be dropped from both sides of equation (1.61), which results in

$$H\psi(q_i) = X\psi(q_i) \qquad \text{...(1.62)}$$

which clearly shows that the time dependence has been separated.

Here, neither the Hamiltonian operator nor the wave function is time dependent. It is this form of the equation that could be used to solve many problems. Hence, the time-independent wave function, ψ, will be normally indicated when we write $H\psi = E\psi$.

For the hydrogen atom, $V = -\dfrac{e^2}{r}$, which remains unchanged in the operator form. Hence, we can write it as :

$$H = -\left(\frac{\hbar^2}{2m}\right)\nabla^2 - \frac{e^2}{r} \qquad \text{...(1.63)}$$

which gives rise to the following equation as :

$$H\psi = E\psi = -\left(\frac{\hbar^2}{2m}\right)\nabla^2\psi - \left(\frac{e^2}{r}\right)\psi \qquad \text{...(1.64)}$$

or,
$$\nabla^2\psi + \left(\frac{2m}{\hbar^2}\right)[E - V]\psi = 0 \qquad \text{...(1.65)}$$

This is the Schrödinger wave equation for the hydrogen atom. Several relatively simple models are capable of being treated by the methods of quantum mechanics. In order to treat these models, we use the above four 'postulates' in a relatively straight forward manner. For any of these models, we always begin with

$$H\psi = E\psi \qquad \text{...(1.66)}$$

and use the approximate expression for the operators corresponding to the potential and kinetic energies. In practice, we will find that there is a rather limited number of potential functions, the most common being a Coulombic (electro-static) potential [1 – 4].

The quantum mechanical models need to be presented, because they can be applied to several systems which are of considerable interest. For example :

(*a*) The 'rigid rotor' and 'harmonic oscillator' models are useful as models in rotational and vibrational spectroscopy, and obviously for understanding the thermal properties of materials.

(*b*) The 'barrier penetration phenomenon' has application as a model for nuclear decay and transition state theory (not discussed here).

(*c*) The particle in a box model has some utility in treating electrons in metals or conjugated molecules (also not discussed here due to limited applicability).

Out of the above utilities or applications of quantum mechanics, only (*a*) or Harmonic Oscillator problem has direct relevance to explain many thermal behaviour of materials, since we need heat to produce a wide range of materials including the "nano materials".

1.3 THE HARMONIC OSCILLATOR

1.3.1 The Vibrating Object

The vibrations in molecular systems constitute one of the most important properties, which provide the basis for studying molecular structure by various spectroscopic methods (I. R./FTIR, Raman Spectroscopy). Let us start with a **vibrating object** $\rightarrow$ For an object attached to a spring, Hook's law describes the system in terms of the force (F) on the object and the displacement (*x*) from the equilibrium position as

$$F = -kx$$

where k = Spring Constant or Force Constant (Newton m or Dynes/cm)

The negative sign means that the restoring force or spring tension is in the direction opposite to the displacement. The work or energy needed to cause this displacement (*i.e.* Potential Energy) is expressed by the "Force Law", which is integrated over the interval, 0 to *x*, that the spring is stretched

$$\int_0^x F(x)\, dx = \int_0^x -kx\, dx = \left(\frac{1}{2}\right) kx^2$$

If the mass (*m*) is displaced by a distance of *x* and released, the object vibrates in simple harmonic motion. The 'angular frequency' of this vibration (ω) is given by

$$\omega = \sqrt{\frac{k}{m}}$$

where the classical or vibrational frequency (ν) is given by

$$\nu = \left(\frac{1}{2\pi}\right)\sqrt{\frac{k}{m}}$$

It is now clear that $\omega = 2\pi\nu$. The maximum displacement from the equilibrium position is called the "amplitude" and the variation of the displacement with time is given by Newton's 2nd Law of

Motion, $F = m \cdot a$. The velocity is the 1st derivative of distance with time $\left(\dfrac{dx}{dt}\right)$ and acceleration is the derivative of velocity with time $\left(\dfrac{d^2x}{dt^2}\right)$. Therefore, the force $(F = m \cdot a)$ can be written as:

$$m \, \frac{d^2x}{dt^2} = -\, kx$$

or,

$$\frac{d^2x}{dt^2} + \left(\frac{k}{m}\right)x = 0$$

This is a linear differential equation with constant coefficients, which can be solved by using the formalism presented above. It is thus seen that the problem of the classical vibrating object serves to introduce the terminology and techniques for the quantum mechanical oscillator, which is much more complex than the classical harmonic oscillator [5 – 6].

