CHAPTER 1

Quantum Mechanics – I

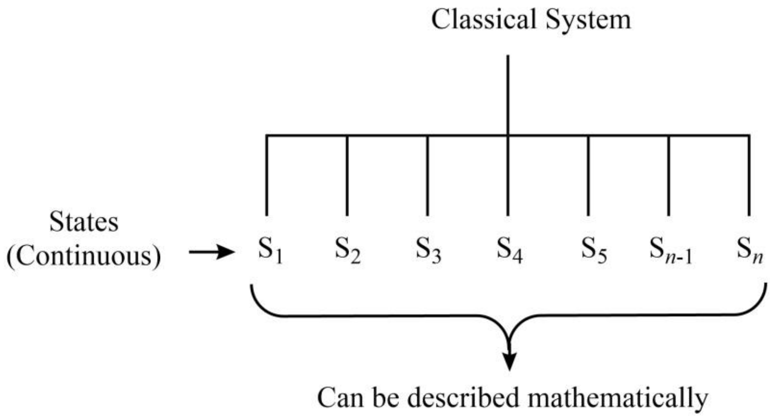
❖ Postulates of Quantum Mechanics

In modern quantum theory, the postulates of quantum mechanics are simply the step-to-step procedure to solve a simple quantum mechanical problem. In other words, it is like the manual that must be followed to retrieve the information about various states of any quantum mechanical system. We will first learn about the nature and the significance of these postulates, and then we will apply them to some real problems like the particle in a one-dimensional box or the harmonic oscillator.

➢ *The First Postulate*

All time-independent states of any quantum mechanical system can be described mathematically as long as the function used is single-valued, continuous and finite.

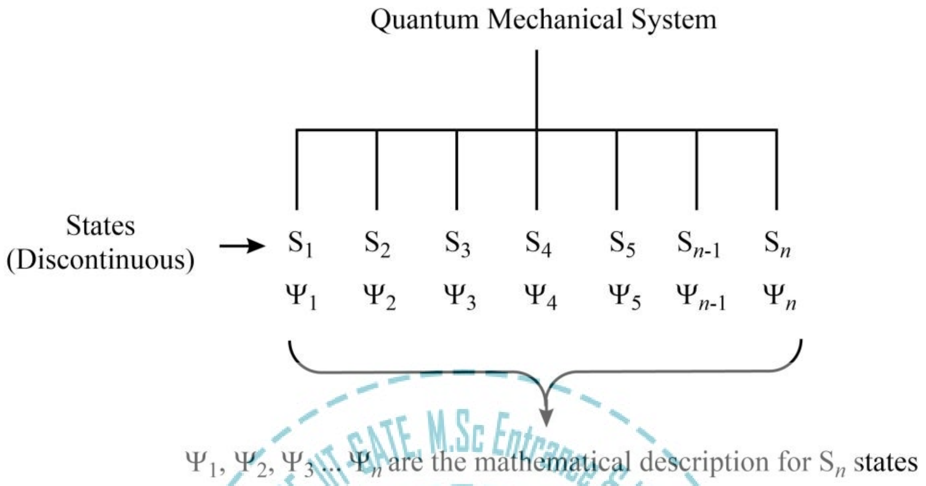
Explanation: The systems around us can be broadly classified into two categories; the first is classical and the other one as quantum mechanical. The classical systems simply refer to the systems which are governed by the classical or the Newtonian mechanics. Now because all the macroscopic objects follow Newton's laws of motion, they fall in the category of classical systems; for example, a rotating gym dumbbell, the vibrating spring of steel, or an athlete running in the playground. Every classical system can possess many states which belong to a continuous domain, and each state can be described mathematically.



However, if the rotating gym dumbbell is replaced by the rotating diatomic molecule, the system would not remain classical anymore and would start violating classical laws. The states of such microscopic systems (here it just means the extremely small) belong to a discontinuous domain and can also be described mathematically. These mathematical descriptions are labeled as ψ_1, ψ_2, ψ_3 ….. ψ_n and generally called as the "wave functions". The term "wave function" is used because as we go from the macroscopic to the microscopic world i.e. from classical to the quantum mechanical world, things start behaving like waves rather particle. All of the states are wave-like; and because every wave we see around us is continuous, single-valued and finite;

Copyright © Mandeep Dalal

only continuous, single-valued and finite expressions can represent those states. For instance, when you drop a stone in a standstill pond, the waves are generated which travel from the center to the boundary of the pond; and you don't see any discontinuity in it.



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector-14, Rohtak, Haryana

Hence, if a function is not single-valued, continuous and finite; it will not be able to represent any wave-like behavior at all. That is why every function that correlates a quantum mechanical state must be single-valued, continuous and finite; and this function describes the corresponding state completely.

- ***The Second Postulate***

For every physical property like linear momentum or the kinetic energy, a particular operator exists in quantum mechanics, the nature of which depends upon the classical expression of the same property.

Explanation: In classical mechanics, there are simply straight forward formulas for all physical properties; like linear momentum can simply be calculated by multiplying the mass with velocity. However, in case of quantum mechanical systems, the value of a certain physical property for a particular state cannot be calculated simply by using its classical formula but from an operator. It does sound silly but the classical formulas which are so well-tested on the scale of time fail in quantum world. For instance, you can use the $mv^2/2$ to calculate the kinetic energy of a moving particle in classical world by just putting its mass and velocity; but if the mass of the moving particle is extremely less, you will not get any rational results.

It is also worthy to note it again that though the classical formulas fail to give the value of physical property, they are still important as they form the basis of the derivations for corresponding quantum mechanical operators. For instance, the operator for kinetic energy (T) along x-axis can be derived as:

$$K.E.(T) = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m} \tag{1}$$

Where m and v are mass and the velocity, respectively; and p represents the angular momentum whose squared operator is:

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\hat{p}_x^2 = \frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2} \tag{2}$$

Now putting the value of momentum squared from equation (2) into equation (1), we get:

$$\hat{T}_x = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} \tag{3}$$

The expressions of various quantum mechanical operators are given below.

Table 1. Various important physical properties and their corresponding quantum mechanical operators.

Physical property		Operator	
Name	*Symbol*	*Symbol*	*Operation*
Position	x	$\hat{x}$	Multiplication by x
Position squared	x^2	$\hat{x}^2$	Multiplication by x^2
Momentum	p_x	$\hat{p}_x$	$\frac{h}{2\pi i}\frac{\partial}{\partial x}$
Momentum squared	p_x^2	$\hat{p}_x^2$	$\frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}$
Kinetic energy	$T = \frac{P^2}{2m}$	$\hat{T}_x$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiplication by $V(x)$
Total energy	$E = T + V(x)$	$\hat{H}$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

For three dimensional systems, the total operator can be obtained by summing the individual operators along three different axes. For instance, some important three-dimensional operators are:

$$\hat{T} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{4}$$

$$\hat{p} = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) \tag{5}$$

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z) \tag{6}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

➢ *The Third Postulate*

If ψ is a well-behaved function for the given state of system and $\hat{A}$ is a suitable operator for a particular physical property, then the operation on ψ by the operator $\hat{A}$ gives the function ψ multiplied by the value of the physical property which can be constant or variable but always real (R). Mathematically, it can be shown as:

$$\hat{A}\psi = R\psi \tag{7}$$

Explanation: The third postulate of quantum mechanics actually connects the first and second postulate of quantum mechanics. The first postulate talks about the possibility of describing a quantum mechanical state mathematically, while the second postulate says that the values of all physical properties in the quantum world are obtained by the operator rather than the simple classical formula. Now the third postulate says that if we operate the operator (from second postulate) over the wave function (from first postulate), we will get the value of the corresponding physical property.

However, at this point, a new problem arises as we do not know the exact mathematical description i.e. the wave function of any quantum mechanical state; and the operators need the absolute mathematical description of the quantum mechanical state to yield any actual result. Now though we know the expressions of different operators proposed by the second postulate; the first postulate speaks only about the presence of a single-valued, continuous and finite mathematical function but does not give actual function itself; and without the knowledge of actual "wave functions", the operators are pretty much useless. Therefore, one would think that there must be some route by which the wave functions are obtained first, which would be used as operand afterward. However, the procedure to find the exact mathematical descriptions of various quantum mechanical states is somewhat more synergistic. The "magic mystery" is that all the operators need absolute expression of the wave function that defines the quantum mechanical state except one, the most famous "Hamiltonian operator". The special thing about the Hamiltonian operator is that it does not necessarily need the absolute form but the symbolic form only to yield the value of its physical property i.e. energy. Nevertheless, in the process of applying the Hamiltonian operator over the symbolic form of the wave function, the absolute expression is also obtained. Mathematically,

$$\hat{H}\psi = E\psi \tag{8}$$

After putting the expression of the Hamiltonian operator in equation (8) and then rearranging, we get:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0 \tag{9}$$

The second-order differential equation i.e. equation (9) is the famous Schrodinger wave equation, the solution of which gives not only the energy but the wave function as well. Now, once the exact expression of the wave function representing a particular state is known, other operators can be operated over it to find their values.

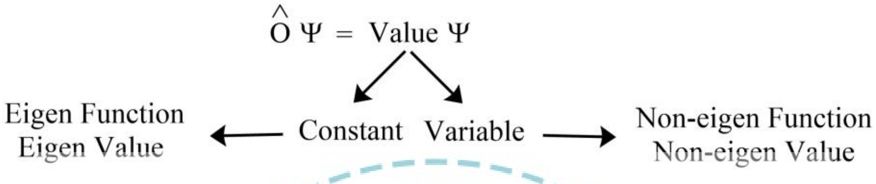
Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

➢ *The Fourth Postulate*

If the value of the physical property obtained after multiplying the wave function by the corresponding operator is constant (postulate 3), the value is called as the eigen-value and is directly reportable; and the wave function will be labeled as the eigen-function of the operator used.