1.3.2 Quantum Mechanical Harmonic Oscillator

For studying molecular vibrations and the structure, the harmonic oscillator is a very useful model in quantum mechanics. It was shown in the above description that for a vibrating object, the potential energy (V) is given by

$$V = \frac{1}{2} kx^2$$

which can also be written as

$$V = \frac{1}{2} \, m \, x^2 \, \omega^2$$

The total energy is the sum of the potential energy and kinetic energy. Now, we must start with the Schrödinger equation as

$$H\psi = E\psi$$

Before we write the full form of the Schrödinger equation, we have to find out $\rightarrow$

What is the form of the Hamiltonian Operator?

Before we find the form of this Hamiltonian operator, the kinetic energy (K) must be known, which is written as

$$K = \left(-\frac{\hbar^2}{2m}\right) \frac{\partial^2}{\partial x^2}$$

The potential energy is $2\pi^2\nu^2 \, mx^2$, so that the Hamiltonian operator can now be written as

$$H = \left\{\left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} + 2\pi^2\nu^2 \, mx^2\right\}$$

Therefore, the Schrödinger wave equation $(H\psi = E\psi)$ becomes

$$\left\{\left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} + 2\pi^2\nu^2 \, mx^2\right\}\psi = E\psi$$

By simplifying this equation by multiplying by $-2m$ and dividing by $\hbar^2$ gives

$$\left(\frac{\partial^2}{\partial x^2} - \frac{4\pi^2\nu^2 \, m^2x^2}{\hbar^2}\right)\psi = \left(-\frac{2mE}{\hbar^2}\right)\psi$$

which can be rearranged by putting $\alpha = 2m\dfrac{E}{\hbar}$, $\beta = 2\pi\nu\dfrac{m}{\hbar} = m\dfrac{\omega}{\hbar}$ as

$$\frac{\partial^2\psi}{\partial x^2} + \{\alpha - \beta^2 \, x^2\}\psi = 0 \qquad\qquad\qquad \dots(1.67)$$

This is the usual form of Schrödinger equation. In this equation, the potential varies as x^2, and since it is a non-linear function, this is much more complex than the classical harmonic oscillator or the particle in the one-dimensional box.

A close look of the above wave equation shows that the "solution" must be a function such that its second derivative contains both the original function and a factor of x^2. For very large x, we could assume that a function like $\exp(-\beta x^2)$ satisfies the requirement as

$$\psi = c[\exp(-bx^2)]$$

where, $b \; (= \beta/2)$ and c are constants.

The other solution is

$$\psi = c[\exp(+bx^2)]$$

which is not a viable solution, since this solution becomes infinity as $x \to \pm \infty$, which is in direct violation of one of the 'Born conditions'.

In order to check the first solution, we start by taking the required derivatives as

$$\frac{d\psi}{dx} = -2bxc[\exp(-bx^2)]$$

$$\frac{d^2\psi}{dx^2} = -2bc[\exp(-bx^2)] + 4b^2cx^2[\exp(-bx^2)] \qquad\qquad \dots(1.68)$$

Now, working with the second term of the equation (1.67), we notice that

$$-\left\{\frac{2mE}{\hbar^2} - \beta^2 x^2\right\}\psi = -\left(\frac{2mE}{\hbar^2}\right)c[\exp(-bx^2)] + \left(\frac{m^2\omega^2}{\hbar^2}\right)x^2c[\exp(-bx^2)] \qquad \dots(1.69)$$

It should be noted that both the equations (1.68) and (1.69) contain terms in x^2 and terms that do not contain x except in the exponential. Hence, we can equate the terms that contain x^2 as

$$\left(\frac{m^2\omega^2}{\hbar^2}\right)x^2 \, c[\exp(-bx^2)] = 4b^2 \, cx^2[\exp(-bx^2)]$$