Explanation: The third postulate said that when the wave function of a particular quantum mechanical state is multiplied by the operator of an observable quantity, we get a real value multiplied by the wave function itself; however, the value obtained so can be constant or variable. Mathematically,



The constant value of the observable quantity can be reported directly, and the function is called the eigenfunction of the operator under consideration.

➢ *The Fifth Postulate*

If the value of the physical property obtained after multiplying the wave function by the corresponding operator is variable i.e. non-eigen, the value can be reported only after averaging it over the whole configurational space.

$$< a > or\ \bar{a} = \frac{\oint \psi^* \hat{O} \psi \, d\tau}{\oint \psi^* \psi \, d\tau} \tag{10}$$

Explanation: As we have seen in the fourth postulate that the value obtained by multiplying the Hermitian operator with any quantum mechanical state can also be variable in nature. For instance, if we multiply a wave function simply by position operator, we will get

$$\hat{x}\psi = x\psi \tag{11}$$

or

$$\hat{x} = \frac{x\psi}{\psi} \tag{12}$$

Now because "*x*" is a variable number, it must have reported as an average value before any further rational argument is made.

Therefore, we can say that the fifth postulate is simply an extension of the fourth postulate; i.e. the fourth postulate is used to obtain the value of a particular physical property if it is an eigenvalue, however, the fifth postulate is employed to calculate all non-eigenvalues.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

❖ Derivation of Schrodinger Wave Equation

The Schrodinger wave equation can be derived from the classical wave equation as well as from the third postulate of quantum mechanics. Now though the two routes may appear completely different, the final result is just the same indicating the objectivity of the quantum mechanical system.

➢ *The Derivation of Schrodinger Wave Equation from Classical Wave Equation*

After the failure of the Bohr atomic model to comply with the Heisenberg's uncertainty principle and dual character proposed by Louis de Broglie in 1924, an Austrian physicist Erwin Schrodinger developed his legendary equation by making the use of wave-particle duality and classical wave equation. In order to understand the concept involved, consider a wave traveling in a string along the *x*-axis with velocity *v*.

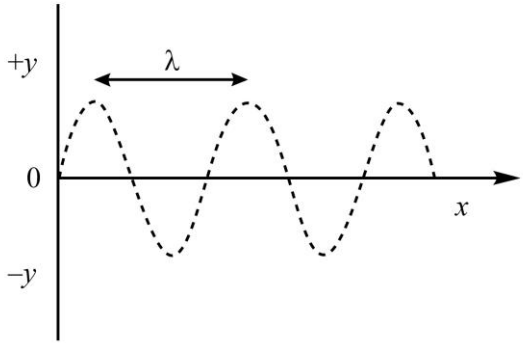


Figure 1. The wave motion in a string.

It can be clearly seen that the amplitude of the wave at any time *t* is the function of displacement *x*, and the equation for wave motion can be formulated as given below.

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \tag{13}$$

Therefore, we can say that y is a function of *x* well at *t*.

$$y = f(x)f'(t) \tag{14}$$

Where *f(x)* and *f′(t)* are the functions of coordinate *x* and time, respectively. The nature of the function *f(x)* can be understood by taking the example of stationary or the standing wave.

A standing wave is created in a string fixed between two points with a wave traveling in one direction, and when it strikes the other end, it gets reflected with the same velocity but in negative amplitude. This would create vibrations in that string with or without nodes depending upon the frequency incorporated. We can create fundamental mode (0 node), first overtone (1 node) or second overtone (2 nodes) just by changing the vibrational frequency. The nature of these standing or stationary waves can be understood more clearly by the diagram given below.

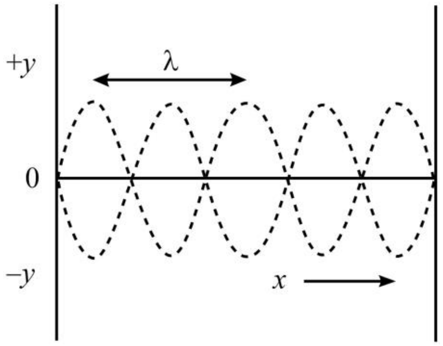


Figure 2. Standing waves in a string.

The mathematical description for such a wave motion is

$$f'(t) = A \sin 2\pi\nu t \tag{15}$$

Where A is a constant representing maximum amplitude and ν is the frequency of the vibration. Now putting the value of $f'(t)$ from equation (15) in equation (14), we get

$$y = f(x)\, A\, Sin\, 2\pi\nu t \tag{16}$$

Differentiating the above equation w.r.t. t, we are left with

$$\frac{\partial y}{\partial t} = f(x)\, A 2\pi\nu\, Cos\, 2\pi\nu t \tag{17}$$

Differentiating again

$$\frac{\partial^2 y}{\partial t^2} = -f(x)\, 4\pi^2\nu^2\, A\, Sin\, 2\pi\nu t \tag{18}$$

$$\frac{\partial^2 y}{\partial t^2} = -4\pi^2\nu^2 f(x)\, f'(t) \tag{19}$$

Now differentiating equation (14) w.r.t. x only, we get

$$\frac{\partial y}{\partial x} = f'(t) \frac{\partial f(x)}{\partial x} \tag{20}$$

Differentiating again

$$\frac{\partial^2 y}{\partial x^2} = f'(t) \frac{\partial^2 f(x)}{\partial x^2} \tag{21}$$

Now put the value of equation (19) and (21) in equation (13), we get

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$f'(t)\frac{\partial^2 f(x)}{\partial x^2} = \left(\frac{1}{v^2}\right)[-4\pi^2\nu^2 f(x)\, f'(t)] \tag{22}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{v^2} f(x) \tag{23}$$

The equation (23) is now time-independent; and therefore, shows the amplitude dependence only upon the coordinate x. Since $c = \nu\lambda$ ($\nu = c/\lambda$), the velocity of the wave can also be replaced by the multiplication of frequency and wavelength i.e. $v = \nu\lambda$.

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{\nu^2\lambda^2} f(x) \tag{24}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \tag{25}$$

The symbol of the function $f(x)$ is replaced by popular $\psi(x)$ or simply the ψ.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2}{\lambda^2}\psi \tag{26}$$

Also, as we know that $\lambda = h/mv$, the equation (26) becomes

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2 m^2 v^2}{h^2}\psi \tag{27}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \tag{28}$$

Furthermore, as the total energy (E) is simply the sum of the potential (V) and kinetic energy, we can say that

$$E = \frac{mv^2}{2} + V \tag{29}$$

$$mv^2 = 2(E - V) \tag{30}$$

After putting the value of mv^2 from equation (30) in equation (28), we get

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{31}$$

For three-dimension i.e. $\psi(x, y, z)$, the above equation can be extended to following

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{32}$$

The above-mentioned second order differential equation i.e. equation (32) is our popular form of the Schrodinger wave equation.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

➢ *The Derivation of Schrodinger Wave Equation from the Postulates of Quantum Mechanics*

The Schrodinger wave equation can be derived using the first three postulates of quantum mechanics. In other words, we can say that the Schrodinger wave equation is nothing but the rearranged form of the following equation:

$$\hat{H}\psi = E\psi \tag{12}$$

In order to prove the above claim, consider a single particle having "m" mass that moves with a velocity "v" in the three-dimensional region. The sum of its kinetic and potential energy can be given as:

$$E = T + V \tag{13}$$

However, we know that

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{14}$$

Where "p" represents the total linear momentum of the particle under consideration. Furthermore, as we also know that

$$p^2 = p_x^2 + p_y^2 + p_z^2 \tag{15}$$

Where p_x, p_y and p_z are the magnitudes of total linear momentum along x, y and z-axis, respectively. Now putting the value of p^2 from equation (15) into equation (14), we get the following

$$T = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{16}$$

And now put the value of kinetic energy from equation (16) into equation (13). We get

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \tag{17}$$

However, from the second postulate of quantum mechanics, we know that the expressions for linear momentum operator along three different directions are:

$$\widehat{p_x} = \frac{h}{2\pi i}\frac{\partial}{\partial x} \tag{18}$$

$$\widehat{p_y} = \frac{h}{2\pi i}\frac{\partial}{\partial y} \tag{19}$$

$$\widehat{p_z} = \frac{h}{2\pi i}\frac{\partial}{\partial z} \tag{20}$$

The operator of "V" is simply itself as it is a function of position coordinates only.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

Hence, after putting values of linear momentum operators and potential energy operator in equation (17), the operator for total energy (Hamiltonian operator) becomes

$$\hat{H} = \frac{1}{2m}\left[\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2\right] + V \tag{21}$$

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \tag{22}$$

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \tag{23}$$

Where

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

represents the Laplacian operator.

Now, after putting the value of Hamiltonian operator from equation (22) into equation (12) i.e. given by the third postulate of quantum mechanics, get

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi \tag{24}$$

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi - E\psi = 0 \tag{25}$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} - \frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial y^2} - \frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial z^2} + V\psi - E\psi = 0 \tag{26}$$

Multiplying the equation (26) throughout by

$$-\frac{8\pi^2 m}{h^2}$$

we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{8\pi^2 m}{h^2}V\psi + \frac{8\pi^2 m}{h^2}E\psi = 0 \tag{27}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{28}$$

Equation (28) is the most popular form of the Schrodinger wave equation for three dimensional systems. In the case of two and one dimensional systems first three terms can be reduced to two and one, respectively.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

❖ Max-Born Interpretation of Wave Functions

In 1926, a German physicist Max Born formulated a rule which is generally called as the Born law or Born's rule of quantum mechanics, giving the probability that a measurement on a quantum system will yield a given result. In other words, it states that the probability density of finding the particle at a given point is proportional to the square of the magnitude of the particle's wavefunction at that point. The Max-Born interpretation is one of the key concepts of quantum mechanics to understand wave-particle duality.