By canceling the common factors from both sides, we get

$$4b^2 = \left(\frac{m^2 \omega^2}{\hbar^2} \right)$$

or,
$$b = \frac{m\omega}{2\hbar}$$

By working with the terms that do not contain x as a factor, we get

$$E = b \left(\frac{\hbar^2}{m} \right)$$

or,
$$E = \frac{1}{2} \omega\hbar \qquad\qquad ...(1.70)$$

Therefore, when $b = \dfrac{m\omega}{2\hbar}$ and $E = \dfrac{1}{2}\omega\hbar$, the function: $\psi = c[\exp(- bx^2)]$ satisfies the Schrödinger equation. By using the value obtained for b, we can write the 'solution' as

$$\psi = c \left[\exp\left(-\frac{m\omega x^2}{2\hbar} \right) \right]$$

In fact, this is the solution for the harmonic oscillator in its lowest energy state.

The "solution" of the harmonic oscillator problem will now be addressed by starting with the wave equation as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left\{ E - \frac{1}{2} kx^2 \right\} \psi = 0$$

Now let us put $\alpha = \dfrac{2mE}{\hbar^2}$ and $\beta = \dfrac{(mk)^{1/2}}{\hbar}$, then the differential equation becomes

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2)\psi = 0$$

In order to solve this 'eigenvalue' problem, it is now necessary to find a set of wave equations (ψ) which satisfies this equation from $-\infty$ to $+\infty$. The function must also obey four 'Born Conditions'. In order to solve the above differential equation, a first solution is found in the limit that x becomes large. Once $x \to \infty$ solution is found, a "power series" is introduced to make the large x solution valid for all x. This is normally called the 'Polynomial Method', known since 1880. By the change of variables to z and after following 'Born Condition', we arrive at the famous Hermite's equation. Without going into a lengthy process, the general form of the Hermite polynomials is written as

$$H_n(z) = (- 1)^n \exp(z^2) \frac{d^n}{dz^n} \exp\left(-\frac{z^2}{2} \right)$$

The first few Hermite polynomials can be written as

$$H_0(z) = 1,$$
$$H_1(z) = 2z,$$
$$H_2(z) = 4z^2 - 2,$$
$$H_3(z) = 8z^3 - 12z,$$
$$H_4(z) = 16z^4 - 48z^2 + 12$$

The wave functions for the 'harmonic oscillator' (ψ_i) have to be expressed as a normalization constant (N_i) times $H_i(z)$ to be able to ultimately give a set of normalized wave functions as

$$\psi_0 = N_0 \exp\left(-\frac{z^2}{2}\right)$$

$$\psi_1 = N_1 (2z) \exp\left(-\frac{z^2}{2}\right)$$

$$\psi_2 = N_2 (4z^2 - 2) \exp\left(-\frac{z^2}{2}\right)$$

$$\psi_3 = N_3 (8z^3 - 12z) \exp\left(-\frac{z^2}{2}\right)$$

The above is just an outline of some of the necessary steps in the full solution of the 'harmonic oscillator' model using quantum mechanics [5 – 6]

The above description is useful for vibrational spectroscopy for the determination of various 'vibration states' between 'two bonding atoms' in a molecule of nano-size or higher. This is obviously useful for some thermal properties like thermal expansion containing various phonon branches, specific heat involving optical and acoustic phonon vibrations in both the longitudinal and transverse modes, and finally on the thermal conductivity that involves the motion of both phonons and electrons. However, in order to have a better knowledge on nano materials, there are many useful properties, like magnetic, electronic and optical, which have to be properly understood in the context of quantum mechanics [7]. These properties are discussed in some details in order get a basic idea about these topics in the following subsections.

1.4 MAGNETIC PHENOMENA

Preamble

In classical physics, a classical charge distribution with angular momentum, which is a 'rotating' or 'spinning' charge distribution, gives rise to magnetic moment. Similarly, in quantum mechanics, the 'angular momentum' is referred to as 'electron spin'. In the mathematical treatment of hydrogen by Schrödinger, we get only "three" quantum numbers : n, l and m_l. The subscript l on the magnetic quantum number m_l shows that this m_l value is associated with the orbital angular momentum, which gives rise to s, p, d and f orbitals, but this treatment does not include the intrinsic angular momentum of the electron. Paul Dirac solved the hydrogen atom problem both from the point of non-relativistic quantum mechanics and the theory of relativity, and showed an additional quantum number m_s which is

associated with the 'intrinsic angular momentum' of the electron, called s. The m_s is actually the projection of this momentum on the z-axis, and due to this momentum, the electron has a 'permanent magnetic dipole'. This is how we can see the relation between the 'electron spin' and the 'magnetic moment'.