Let us suppose that the particle under consideration is an electron whose way of existence is represented by a mathematical expression ψ which is a function of the electron's coordinates i.e. x, y, and z. Max Born actually suggested that because this mathematical expression is single-valued, continuous and finite i.e. wave-like; one can opt the same route to find it's intensity as we use in case of light or sound waves. In the case of light or sound waves, the intensity at any point can simply be obtained by squaring the amplitude i.e. ψ of the wave at the same point. Therefore, in the case of the electron, the square of the amplitude of electron wave (ψ^2) at a particular point also gives the intensity of the electron wave at the same point. In other words, the density of electron wave (probability density) at a point for a quantum mechanical state is simply obtained by the square of the magnitude of the corresponding wavefunction at the same point. Mathematically, we can show this as:

$$Probability\ density = |\psi|^2 = \psi\psi^* \tag{29}$$

Where ψ^* designates a complex conjugate of the wave function ψ. The reason for using ψ^* lies in the fact that the wave function representing a quantum mechanical state is not always real but be imaginary as well. However, as the probability density should always be real, $\psi\psi^*$ is more appropriate than simple ψ^2. In other words, if the wave function defining the quantum mechanical state is real, we can use ψ^2 as the probability density; nevertheless, if the wave function does contain the imaginary part (like $\psi = a + ib$), $\psi\psi^*$ must be used to yield real values. This can be explained by taking an imaginary expression ψ and then multiplying it by its complex conjugate ψ^* to yield real value.

$$\psi = a + ib; \qquad \psi^* = a - ib \tag{30}$$

or

$$\psi\psi^* = (a + ib)\ \times\ (a - ib) \tag{31}$$

or

$$\psi\psi^* = a^2 + b^2 \tag{32}$$

Moreover, if ψ is real, $\psi = \psi^*$, $\psi\psi^*$ becomes ψ^2, the value we have already discussed.

Now though the probability density in space is not a constant parameter (ψ is not constant), in a very small segment it can be considered constant. Now let us discuss the Max-Born interpretation for one, two and three dimensional systems.

➢ *One Dimensional Systems*

The probability of finding the particle in any one-dimensional system in the region from x to $x+dx$ must be obtained by integrating ψ^2 from x to $x+dx$ i.e. by finding the area under the curve from x to $x+dx$.

Now although the ψ^2 or $\psi\psi^*$ (because ψ is continuous) varies continuously with x, the decrease or increase in ψ^2 can be neglected and it can be assumed that it remains constant as we move from x to $x+dx$.

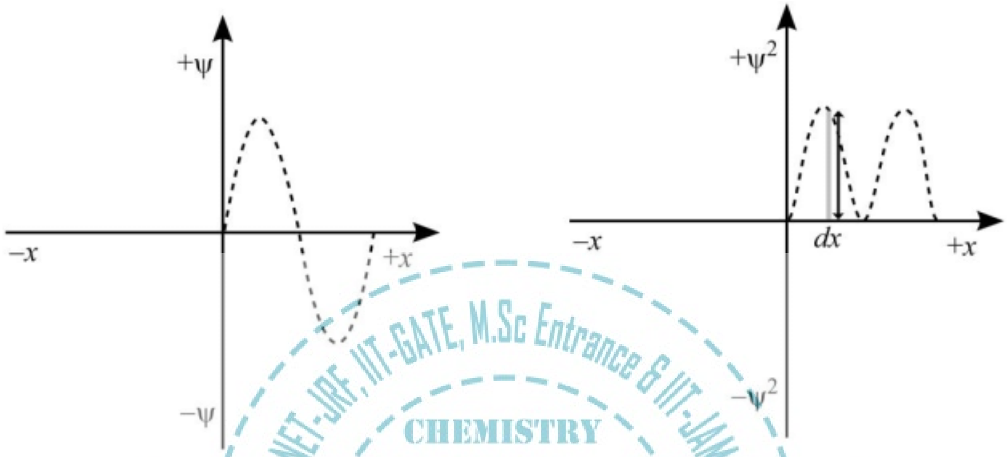


Figure 3. Born interpretation of wave function and probability density in a one-dimensional system.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Therefore, the area of the shaded region and hence the probability of finding the particle can be obtained just by multiplying the length (or height i.e. ψ^2) with the width (dx) of the narrow rectangle. Thus we can say that

$$Probability = |\psi|^2 \times (dx) = \psi\psi^* dx = \psi^2 dx \tag{33}$$

Since the chances of finding the particle over whole length (whole configurational space) must be unity, we get the following

$$\oint |\psi|^2 \times (dx) = \oint \psi\psi^* dx = \oint \psi^2 dx \tag{34}$$

➢ *Two Dimensional Systems*

The probability of finding the particle in an area element $dx\, dy$ (dA), situated at a distance r distance from the center, would be $\psi\ (x, y) \times \psi^*\ (x, y) \times dx \times dy$; or in short can be written as $\psi\psi^* dA$. Hence, it must be obtained by integrating ψ^2 from (x, y) to $(x+dx, y+dy)$ i.e. by finding the area under the curve dA. Now although the ψ^2 or $\psi\psi^*$ (because ψ is continuous) varies continuously with coordinates (x y), the decrease or increase in ψ^2 can be neglected and it can be assumed that it remains constant as we move from (x, y) to $(x+dx, y+dy)$.

Therefore, the area of the shaded region and hence the probability of finding the particle can be obtained just by multiplying the magnitude of the wave function (ψ^2) with the area (dA) of the area element. Thus we can say that

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$Probability = |\psi|^2 \times (dA) = \psi\psi^* dA = \psi^2 dA \tag{35}$$

Since the chances of finding the particle over the whole area (whole configurational space) must be unity, we get the following

$$\oint |\psi|^2 \times (dA) = \oint \psi\psi^* dA = \oint \psi^2 dA \tag{36}$$

The pictorial representation of the area element is given below.

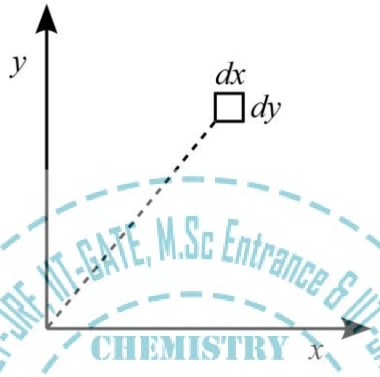


Figure 2. Born interpretation of wave function and probability density in two dimensional systems.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

- ***Three Dimensional System***

The probability of finding the particle in a volume element *dx dy dz* (*dV*), situated at a distance *r* distance from the center, would be ψ (*x, y, z*) × ψ^* (*x, y, z*) × *dx* × *dy*× *dz*; or in short can be written as $\psi\psi^* dV$. must be obtained by integrating ψ^2 from (*x, y, z*) to (*x*+*dx, y*+*dy, z*+*dz*) i.e. by finding the area under the curve from (*x, y, z*) to (*x*+*dx, y*+*dy, z*+*dz*). Now although the ψ^2 or $\psi\psi^*$ (because ψ is continuous) varies continuously with coordinates (*x, y, z*), the decrease or increase in ψ^2 can neglected and it can be assumed that it remains constant as we move from (*x, y, z*) to (*x*+*dx, y*+*dy, z*+*dz*).

Therefore, the probability of finding the particle can be obtained just by multiplying the magnitude of the wave function (ψ^2) with the volume (*dV*) of the area element. Thus we can say that

$$Probability = |\psi|^2 \times (dV) = \psi\psi^* dV = \psi^2 dV \tag{35}$$

Since the chances of finding the particle over the whole area (whole configurational space) must be unity, we get the following

$$\oint |\psi|^2 \times (dV) = \oint \psi\psi^* dV = \oint \psi^2 dV \tag{36}$$

The pictorial representation of the area element is given below.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

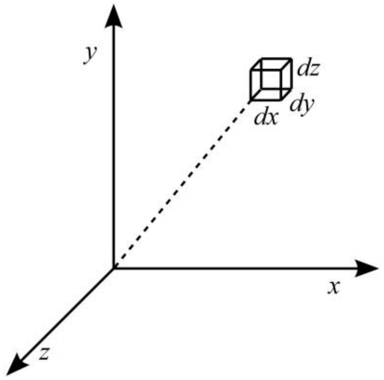


Figure 3. Born interpretation of wave function and probability density in three dimensional systems.

❖ The Heisenberg’s Uncertainty Principle

In quantum mechanical world, the Heisenberg's uncertainty principle (or simply the uncertainty principle) is one of a variety of mathematical inequalities asserting a fundamental limit to the precision with which certain pairs of physical properties of a particle, known as complementary variables or canonically conjugate variables such as position x and momentum p, can be known. The concept was first introduced in 1927, by a German physicist Werner Heisenberg.

The Heisenberg’s uncertainty principle states that the more precisely the position of some particle is determined, the less precisely its momentum can be known, and vice versa.

The formal inequality relating the standard deviation of position Δx and the standard deviation of momentum Δp_x was derived by Earle Hesse Kennard later that year and by Hermann Weyl in 1928:

$$\Delta x.\Delta p_x \geq \frac{h}{4\pi} \tag{37}$$

or

$$\Delta x\ .\ \Delta p_x \geq \hbar/2 \tag{38}$$

Where $\hbar$ is the reduced Planck’s constant, which is obviously equal to the Planck’s constant divided by 2π. Besides the equation (37), the is also an energy-time uncertainty relation given by W. Heisenberg which states that higher the lifetime of a quantum mechanical state, less uncertain would be the energy value. Mathematically, it can be shown as:

$$\Delta E.\Delta t \geq \frac{h}{2\pi} \tag{39}$$

Where ΔE and Δt represent the uncertainties in the energy and time respectively.

➢ *Position Momentum Uncertainty*

Among various kinds of uncertainties, the position-momentum uncertainty is one of the popular kind that arises as a consequence of wave-particle duality. In order to understand the relation, we first need to study the effect of wave behavior on the simultaneous measurement of position about x-coordinate and the linear momentum component along the x-axis for a microscopic particle.

Consider a beam of particles traveling with a momentum "p" along the y-direction, and this beam finally strikes a narrow slit of width "w". Now, from the principles of optics, we know that the uncertainty in the position of the particle along x-axis must be equal to the slit width. In other words, as the width of the slit is along x-axis, any particle that strikes the detector must have crossed the Δx region i.e. w, the slit width available. However, we exactly don't know where it does cross from. It could be along the center of the slit, or along a line slightly above or below the central trajectory. Therefore, the slit width ($w = \Delta x$) would be equal to a crossing domain that we are uncertain about. However, a diffraction pattern will be observed in the case of microscopic particles because of their wave-like character. The amplitude of the wave at a particular point on the detector represents the number of the particles reaching that point. Now because of this diffraction, the incident beam does not strike only at the central point O but also at the above and below to it. It means that some particles do reach upward and downward to O, suggesting that the part of their linear momentum is transferred along x-axis also.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

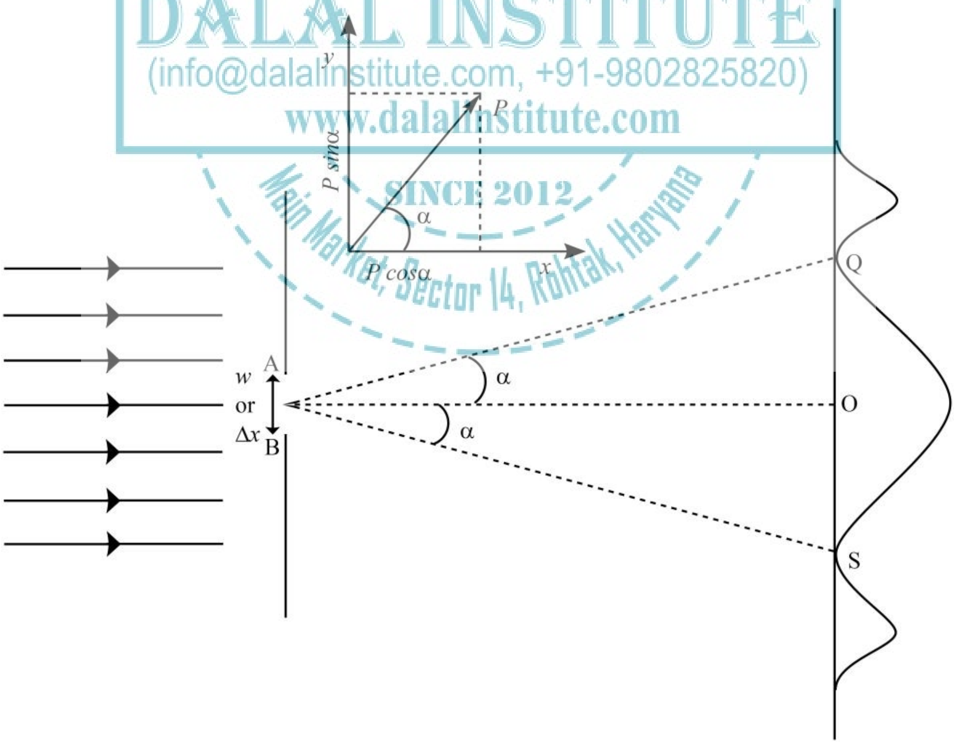


Figure 4. The diffraction of electron waves by single slit systems.

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

The x-component of linear momentum of the wave (aka particle) diffracted at an angle α can be obtained by the rectangular resolution of the linear momentum vector. The particles diffracted upward and downward at an angle α will yield the x-component as P sinα and $-P$ sinα, respectively. Now because a large number of particles reach the plate in between +α to −α i.e in between the first minimums, half of the momentum spread in the central diffraction peak should give the uncertainty in the momentum along x-axis. Mathematically, we can say that

$$\Delta p_x = P\ sin\alpha \tag{40}$$

Multiplying the above equation by the uncertainty in the position i.e. width of the slit used for the measurement purpose, we get

$$\Delta x.\Delta p_x = w.P\ sin\alpha \tag{41}$$

Here, it is very important to recall the fact that the condition which must be satisfied to obtain the first minima is that the path difference between the waves reaching the minima point should be an integral multiple of λ/2.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Figure 5. The calculation for 1st order diffraction for electron wave in single slit systems.

Hence we have the following equalities from the diagram given above.

$$AQ = DQ \tag{42}$$

$$CQ = difference\ in\ the\ path\ length \tag{43}$$

Now because the distance of the detector is very large as compared to the slit width, AQ and CQ can be considered parallel to each other i.e. AQ ∥ DQ. Hence, we can say that

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$< ADC = 90° \tag{44}$$

$$< CAD = \alpha \tag{45}$$

also

$$AC = \frac{w}{2} \tag{46}$$

$$CD = \frac{\lambda}{2} \tag{47}$$

From the trigonometric relations, we get

$$\frac{CD}{AC} = Sin\ \alpha \tag{48}$$

$$CD = AC\ Sin\ \alpha \tag{49}$$

Putting the values of AC and CD from equation (46) and (47) in equation (49), we get

$$\frac{\lambda}{2} = \frac{w}{2}\ Sin\ \alpha \tag{50}$$

$$\lambda = w\ Sin\ \alpha \tag{51}$$

Now, after putting the value of *w* from equation (51) in equation (41), we get

$$\Delta x.\Delta p_x = \frac{\lambda}{Sin\ \alpha}.P\ sin\alpha \tag{52}$$

$$\Delta x.\Delta p_x = \lambda.P \tag{53}$$

Using the de Broglie relation ($\lambda = h/p$) in equation (53), we get

$$\Delta x.\Delta p_x = \frac{h}{P}.P \tag{54}$$

$$\Delta x.\Delta p_x = h \tag{55}$$

Now because we didn't define the uncertainty very precisely, we should not use the "equal" sign. Therefore, the above equation can be reduced to the following.

$$\Delta x.\Delta p_x \approx h \tag{56}$$

This eventually means that decreasing the uncertainty in the position of the incident particle (decreasing the slit width) would result in a higher uncertainty in the momentum along *x*-axis; while the higher slit width does give more precise momentum but small precision in the calculation of the position of the incident particle.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

➢ ***Energy Time Uncertainty***

The uncertainty principle doesn't limit itself to position-momentum only but can also be applied to some other pairs of conjugate variables. All the variable pairs whose products have the same dimension as the Plank's constant h (Js) are said to be a conjugate pair. Besides the position-momentum, another famous uncertainty is relation energy-time because the product of these two quantities (energy × time) also has the unit of h (Js).

$$\Delta E.\Delta t \approx h \tag{57}$$

Where ΔE and Δt are uncertainties in energy and time, respectively. This popular relation can be derived directly from the concept of wave-particle duality. In the quantum mechanical world, a particle is supposed to possess a wave packet. Now, let us consider that this wave packet occupies the Δx region along the direction x-direction and travels with a velocity v. The time it needs to pass a certain point in x-direction has an uncertainty magnitude of Δt, and can be formulated as:

$$\Delta t = \frac{\Delta x}{v} \tag{58}$$

Now because this wave packet occupies the region Δx, the momentum uncertainty along x-axis can be given by the following relation.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

$$\Delta p_x = \frac{h}{\Delta x} \tag{59}$$

or

$$\Delta x = \frac{h}{\Delta p_x} \tag{60}$$

Putting the value of Δx from equation (60) in equation (58), we get

$$\Delta t = \frac{h}{v\Delta p_x} \tag{61}$$

Moreover, we also know that

$$E = \frac{p_x^2}{2m} \tag{62}$$

Differentiating the above equation w.r.t p_x, we get

$$\frac{dE}{dp_x} = \frac{\Delta E}{\Delta p_x} = \frac{p_x}{m} = \frac{mv}{m} = v \tag{63}$$

$$\Delta E = \frac{dE}{dp_x}\Delta p_x = v.\Delta p_x \tag{64}$$

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

Multiplying equation (63) and (64), we get

$$\Delta E . \Delta t = v \Delta p_x . \frac{h}{v \Delta p_x} \tag{65}$$

$$\Delta E . \Delta t \approx h \tag{66}$$

The physical interpretation of the above relation can be viewed in terms of fluctuating energy level with a total ΔE uncertainty if the system does not stay in it longer than Δt interval of time i.e. lifetime of the state.

❖ Quantum Mechanical Operators and Their Commutation Relations

An operator may be simply defined as a mathematical procedure or instruction which is carried out over a function to yield another function.

$$\text{(Operator) . (Function) = (Another function)} \tag{67}$$

The function used on the left-hand side of the equation (67) is called as the operand i.e. the function over which the operation is actually carried out. The operator alone has no significance but when operated over a certain mathematical description, these operators can provide very detailed insights into those functions. Some of the simple illustrations of equation (67) are given below.

i) Consider the differential operator d/dx whose operation has to be studied over the function $y = x^5$. The mathematical treatment is

$$\frac{dy}{dx} = \frac{d}{dx} x^5 = 5x^4 \tag{68}$$

The operation of d/dx on y means that the rate of change of function y w.r.t. the variable x. The expression x^5 is the operand while the $5x^4$ is the final result of our differential operator.

ii) Consider the integral operator $\int (y)\, dx$ whose operation has to be studied over the function $y = x^5$. The mathematical treatment is

$$\int y(dx) = \int x^5 (dx) = \frac{x^6}{6} \tag{69}$$

The operation of $\int dx$ on y means that we can find the function whose derivative is x^5. The expression x^5 is the operand while the $x^6/6$ is the final result of our integral operator.