Stern and Gerlach made a 'dramatic demonstration' of the existence of 'electron spin' by heating silver atom, and making the vapour pass through a baffle and then through an inhomogenous magnetic field (defined as the z-axis) onto a glass plate. This showed two distinct spots for the unpaired $5s$ electron of silver $\left(s = \dfrac{1}{2} \right)$ with two possible projections on the z-axis with $m_s = \pm \dfrac{1}{2}$. Obviously, it was already known that a magnetic dipole in an inhomogeneous magnetic field experiences a force, which deflects the 'dipole' in a direction that depends on the orientation of the dipole relative to the magnetic field.

1.4.1 Fundamentals of Magnetism

The "spin state" of electrons in an atom determine the magnetic property of the atom. Depending on this spin state of the electrons, the atoms may be classified into mainly : Diamagnetic and Paramagnetic.

(*a*) Diamagnetic atoms (or ions) are those in which there are no uncoupled or uncompensated electron spins.

(*b*) Paramagnetic atoms (or ions) are those with uncoupled or unpaired electron spins in the orbital giving rise a "net magnetic (spin) moment".

The magnetic moment of an uncoupled electron is given as Bohr magneton, μ_B. One Bohr magneton represents the magnetic moment of 'one uncoupled' electron. Therefore, for example, the net magnetic moment for the Fe^{3+} atom is $5\mu_B$, since it has '5 uncoupled' electrons. Different types of magnetism are shown below :
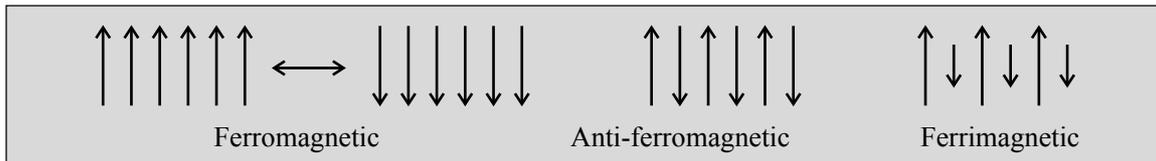
Although paramagnetic atoms have 'net magnetic moments', the overall magnetic moment of crystalline solid may be zero due to the interaction of the atoms in the crystalline lattice. Depending on the 'nature' of this interaction, the atoms may be further classified as 'ferromagnetic', 'anti-ferromagnetic', 'ferrimagnetic'.

A crystal is called a ferromagnetic, if the participating atoms are 'paramagnetic' and their 'directions' are aligned in one direction, which can be switched in the 'opposite direction'. Anti-ferromagnetic crystal is the one whose 'total magnetic moment' is zero, since the magnetic moment of the atoms aligned in one direction is compensated by other atoms, whose magnetic moments are aligned in the opposite direction.

In a ferrimagnetic crystal, the magnetic moments of the atoms are arranged in a similar way to anti-ferromagnetic crystal. However, if the magnetic moment in one direction is larger than the other direction, the result is a "non-zero" overall magnetic moment. Even in ferromagnetic crystal, both up and down magnetic moments coexist. The difference between ferromagnetic and ferrimagnetic is that

up and down moments coexist 'intrinsically' within the crystal for ferrimagnetic → while they are formed by two distinct regions (called 'domains') of the crystal in ferromagnetic materials. Hence, only 'one direction' of magnetic moment exists in a domain of ferromagnetic crystals.

In this book, we are dealing with nano materials. In **chapter – 5**, the magnetic properties of the nano particles of magnetite (*i.e.,* a ferrite with a spinel structure) that are embedded in a glassy diamagnetic matrix are discussed in details. These small particles show a phenomenon of 'super-paramagnetism' and also within the nano domain for a slightly higher particle size, these nano particles show 'ferrimagnetism', as per the above description. In the continuation of this section, we would like to give some details on diamagnetism and paramagnetism along with symmetrization and antisymmetrization, which are very important concepts. Moreover, Pauli's principle on the 'electron spin' is discussed with a mathematical treatment in terms of 'determinants' so that a theoretical understanding is developed for the readers to appreciate some intricate details of the 'magnetic properties', *i.e.,* the 'spin properties', of nano materials. The necessary concept on the 'magnetic properties' of the nano materials can be obtained from the theoretical aspects of Mössbauer and ESR spectra, as detailed in the **sections – 1.6.1 and 1.6.2.**

The concept of antisymmetrization is important in the quantum level, which can have some consequences on the magnetic properties of solids containing nano particles. So, here is a brief discussion on this subject.