In a similar way, the multiplication of a function by a constant number, or taking the square and cube roots of any function are also the operators which give some other function after operating them over the operand. The symbol of the operator typically carries a cap over it ($\hat{A}$) which differentiates it from the function used in the whole procedure.

➢ *Algebra of Operators*

Just like the normal algebra, the resultants like addition or the multiplication of operators also follow certain rules; however, these rules are different from the typical algebra. Some of the most important rules of operator algebra are given below.

1. Addition and subtraction of operators: Let A and B as two different operators; *f* as the function that has to be used as the operand. Then, the addition and subtraction of these two operators must be carried out in the manner discussed below.

$$(\hat{A}+\hat{B})f = \hat{A}f + \hat{B}f \tag{70}$$

and

$$(\hat{A}-\hat{B})f = \hat{A}f - \hat{B}f \tag{71}$$

2. Multiplication of operators: If A and B as two different operators; and *f* as the function that has to be used as operand. Then, the multiplication of these two operators must be carried out in the manner discussed below.

$$\hat{A}\hat{B}f = f'' \tag{72}$$

The interpretation of the above equation is that first we need to operate B on *f*, which would give us another function f', which in turn is further used as the operand for operator giving the final result f''. In other words, we can say that when multiplication of two or more operators is used, we should follow from left to right. Moreover, the square or cube of a particular operator must be considered as double or triple multiplication of the operator itself; mathematically, it can be shown as given below.

$$\hat{A}^2 f = \hat{A}\hat{A}f \tag{73}$$

At this point it also very important to discuss one of the most fundamental properties of operator multiplication, the commutation relation or the commutation rule. Consider two operators, A and B which can be operated over the function *f*.

$$\hat{A} = \frac{d}{dx}; \quad \hat{B} = x; \quad f = x^3 \tag{74}$$

Now

$$\hat{A}\hat{B}f = \frac{d}{dx}x(x^3) = \frac{d}{dx}x^4 = 4x^3 \tag{75}$$

And

$$\hat{B}\hat{A}f = x\frac{d}{dx}(x^3) = x(3x^2) = 3x^3 \tag{76}$$

From equation (75) and (76), it the clear that in this case

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\hat{A}\hat{B}f \neq \hat{B}\hat{A}f \tag{77}$$

These operators are said to be non-commutating with the commutator given below.

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 4x^3 - 3x^3 \tag{78}$$

However, the two operators are said to be commute if their result is the same even after reverting their order of application. Mathematically, it can be stated as given by equation (79).

$$\hat{A}\hat{B}f = \hat{B}\hat{A}f \tag{79}$$

This is quite different from the normal algebra in which the product of two numbers is always the same irrespective of the order of multiplication ($x.y = y.x$). Summarizing the commutation rule, it can be concluded that

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \ \rightarrow Commutating \tag{80}$$

and

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0 \ \rightarrow Non\text{-}commutating \tag{81}$$

3. Linear Operator: An operator Â is said to be a linear operator if its application on the sum of two functions *f* and *g* gives the same result as the sum of its individual operations. Mathematically, it can be shown as given below.

$$\hat{A}(f + g) = \hat{A}f + \hat{A}g \tag{82}$$

For example, consider the differential operator A; with *f* and *g* as the functions which have to be used as the operand.

$$\hat{A} = \frac{d}{dx}; \quad f = 2x^2; \quad g = 3x^2 \tag{83}$$

or

$$\hat{A}(f + g) = \frac{d}{dx}(2x^2 + 3x^2) = \frac{d}{dx}(5x^2) = 10x \tag{84}$$

or

$$\hat{A}f + \hat{A}g = \frac{d}{dx}(2x^2) + \frac{d}{dx}(3x^2) = 4x + 6x = 10x \tag{85}$$

Hence, from equation (84) and equation (85), it is clear that the differential operator is clearly linear in nature. On the other hand, the "square root" operator is not linear as it does not give the same result when operated individually.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

➢ *Some Important Quantum Mechanical Operators*

One of the most basic and very popular operators in quantum mechanics is the Laplacian operator, typically symbolized as ∇^2, and is given by the following expression.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{86}$$

The popular form of the Schrodinger equation can be written in terms of Laplacian operator as well.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{87}$$

or

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{88}$$

The Laplacian operator is pronounced as "del squared". This operator is also a part of the "mighty" Hamiltonian operator which forms the basis for value evaluation for other operators, as we have already discussed in the postulates of quantum mechanics. The Hamiltonian operator is typically symbolized as $\hat{H}$ and is given by the following expression.

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \tag{89}$$

or

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \tag{90}$$

The popular form of the Schrodinger equation is written in terms of the Hamiltonian operator as well.

$$\hat{H}\psi = E\psi \tag{91}$$

or

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi \tag{92}$$

or

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)\psi = E\psi \tag{93}$$

Furthermore, we know from the third postulate of quantum mechanics that owing to the constant value of E (eigenvalue) the wave function ψ can be labeled as eigenfunction.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

Therefore, the Schrodinger equation is also called as the “eigen value equation”. Simplifying this, we can say that

$$(Energy\ operator)(Wave\ function) = (Energy)(Wave\ function) \tag{94}$$

The equation (94) is applicable to observables in the quantum mechanical world.

For three dimensional systems, like the Hamiltonian, the operator can be obtained by summing the individual operators along three different axes. For instance, some important three-dimensional operators are:

$$\hat{T} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{95}$$

$$\hat{p} = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) \tag{96}$$

The list of various important quantum mechanical operators in one dimension, along with their mode of operation is given below.

Table 2. Name and symbols of various important physical properties and their corresponding quantum mechanical operators.

Physical property		Operator	
Name	*Symbol*	*Symbol*	*Operation*
Position	x	$\hat{x}$	Multiplication by x
Position squared	x^2	$\hat{x}^2$	Multiplication by x^2
Position cubed	x^3	$\hat{x}^2$	Multiplication by x^3
Momentum	p_x	$\hat{p}_x$	$\frac{h}{2\pi i}\frac{\partial}{\partial x}$
Momentum squared	p_x^2	$\hat{p}_x^2$	$\frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}$
Kinetic energy	$T = \frac{P^2}{2m}$	$\hat{T}_x$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiplication by $V(x)$
Total energy	$E = T + V(x)$	$\hat{H}$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

Besides the record of different operators presented in ‘Table 2’, there still many operators which are extremely important like angular momentum, parity, or the step-up–step-down operators. The discussion of every operator is beyond the scope of this book; however, a brief discussion of the essential operators in quantum mechanics is given below.

1. Angular momentum operator: In order to understand the angular momentum operator in the quantum mechanical world, we first need to understand the classical mechanics of one particle angular momentum. Let us consider a particle of mass *m* which moves within a cartesian coordinate system with a position vector “*r*”. Hence, we can say that

$$r = ix + jy + kz \tag{97}$$

The coordinates *x*. *y* and *z* are the functions of time, and therefore, we can define the velocity as the time derivative of the position vector as given below.

$$v = \frac{dr}{dt} = i\frac{dx}{dt} + j\frac{dy}{dt} + k\frac{dz}{dt} \tag{98}$$

or

$$v = v_x + v_y + v_z \tag{99}$$

Now, since we that $p = mv$, we can say that

$$p_x = mv_x; \quad p_y = mv_y; \quad p_z = mv_z \tag{100}$$

The angular momentum of a particle with mass *m* and distance *r* from the origin is given by the following relation.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

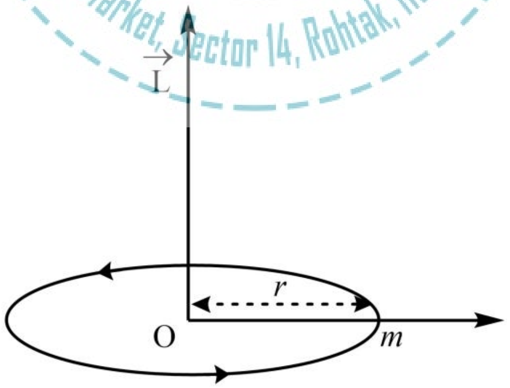


Figure 6. The angular momentum vector.

$$\vec{L} = \vec{v} \times m \times \vec{r} \tag{101}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\vec{L} = \vec{p} \times \vec{r} \tag{102}$$

Equation (102) can also be written in the form of a matrix as:

$$L = \begin{bmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{bmatrix} \tag{103}$$

$$L_x = yp_z - zp_y; \quad L_y = zp_x - xp_z; \quad L_z = xp_y - yp_x \tag{104}$$

Where i, j, k are the unit vectors along x, y, z axis and L_x, L_y, L_z are the component of angular momentum along x, y, z axis. Moreover, it is also worthy to note that the angular momentum vector is always perpendicular to the direction of the position vector of the particle i.e. the plane in which the particle is moving.