1.4.2 Antisymmetrization

It is known that the 'total wave function' of an electron in a solid consists of a 'spatial function' and a 'spin function', and for a 'symmetric spatial function', the spin function is 'antisymmetric', and vice versa. The 'spatial' part can be symmetric or antisymmetric. The 'spin' part can be symmetric or antisymmetric → but the 'total function' must be antisymmetric, since the totally symmetric wavefunction are not valid wave functions.

No additional terms in the Hamiltonian can mix symmetric and antisymmetric states. For the states to mix, a non-zero matrix element must exist. The Hamiltonian including any additional terms is symmetric. The product of a symmetric function and an antisymmetric function is always 'antisymmetric'. In order to calculate the value of a matrix element, an integration is performed over all space → *i.e.,* in a symmetric region. Since the product is 'antisymmetric', the integral will vanish. Therefore, the 'totally symmetric' functions and the 'totally antisymmetric' functions are two completely independent to each other, which never mix → *i.e.,* they can have no interaction with each other and hence only one of the two types of states can exist in nature. This point should be clearly understood.

The Question is → Which Type of Function Occurs in Nature?

This question has been answered by experiments. All experimental observations show that the states occurring in nature are totally 'antisymmetric'. Let us take an example of He atom, whose ground state is triply degenerate ($s = 1$) spin state, where the electron spins are 'unpaired', if the wavefunction is totally symmetric → whereas for a 'non-degenerate' ground state ($s = 0$), the spin state, where the electron spins are 'paired', if the wavefunction is totally antisymmetric.

The $s = 1$ state would be paramagnetic because of the combined magnetic dipole moments of the two electrons. By contrast, the $s = 0$ state is diamagnetic. The experiments show that the ground state of He is not paramagnetic. For example → a non-magnetic glass container with liquid helium cannot be picked up by a magnet. For the totally symmetric states, the $s = 0$ (singlet) states are lower in energy

than the *s = 1* (triplet) states for the states involving the same orbitals. The opposite is true for totally antisymmetric states.

Actually, spectroscopic experiments-which involves 'transitions' between two different energy states -- show that for the same orbitals, the triplet states are 'always' lower in energy than the singlet states.

This is due the 'qualitative' statement of the "Pauli Exclusion Principle" that →

All Total Many-Electron Wavefunctions Must be Antisymmetric

Since the 'permutation' symmetry of many-body wavefunctions can only be determined experimentally, it is necessary to bring the "Antisymmetrization Property" into quantum mechanical theory as an 'assumption'.

The Assumption →

The wavefunctions representing an actual state of a system containing two or more electrons must be completely 'antisymmetric' in the coordinates of the electrons → *i.e.,* "on interchanging the coordinates of any two electrons" → *"the sign of the wavefunction must change".*

In fact, this assumption is the 'quantum mechanical statement' of the Pauli Exclusion Principle'. This can be better understood by two important properties of the 'determinants', which should be elaborated little further as follows:

First Property of the Determinant →

The antisymmetric wavefunctions can be expressed as determinants : Let us take A(1) as an "orbit × spin" function for one electron, such as $1s\alpha$, and B, C, ... N and others, then the total wave function $\psi(x)$ can be written as

$$\begin{vmatrix} A(1) & B(1) & .... & N(1) \\ A(2) & B(2) & .... & N(2) \\ .... & .... & .... & .... \\ A(N) & B(N) & .... & N(N) \end{vmatrix}$$ ...(1.71)

which is completely antisymmetric in the N electrons, since any interchange of any two rows change the sign of the determinant, which is the 'first' property of the determinant. The number in each row is the 'electron label'. Each electron is in every orbital.