Now since the mathematical nature of any quantum mechanical operator is dependent upon the classical expression of the same observable, the angular momentum is not any exception. The quantum mechanical operator for angular momentum is given below.

$$\hat{L} = -i\frac{h}{2\pi}(r \times \nabla) = -i\hbar(r \times \nabla) \tag{105}$$

NET/JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

The angular momentum can be divided into two categories; one is orbital angular momentum (due to the orbital motion of the particle) and the other is spin angular momentum (due to spin motion of the particle). Moreover, being a vector quantity, the operator of angular momentum can also be resolved along different axes.

$$\hat{L} = \hat{L}_x + \hat{L}_y + \hat{L}_z \tag{106}$$

And we know that

$$\hat{L}_x = yp_z - zp_y = y\left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right) - z\left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right) = \frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{107}$$

or

$$\hat{L}_y = zp_x - xp_z = z\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right) - x\left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right) = \frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{108}$$

or

$$\hat{L}_z = xp_y - yp_x = x\left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right) - y\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right) = \frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{109}$$

$$\hat{L} = \frac{h}{2\pi i}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{110}$$

It is also worthy to recall that equation (107) to (110) can also be reported in terms of ħ; or by multiplying and dividing by i, or both.

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

2. Ladder operator: These operators are also called as step-up–step-down or rising-lowering operators. The reason for such terminology lies in the fact that these operators can increase or decrease the eigenvalues. Moreover, it should also be noted that this increase or decrease is always quantized in nature.

$$\widehat{J}_+ = \widehat{J}_x + i\widehat{J}_y \tag{111}$$

and

$$\widehat{J}_+ = \widehat{J}_x - i\widehat{J}_y \tag{112}$$

The equation (111) and (112) represent the step-up and step-down operators respectively. These operators can be used to increase or decrease the eigen values.

- ***Operator Evaluation***

The operator evaluation simply means that we need to find the result by applying the operator over a given function. Some general examples are given below.

i) (d/dx) (x^5): In this case d/dx is the operator while the function x^5 is the operand.

$$\frac{d}{dx}x^5 = 5x^4 \tag{113}$$

ii) ∫(x^5): In this case, ∫ is the operator while the function x^5 is the operand.

$$\int x^5 = \frac{x^6}{6} \tag{114}$$

iii) (d^2/dt^2) (A*Sine* 2π*νt*): In this particular case, (d^2/dt^2) is the operator while the function (A *Sin* 2π*νt*) is the operand.

Let the function is symbolized by *y*. Then, we have

$$y = A\ Sin\ 2\pi\nu t \tag{115}$$

Differentiating with respect to *t*, we get

$$\frac{dy}{dt} = A\ 2\pi\nu\ Cos\ 2\pi\nu t \tag{116}$$

Differentiating again

$$\frac{d^2y}{dt^2} = -A\ 4\pi^2\nu^2\ Sin\ 2\pi\nu t \tag{117}$$

The operator evaluation is frequently used as a part of the commutator calculation and will be discussed in detail in this chapter.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

➢ *Calculation of Resultant Operator*

Sometimes the operator is simplified to another form which is easy to apply over a function. This resultant operator is obtained by the rules of operator algebra. For instance, consider the following cases.

i) Find the resultant expression for the following operator

$$\left(\frac{d}{dx}x\right)^2 \tag{118}$$

In order to find the resultant operator, suppose a function $\psi(x)$ which is used as an operand, then we can say

$$\left(\frac{d}{dx}x\right)^2 \psi = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\right)\psi \tag{119}$$

or

$$\left(\frac{d}{dx}x\right)^2 \psi = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\psi\right) \tag{120}$$

or

$$\left(\frac{d}{dx}x\right)^2 \psi = \left(\frac{d}{dx}x\right)\left(x\frac{d\psi}{dx} + \psi\frac{dx}{dx}\right) \tag{121}$$

$$\left(\frac{d}{dx}x\right)^2 \psi = \frac{d}{dx}\left(x^2\frac{d\psi}{dx} + x\psi\right) \tag{122}$$

$$\left(\frac{d}{dx}x\right)^2 \psi = \left[x^2\frac{d^2\psi}{dx^2} + \frac{d\psi}{dx}(2x)\right] + \left[x\frac{d\psi}{dx} + \psi\frac{dx}{dx}\right] \tag{123}$$

$$\left(\frac{d}{dx}x\right)^2 \psi = x^2\frac{d^2\psi}{dx^2} + 2x\frac{d\psi}{dx} + x\frac{d\psi}{dx} + \psi \tag{124}$$

$$\left(\frac{d}{dx}x\right)^2 \psi = \left[x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1\right]\psi \tag{125}$$

Removing ψ from both sides, we get

$$\left(\frac{d}{dx}x\right)^2 = x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1 \tag{126}$$

ii) Find the resultant expression for the following operator

$$\left(x + \frac{d}{dx}\right)\frac{d}{dx} \tag{127}$$

In order to find the resultant operator, suppose a function $\psi(x)$ which is used as operand, then we can say that

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\left[\left(x+\frac{d}{dx}\right)\frac{d}{dx}\right]\psi=\left(x+\frac{d}{dx}\right)\frac{d\psi}{dx} \tag{128}$$

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

Removing ψ from both sides, we get

$$\left(x+\frac{d}{dx}\right)\frac{d}{dx}=x\frac{d}{dx}+\frac{d^2}{dx^2} \tag{129}$$

iii) Find the resultant expression for the following operator

$$\left(\frac{d}{dx}+x\right)^2 \tag{130}$$

In order to find the resultant operator, suppose a function ψ(*x*) which is used as operand, then we can say that

$$\left[\left(\frac{d}{dx}+x\right)^2\right]\psi=\left[\left(\frac{d}{dx}+x\right)\left(\frac{d}{dx}+x\right)\right]\psi \tag{131}$$

$$\left[\left(\frac{d}{dx}+x\right)^2\right]\psi=\left(\frac{d}{dx}+x\right)\left(\frac{d\psi}{dx}+x\psi\right) \tag{132}$$

$$\left[\left(\frac{d}{dx}+x\right)^2\right]\psi=\frac{d^2\psi}{dx^2}+\frac{d}{dx}x\psi+x\frac{d\psi}{dx}+x^2\psi \tag{133}$$

$$\left[\left(\frac{d}{dx}+x\right)^2\right]\psi=\frac{d^2\psi}{dx^2}+x\frac{d\psi}{dx}+\psi\frac{dx}{dx}+x\frac{d\psi}{dx}+x^2\psi \tag{134}$$

$$\left[\left(\frac{d}{dx}+x\right)^2\right]\psi=\frac{d^2\psi}{dx^2}+2x\frac{d\psi}{dx}+x^2\psi+\psi \tag{135}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Removing ψ from both sides, we get

$$\left(\frac{d}{dx}+x\right)^2=\frac{d^2}{dx^2}+2x\frac{d}{dx}+x^2+1 \tag{136}$$

iv) Find the resultant expression for the following operator

$$\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right) \tag{137}$$

In order to find the resultant operator, suppose a function ψ(*x*) which is used as operand, then we can say that

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\left[\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right)\right]\psi = \left(x+\frac{d}{dx}\right)\left(x\psi-\frac{d\psi}{dx}\right) \tag{138}$$

$$\left[\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right)\right]\psi = xx\psi - x\frac{d\psi}{dx}+\frac{d}{dx}x\psi-\frac{d^2\psi}{dx^2} \tag{139}$$

$$\left[\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right)\right]\psi = x^2\psi - x\frac{d\psi}{dx}+x\frac{d\psi}{dx}+\psi\frac{dx}{dx}-\frac{d^2\psi}{dx^2} \tag{140}$$

$$\left[\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right)\right]\psi = x^2\psi+\psi\frac{dx}{dx}-\frac{d^2\psi}{dx^2} \tag{141}$$

$$\left[\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right)\right]\psi = \left[x^2+\frac{dx}{dx}-\frac{d^2}{dx^2}\right]\psi \tag{142}$$

Removing ψ from both sides, we get

$$\left(x+\frac{d}{dx}\right)\left(x-\frac{d}{dx}\right) = x^2+1-\frac{d^2}{dx^2} \tag{143}$$

The resultant operator calculation is frequently used as a part of the commutator calculation and will be discussed in detail in this chapter.

- ***Commutation Relations of Various Quantum Mechanical Operators***

As we have discussed previously that one of the most fundamental properties of operator multiplication is the commutation relation or the commutation rule. two operators, A and B, are said to be commutating or non-commutating depending upon the value of their commutator.

$$[\hat{A},\hat{B}] = \hat{A}\hat{B}-\hat{B}\hat{A} = 0 \ \rightarrow Commutating \tag{144}$$

$$[\hat{A},\hat{B}] = \hat{A}\hat{B}-\hat{B}\hat{A} \neq 0 \ \rightarrow Non\text{-}commutating \tag{145}$$

The physical significance of the commutation relations is that when two operators commute, it means they are having a simultaneous set of eigenfunctions; and their corresponding physical properties can be calculated simultaneously and accurately. However, if the commutator is non-zero, the respective physical properties cannot be obtained simultaneously and accurately. Some important commutation relations are given below.