Now, let us take an actual example → He atom and write its ground state as a determinant, which will involve the $1s$ orbital, and α and β spin states. The 2×2 determinant is formed and expanded to obtain totally antisymmetric wavefunction

$$\begin{vmatrix} 1s(1)\,\alpha(1) & 1s(1)\,\beta(1) \\ 1s(2)\,\alpha(2) & 1s(2)\,\beta(2) \end{vmatrix}$$ ...(1.72)

$$= 1s(1)\alpha(1).1s(2)\beta(2) - 1s(2)\alpha(2).1s(1)\beta(1)$$
$$= 1s(1)1s(2)[\alpha(1).\beta(2) - \beta(1).\alpha(2)]$$ ...(1.73)

This equation (1.73) correctly represents antisymmetric ground state function. The spatial part is symmetric and the spin part is antisymmetric. The spin part here corresponds to $s = 0, m_s = 0$ → *i.e.,* the electron spins are paired.

Second Property of the Determinant →

Another important property of the determinant is that if two columns are equal → it vanishes. In fact, this property of the determinant builds the 'Pauli Exclusion Principle' into mathematical formalism. For a given one-electron orbital, there are only two possible spatial × spin functions, *i.e.* those obtained by multiplying the spatial function by either of the two spin functions α and β. Thus, no more than two electrons can occupy the same orbital in an atom or molecule and those two must have their spins opposed → *i.e.,* no two electrons can have the same set of values of all four quantum numbers : n, l, m_l and m_s.

But, why it is so?

If all of the quantum numbers are the "same" → then two columns in the 'determinant form' of the wavefunction will be exactly equal → and the wavefunction (*i.e.,* the determinant) will vanish, which is not desirable. Hence, the requirement that all many-electron 'total wavefunctions' (spatial × spin) must be antisymmetric with respect to the interchange of all pairs of electrons → forces the wavefunctions to satisfy the 'Pauli Exclusion Principle'.

Again, let us take an example → for the ground state of the He atom, if we assume that both electrons are in the $1s$ orbital and both have α spin, then it is written as

$$\psi = \begin{vmatrix} 1s(1) & 1s(1) \\ 1s(2) & 1s(2) \end{vmatrix} \qquad \qquad ...(1.74)$$

If we expand this determinant, we find that

$$1s(1)\alpha(1).1s(2)\alpha(2) - 1s(2)\alpha(2).1s(1)\alpha(1) = 0 \qquad ...(1.75)$$

This is the price we pay → if we attempt to write a wavefunction, which "violates" the 'Pauli Exclusion Principle' → a wavefunction which is not totally antisymmetric → gives zero, which is not an 'acceptable' wavefunction. Hence, the concept of 'antisymmetrization' is clear through the 'Pauli Exclusion Principle'.

Since the 'spin state' decides the magnetic property of materials, it is important to discuss various 'spin states' that exist within a quantum system, like singlet state and triplet state.

1.4.3 Concept of Singlet and Triplet States

The Definition

A given 'state' can be obtained by multiplying a symmetric spatial function by the 'single' antisymmetric spin function. For each 'spatial configuration', there is only one such 'state' with $s = 0$ and $m_s = 0$. These states are called "singlet states".

A given 'state' can also be obtained by multiplying an antisymmetric spatial function by a symmetric spin function. Each antisymmetric spatial function can be actually multiplied by 'three' symmetric spin functions with $s = 0$ and $m_s = 1, 0$ and -1. Since each antisymmetric spatial function gives rise to three 'total' spatial × spin functions, these states are called "triplet states".

The three triplet states differ by the value of m_s associated with each one. They are not necessarily degenerate → for example, the 'spin-orbit' coupling can split the degeneracy of the triplet states giving rise to multiplets in the observed spectra. The symbols : ^1S, ^3S and ^1P are called 'term symbols'. ^3S means a triplet state derived from 's' states, while ^1P means a singlet state from 's' and 'p' states. They are useful in understanding the spectroscopic behaviour of solids.

The Energy Consideration

The triplet states have inherently lower energies than the singlet state, which arises from the same orbital configurations. For example → the He excited triplet states involving 1*s*, 2*s* orbitals are lower in energy than the 1*s*, 2*s* singlet state, in spite of the fact that the spatial wavefunctions contain the same orbitals. This difference in energy arises from the permutation symmetry of the spatial wavefunctions.