1. Commutators of some simple operators:

i) Calculate the commutator of the following

$$\left[x,\frac{d}{dx}\right] \tag{146}$$

Let it be operated over a function ψ. We have

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\left[x,\frac{d}{dx}\right]\psi = x\,\frac{d}{dx}\psi - \frac{d}{dx}x\,\psi \tag{147}$$

$$\left[x,\frac{d}{dx}\right]\psi = x\,\frac{d\psi}{dx} - \psi - x\,\frac{d\,\psi}{dx} \tag{148}$$

$$\left[x,\frac{d}{dx}\right]\psi = -\psi \tag{149}$$

or

$$\left[x,\frac{d}{dx}\right] = -1 \tag{150}$$

ii) Calculate the commutator of the following

$$\left[y,\frac{d}{dx}\right] \tag{151}$$

Let it be operated over a function ψ. We have

$$\left[y,\frac{d}{dx}\right]\psi = y\,\frac{d}{dx}\psi - \frac{d}{dx}y\,\psi \tag{152}$$

$$\left[y,\frac{d}{dx}\right]\psi = y\,\frac{d\psi}{dx} - y\,\frac{d\,\psi}{dx} - \psi\,\frac{d\,y}{dx} \tag{153}$$

$$\left[x,\frac{d}{dx}\right]\psi = 0 \tag{154}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

iii) Calculate the commutator of the following

$$\left[\frac{d}{dx},\frac{d^2}{dx^2}\right] \tag{155}$$

Let it be operated over a function ψ. We have

$$\left[\frac{d}{dx},\frac{d^2}{dx^2}\right]\psi = \frac{d}{dx}\frac{d^2}{dx^2}\psi - \frac{d^2}{dx^2}\frac{d}{dx}\,\psi \tag{156}$$

or

$$\left[\frac{d}{dx},\frac{d^2}{dx^2}\right]\psi = \frac{d^3\psi}{dx^3} - \frac{d^3\psi}{dx^3} \tag{157}$$

$$\left[\frac{d}{dx},\frac{d^2}{dx^2}\right]\psi = 0 \tag{158}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

2. Commutators of position and linear momentum operators:

i) Find the commutator of the following

$$[\hat{x}, \hat{p}_x] \tag{159}$$

Let it be operated over a function ψ. We have

$$[\hat{x}, \hat{p}_x]\psi = \hat{x}\,\hat{p}_x\,\psi - \hat{p}_x\,\hat{x}\;\psi \tag{160}$$

$$[\hat{x}, \hat{p}_x\,]\psi = x\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi - \frac{h}{2\pi i}\frac{\partial}{\partial x}x\,\psi \tag{161}$$

$$[\hat{x}, \hat{p}_x\,]\psi = \frac{h}{2\pi i}x\frac{\partial\psi}{\partial x} - \frac{h}{2\pi i}x\frac{\partial\psi}{\partial x} - \frac{h}{2\pi i}\psi\frac{\partial x}{\partial x} \tag{162}$$

$$[\hat{x}, \hat{p}_x\,]\psi = -\frac{h}{2\pi i}\psi$$

$$[\hat{x}, \hat{p}_x] = -\frac{h}{2\pi i} = \frac{hi}{2\pi} = i\hbar \tag{163}$$

ii) Find the commutator of the following

$$[\hat{x}^n, \hat{p}_x] \tag{164}$$

Let it be operated over a function ψ. We have

$$[\hat{x}^n, \hat{p}_x\,]\psi = \hat{x}^n\,\hat{p}_x\,\psi - \hat{p}_x\,\hat{x}^n\;\psi \tag{165}$$

$$[\hat{x}^n, \hat{p}_x\,]\psi = x^n\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi - \frac{h}{2\pi i}\frac{\partial}{\partial x}x^n\,\psi \tag{166}$$

$$[\hat{x}^n, \hat{p}_x\,]\psi = \frac{h}{2\pi i}x^n\frac{\partial\psi}{\partial x} - \frac{h}{2\pi i}x^n\frac{\partial\psi}{\partial x} - \frac{h}{2\pi i}nx^{n-1}\psi \tag{167}$$

$$[\hat{x}^n, \hat{p}_x\,]\psi = -\frac{h}{2\pi i}nx^{n-1}\psi \tag{168}$$

Removing ψ from both sides, we get

$$[\hat{x}^n, \hat{p}_x\,] = -\frac{h}{2\pi i}nx^{n-1} \tag{169}$$

The commutation relations between position and linear momentum can mainly be divided into three categories as discussed below.

(a) When position and momentum are along the same axis:

$$[\hat{x}^n, \hat{p}_x] = ni\hbar x^{n-1} \tag{170}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$[\,\hat{p}_x, \hat{x}^n] = -ni\hbar x^{n-1} \tag{171}$$

and

$$[\hat{x}, \hat{p}_x^n] = ni\hbar p_x^{n-1} \tag{172}$$

$$[\hat{p}_x^n, \hat{x}\,] = -ni\hbar p_x^{n-1} \tag{173}$$

(b) When position and momentum are along different axis:

$$[\hat{x}, \hat{p}_y] = 0 \tag{174}$$

$$[\hat{x}, \hat{p}_z] = 0 \tag{175}$$

$$[\hat{y}, \hat{p}_x] = 0 \tag{176}$$

$$[\hat{y}, \hat{p}_z] = 0 \tag{177}$$

$$[\hat{z}, \hat{p}_x] = 0 \tag{178}$$

$$[\hat{z}, \hat{p}_y] = 0 \tag{179}$$

(b) When positions are along the different axis:

$$[\hat{x}, \hat{y}] = 0 \tag{180}$$

$$[\hat{x}, \hat{z}] = 0 \tag{181}$$

$$[\hat{y}, \hat{z}] = 0 \tag{182}$$

(b) When positions are along the different axis:

$$[\hat{p}_x, \hat{p}_y] = 0 \tag{183}$$

$$[\hat{p}_x, \hat{p}_z] = 0 \tag{184}$$

$$[\hat{p}_y, \hat{p}_z] = 0 \tag{185}$$

3. Commutators of angular momentum operators:

i) The commutator of orbital angular momentum operators along *x* and *y*-axis.

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x \tag{186}$$

Finding the values of $\hat{L}_x\hat{L}_y$, we get

$$\hat{L}_x\hat{L}_y = \left[\frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]\left[\frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \tag{187}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$= -\frac{h^2}{4\pi^2}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \tag{188}$$

$$= -\frac{h^2}{4\pi^2}\left(y\frac{\partial}{\partial z}z\frac{\partial}{\partial x} - z\frac{\partial}{\partial y}z\frac{\partial}{\partial x} - y\frac{\partial}{\partial z}x\frac{\partial}{\partial z} + z\frac{\partial}{\partial y}x\frac{\partial}{\partial z}\right) \tag{189}$$

$$= -\frac{h^2}{4\pi^2}\left(y\frac{\partial}{\partial x}\frac{\partial z}{\partial z} + yz\frac{\partial^2}{\partial^2 zx} - z^2\frac{\partial^2}{\partial^2 yx} - yx\frac{\partial^2}{\partial z^2} + zx\frac{\partial^2}{\partial yz}\right) \tag{190}$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial^2 zx} - z^2\frac{\partial^2}{\partial^2 yx} - yx\frac{\partial^2}{\partial z^2} + zx\frac{\partial^2}{\partial yz}\right) \tag{191}$$

Similarly obtaining the value of $\hat{L}_y\hat{L}_x$, we get

$$\hat{L}_y\hat{L}_x = \left[\frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]\left[\frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{192}$$

$$= -\frac{h^2}{4\pi^2}\left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{193}$$

$$= -\frac{h^2}{4\pi^2}\left(z\frac{\partial}{\partial x}y\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}z\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}y\frac{\partial}{\partial z} + x\frac{\partial}{\partial z}z\frac{\partial}{\partial y}\right) \tag{194}$$

$$= -\frac{h^2}{4\pi^2}\left(zy\frac{\partial^2}{\partial^2 xz} - z^2\frac{\partial^2}{\partial^2 xy} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial zy} + x\frac{\partial}{\partial y}\frac{\partial z}{\partial z}\right) \tag{195}$$

$$= -\hbar^2\left(zy\frac{\partial^2}{\partial^2 xz} - z^2\frac{\partial^2}{\partial^2 xy} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial zy} + x\frac{\partial}{\partial y}\right) \tag{196}$$

Now putting the values of $\hat{L}_x\hat{L}_y$ and $\hat{L}_y\hat{L}_x$ in equation (183), we get the following.

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] = &\left[-\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial^2 zx} - z^2\frac{\partial^2}{\partial^2 yx} - yx\frac{\partial^2}{\partial z^2} + zx\frac{\partial^2}{\partial yz}\right)\right] \\ &- \left[-\hbar^2\left(zy\frac{\partial^2}{\partial^2 xz} - z^2\frac{\partial^2}{\partial^2 xy} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial zy} + x\frac{\partial}{\partial y}\right)\right]\end{aligned} \tag{197}$$

$$[\hat{L}_x, \hat{L}_y] = -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) \tag{198}$$

Taking negative sign common, we get

$$[\hat{L}_x, \hat{L}_y] = \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{199}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$[\hat{L}_x, \hat{L}_y] = i\hbar\left[-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{200}$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \tag{201}$$

ii) The commutator of orbital angular momentum operators along *y* and *z*-axis.

$$[\hat{L}_y, \hat{L}_z] = \hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y \tag{202}$$

Finding the values of $\hat{L}_y\hat{L}_z$, we get

$$\hat{L}_y\hat{L}_z = \left[\frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]\left[\frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{203}$$

$$= -\frac{h^2}{4\pi^2}\left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{204}$$

$$= -\frac{h^2}{4\pi^2}\left(z\frac{\partial}{\partial x}x\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}x\frac{\partial}{\partial y} - z\frac{\partial}{\partial x}y\frac{\partial}{\partial x} + x\frac{\partial}{\partial z}y\frac{\partial}{\partial x}\right) \tag{205}$$

$$= -\frac{h^2}{4\pi^2}\left(z\frac{\partial}{\partial y}\frac{\partial x}{\partial x} + zx\frac{\partial^2}{\partial xy} - x^2\frac{\partial^2}{\partial^2 zy} - zy\frac{\partial}{\partial x^2} + xy\frac{\partial^2}{\partial zx}\right) \tag{206}$$

$$= -\hbar^2\left(z\frac{\partial}{\partial y} + zx\frac{\partial^2}{\partial xy} - x^2\frac{\partial^2}{\partial^2 zy} - zy\frac{\partial}{\partial x^2} + xy\frac{\partial^2}{\partial zx}\right) \tag{207}$$