The triplet states have antisymmetric spatial functions, while the singlet states have symmetric spatial function. The antisymmetric spatial function has a node, *i.e.,* it vanishes if the two electrons are at the same spatial locations, while the symmetric spatial function does not vanish. Let us consider an antisymmetric spatial function

$$\frac{1}{\sqrt{2}} \; [1s(1)2s(2) - 2s(1)1s(2)] \qquad \qquad ...(1.76)$$

Since the electron labels, 1 and 2, represent the coordinates of the two electrons, if the two electron are at the same location, q, the function is expressed as

$$\frac{1}{\sqrt{2}} \; [1s(q)2s(q) - 2s(q)1s(q)] \; = \; 0$$

The triplet electrons are anti-correlated. A plot of a function like (1.76) around the point q would show that the probability of finding the two electrons near each other is small and the probability vanishes at q for all q. By contrast, if the electrons are located at q, the symmetric spatial function is expressed as

$$\frac{1}{\sqrt{2}} \; [1s(q)2s(q) + 2s(q)1s(q)] \neq 0$$

Thus, the symmetric spatial function allows the 'two electrons' to reside at the same point in space, and the probability is not necessarily small for finding the two electrons at the same location or near each other.

The anti-correlation of the triplet electrons, which causes them to be further apart than the singlet electrons on average, reduces the 'triplet-state energy' by reducing the magnitude of 'electron-electron' repulsion. The electron-electron repulsion is a type of 'interaction', which increases the energy of a given state. Hence, the energy of the state is not solely determined by the orbitals, which make up the spatial wavefunction. The 'permutation symmetry' of the spatial wavefunction can play a significant role in determining the energy of a state.

1.4.4 Diamagnetism and Paramagnetism

The physical quantities like the magnetic field strength, H, and the magnetic induction, B, in vacuum, are related by the following relation

$$B = \mu_0 H \qquad \qquad ...(1.77)$$

where, $\mu_0 = 4\pi \times 10^{-7}$ Vs/Amp is the permeability of free space. The magnetic state of a system (often called Sommerfeld System) will be specified by the magnetization M, which is related to B and H as

$$B \; = \mu_0 \, (H + M) \qquad \qquad ...(1.78)$$

The magnetization M is equal to the density of magnetic dipole moments *m* as

$$M \; = \; m \; (N/V) \qquad \qquad ...(1.79)$$

Generally, instead of the external field H, it is convenient to introduce an external 'induction' B_0 = $\mu_0 H$, and we can call the quantity B as simply the 'magnetic field strength'. In most cases in solids, there is a linear relation between the 'field' B_0 and the magnetization M as

$$\mu_0 M = \chi B_0 \qquad ...(1.80)$$

where, χ is the 'magnetic susceptibility. The value of χ is important in determining whether the material is diamagnetic or paramagnetic.

If the value of χ is negative, then the induced magnetic polarization is opposite in sign to the applied field. Such behaviour is termed as "diamagnetic", while the reverse behaviour is termed as "paramagnetic", and is characterized by $\chi > 0$. In general, the susceptibility of atoms, and hence of solids, consist of a dia-magnetic and a para-magnetic component, which are denoted by χ_D and χ_P. The paramagnetic component is related to the 'intrinsic magnetic moments', which originate from the angular momentum and the spin of the electrons. For example, the magnetic dipole moment of an electron due to angular momentum can be written as

$$m = -\left(\frac{e}{2m}\right) \Sigma_i\, r_i \times p_i = -\mu_B L \qquad ...(1.81)$$

with $\hbar L = \Sigma_i\, r_i \times p_i$ and the Bohr Magneton $\mu_B = \dfrac{e\hbar}{2m}$ = 5.7884×10^{-5} eV/T = 9.2742×10^{-24} J/T

$(1T = 1 \text{ Tesla} = 1 \text{ Vs/m}^2 = 10^4 \text{ Gauss})$.

The negative sign in (1.81) follows from the fact that the electric current has the opposite sense to that of the particle current due to the negative charge of the electron. Apart from the magnetic moment due to the angular momentum, the electrons also possess a magnetic moment due to 'spin', and the summation of this factor gives the spin moment of the whole atom as

$$m = \mu_B g_0 \Sigma_i s_i = \mu_B g_0 S \qquad ...(1.82)$$

Here, g_0 is the 'electronic g factor' or 'Lande g factor' (= 2.0023 for free electron value) and s_i are the (negative) electron spins. As already shown in (1.81) and (1.82), L and S can be treated as 'operators'. The choice of sign of the 'spin operator' is best made so that the spin operator and the magnetic moment have the same sign. At this stage, it is better to talk about the spin-orbit coupling or L – S coupling.

Spin-Orbit Coupling

The importance of these operators needs to be understood in the light of 'spin-orbit' coupling, which lifts the 'degeneracy' of electronic states. In the Schrödinger treatment of hydrogen like atoms, the terms in the Hamiltonian arising from the electron spin have not been included. Thus, the six states of a single p electron in sodium, for example, would be degenerate, which is important for the understanding of the fluorescence of Na – D lines. However, the 'intrinsic angular momentum' of the electron gives rise to a magnetic dipole, which is moving in the electric field of the atom or molecule. The 'interaction' of a moving dipole with an electric field produces 'changes' in the electronic energy $\rightarrow$ and that's how the 'degeneracy' is lifted by the spin-orbit coupling or L – S coupling. For a hydrogen like atom, the spin-orbit coupling portion of the Hamiltonian is given by

$$H_{so} = \frac{Ze^2}{8\pi\varepsilon_0\, m^2 c} \left(\frac{1}{r^3}\right) [r \times p].S$$

$$= \frac{Ze^2}{8\pi\varepsilon_0\, m^2 c}\, \left(\frac{1}{r^3}\right) \text{L.S} \qquad\qquad ...(1.83)$$

since $(r \times p)$ is the orbital angular momentum (L). S operates on the electron spin wavefunction. L operates on the orbital angular momentum wavefunction (the spherical harmonics), and $\frac{1}{r^3}$ operates on the radial part of the wavefunction, and finally the Hamiltonian is expressed as

$\text{H}_{so} = a(r)\, \text{L.S}$

For hydrogen like atoms, the value of the coefficient of L.S is expressed as

$a(r) \propto Z^4$

The Z^4 dependence gives rise to 'heavy atom effect' $\rightarrow$ *i.e.,* the 'spin-orbit' coupling increases very rapidly with nuclear charge (Z) of the atoms or molecules. Since atomic or molecular wavefunctions are spatially 'extended', there is some probability of finding a molecule's electrons on the 'heavy atoms' of the solvent. The electron delocalization is responsible for the 'external' heavy atom effect.

Finally, by evaluating the expectation values of the operators L and S for atoms, it can be seen that a non-vanishing expectation value results only for open shells. For closed shells, the sum of the angular momentum and spins is zero. In solids, we have 'open shells' for transition metals and rare earths. The paramagnetic behaviour is thus expected for solids containing both these elements with a finite expectation value (see **section 1.2.5** for expectation value).

Apart from paramagnetism due to the electrons, we must also consider diamagnetism. The latter results from the induction of 'eddy' currents by an external magnetic field. According to the Lenz's rule, the magnetic moment of these induced currents is opposed to the applied field. The susceptibility thereby acquires a negative diamagnetic contribution. The susceptibility relation is written as

$$\chi = - \left(\frac{e^2 n}{6m}\right)\mu_0\, \Sigma_i < \phi \mid r_i^2 \mid \phi > \qquad\qquad ...(1.84)$$

where *n* is the number of atoms per unit volume. In the sum over the matrix elements, the electrons in the outer shells are naturally of great importance, since their mean square distance from the nucleus is the largest. If the number of outer electrons is Z_a and we include the square of the atomic or ionic radii r_a in place of the mean of r_i^2, then we get

$$\chi = - \left(\frac{e^2}{6m}\right)\mu_0\, n\, Z_a\, r_a^{\,2} \qquad\qquad ...(1.85)$$

The measured values of the diamagnetic susceptibility for atoms and ions with closed shells are indeed found to be in good agreement with $Z_a r_a^{\,2}$. A similar order of magnitude results for paramagnetic contributions. For a typical solid state density of 0.2 mol/cc, the susceptibility is about 10^{-4} (SI units), *i.e.,* small compared with 1. Therefore, apart from the solids showing ferromagnetism, the magnetic susceptibility of solids is small. By contrast, the electric susceptibility is of the order of 1 or larger.

Now, this should explain why in solid state spectroscopy with 'electromagnetic radiation', which is one of the most important experimental methods, we usually consider only electronic effects.