Similarly obtaining the value of $\hat{L}_z\hat{L}_y$, we get

$$\hat{L}_z\hat{L}_y = \left[\frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\left[\frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \tag{208}$$

$$= -\frac{h^2}{4\pi^2}\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \tag{209}$$

$$= -\frac{h^2}{4\pi^2}\left(x\frac{\partial}{\partial y}z\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}x\frac{\partial}{\partial z} - y\frac{\partial}{\partial x}z\frac{\partial}{\partial x} + y\frac{\partial}{\partial x}x\frac{\partial}{\partial z}\right) \tag{210}$$

$$= -\frac{h^2}{4\pi^2}\left(xz\frac{\partial^2}{\partial yx} - x^2\frac{\partial^2}{\partial yz} - yz\frac{\partial^2}{\partial x^2} + yx\frac{\partial^2}{\partial xz} + y\frac{\partial}{\partial z}\frac{\partial x}{\partial x}\right) \tag{211}$$

$$= -\hbar^2\left(xz\frac{\partial^2}{\partial yx} - x^2\frac{\partial^2}{\partial yz} - yz\frac{\partial^2}{\partial x^2} + yx\frac{\partial^2}{\partial xz} + y\frac{\partial}{\partial z}\right) \tag{212}$$

Now putting the values of $\hat{L}_y\hat{L}_z$ and $\hat{L}_z\hat{L}_y$ in equation (212), we get the following.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$[\hat{L}_y, \hat{L}_z] = \left[-\hbar^2\left(z\frac{\partial}{\partial y} + zx\frac{\partial^2}{\partial xy} - x^2\frac{\partial^2}{\partial^2 zy} - zy\frac{\partial}{\partial x^2} + xy\frac{\partial^2}{\partial zx}\right)\right] - \left[-\hbar^2\left(xz\frac{\partial^2}{\partial yx} - x^2\frac{\partial^2}{\partial yz} - yz\frac{\partial^2}{\partial x^2} + yx\frac{\partial^2}{\partial xz} + y\frac{\partial}{\partial z}\right)\right] \tag{213}$$

$$[\hat{L}_y, \hat{L}_z] = -\hbar^2\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) \tag{214}$$

Taking negative sign common, we get

$$[\hat{L}_y, \hat{L}_z] = \hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{215}$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\left[-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{216}$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \tag{217}$$

iii) The commutator of orbital angular momentum operators along *z* and *x*-axis.

$$[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z \tag{218}$$

Finding the values of $\hat{L}_z\hat{L}_x$, we get

$$\hat{L}_z\hat{L}_x = \left[\frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\left[\frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{219}$$

$$= -\frac{h^2}{4\pi^2}\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{220}$$

$$= -\frac{h^2}{4\pi^2}\left(x\frac{\partial}{\partial y}y\frac{\partial}{\partial z} - x\frac{\partial}{\partial y}z\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}y\frac{\partial}{\partial z} + y\frac{\partial}{\partial x}z\frac{\partial}{\partial y}\right) \tag{221}$$

$$= -\frac{h^2}{4\pi^2}\left(x\frac{\partial}{\partial z}\frac{\partial y}{\partial y} + xy\frac{\partial^2}{\partial yz} - xz\frac{\partial^2}{\partial y^2} - y^2\frac{\partial^2}{\partial xz} + yz\frac{\partial^2}{\partial xy}\right) \tag{222}$$

$$= -\hbar^2\left(x\frac{\partial}{\partial z} + xy\frac{\partial^2}{\partial yz} - xz\frac{\partial^2}{\partial y^2} - y^2\frac{\partial^2}{\partial xz} + yz\frac{\partial^2}{\partial xy}\right) \tag{223}$$

Similarly obtaining the value of $\hat{L}_x\hat{L}_z$, we get

$$\hat{L}_x\hat{L}_z = \left[\frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]\left[\frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{224}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$= -\frac{h^2}{4\pi^2}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{225}$$

or

$$= -\frac{h^2}{4\pi^2}\left(y\frac{\partial}{\partial z}x\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}y\frac{\partial}{\partial x} - z\frac{\partial}{\partial y}x\frac{\partial}{\partial y} + z\frac{\partial}{\partial y}y\frac{\partial}{\partial x}\right) \tag{226}$$

$$= -\frac{h^2}{4\pi^2}\left(yx\frac{\partial^2}{\partial zy} - y^2\frac{\partial^2}{\partial zx} - zx\frac{\partial^2}{\partial y^2} + z\frac{\partial}{\partial x}\frac{\partial y}{\partial y} + zy\frac{\partial^2}{\partial yx}\right) \tag{227}$$

$$= -\hbar^2\left(yx\frac{\partial^2}{\partial zy} - y^2\frac{\partial^2}{\partial zx} - zx\frac{\partial^2}{\partial y^2} + z\frac{\partial}{\partial x} + zy\frac{\partial^2}{\partial yx}\right) \tag{228}$$

Now putting the values of $\hat{L}_z\hat{L}_x$ and $\hat{L}_x\hat{L}_z$ in equation (218), we get the following.

$$[\hat{L}_z, \hat{L}_x] = \left[-\hbar^2\left(x\frac{\partial}{\partial z} + xy\frac{\partial^2}{\partial yz} - xz\frac{\partial^2}{\partial y^2} - y^2\frac{\partial^2}{\partial xz} + yz\frac{\partial^2}{\partial xy}\right)\right] - \left[-\hbar^2\left(yx\frac{\partial^2}{\partial zy} - y^2\frac{\partial^2}{\partial zx} - zx\frac{\partial^2}{\partial y^2} + z\frac{\partial}{\partial x} + zy\frac{\partial^2}{\partial yx}\right)\right] \tag{229}$$

$$[\hat{L}_z, \hat{L}_x] = -\hbar^2\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right) \tag{230}$$

Taking negative sign common, we get

$$[\hat{L}_z, \hat{L}_x] = \hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{231}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\left[-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{232}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \tag{233}$$

iv) The commutator of total orbital angular momentum squared operator and orbital angular momentum along one of the three-axis.

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_z] \tag{234}$$

$$= [\hat{L}_x^2\,\hat{L}_z + \hat{L}_y^2\,\hat{L}_z + \hat{L}_z^2\,\hat{L}_z - \hat{L}_z\hat{L}_x^2 - \hat{L}_z\hat{L}_y^2 - \hat{L}_z\hat{L}_z^2] \tag{235}$$

$$= [(\hat{L}_x^2\,\hat{L}_z - \hat{L}_z\hat{L}_x^2) + (\hat{L}_y^2\,\hat{L}_z - \hat{L}_z\hat{L}_y^2) + (\hat{L}_z^2\,\hat{L}_z - \hat{L}_z\hat{L}_z^2)] \tag{236}$$

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2\,, \hat{L}_z] + [\hat{L}_y^2\,\hat{L}_z] + [\hat{L}_z^2\,\hat{L}_z] \tag{237}$$

Now finding $[\hat{L}_x^2\,, \hat{L}_z]$ first, we get

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$[\hat{L}_x^2\,,\hat{L}_z] = \hat{L}_x^2\,\hat{L}_z - \hat{L}_z\hat{L}_x^2 \tag{238}$$

$$= \hat{L}_x\hat{L}_x\,\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x \tag{239}$$

$$= [\hat{L}_x\hat{L}_x\,\hat{L}_z - \hat{L}_x\hat{L}_z\,\hat{L}_x] - [\hat{L}_z\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_z\,\hat{L}_x] \tag{240}$$

$$= \hat{L}_x\,[\hat{L}_x\hat{L}_z - \hat{L}_z\,\hat{L}_x] - [\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\,]\hat{L}_x \tag{241}$$

$$= \hat{L}_x\,[\hat{L}_x\hat{L}_z - \hat{L}_z\,\hat{L}_x] + [\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\,]\hat{L}_x \tag{242}$$

$$= \hat{L}_x\,[-i\hbar\hat{L}_y\,] + [-i\hbar\hat{L}_y\,]\hat{L}_x \tag{243}$$

$$= -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x = -i\hbar[\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x] \tag{244}$$

Similarly,

$$[\hat{L}_y^2\,,\hat{L}_z] = \hat{L}_y^2\,\hat{L}_z - \hat{L}_z\hat{L}_y^2 \tag{245}$$

$$= \hat{L}_y\hat{L}_y\,\hat{L}_z - \hat{L}_z\hat{L}_y\hat{L}_y \tag{246}$$

$$= [\hat{L}_y\hat{L}_y\,\hat{L}_z - \hat{L}_y\hat{L}_z\hat{L}_y] - [\hat{L}_z\hat{L}_y\hat{L}_y - \hat{L}_y\hat{L}_z\hat{L}_y]$$

$$= \hat{L}_y\,[\hat{L}_y\hat{L}_z - \hat{L}_z\,\hat{L}_y] - [\hat{L}_z\hat{L}_y - \hat{L}_y\hat{L}_z\,]\hat{L}_y$$

$$= \hat{L}_y\,[\hat{L}_y\hat{L}_z - \hat{L}_z\,\hat{L}_y] + [\hat{L}_y\hat{L}_z - \hat{L}_z\,\hat{L}_y\,]\hat{L}_y$$

$$= \hat{L}_y\,[i\hbar\hat{L}_x\,] + [i\hbar\hat{L}_x\,]\hat{L}_y$$

$$= i\hbar\hat{L}_y\hat{L}_x + i\hbar\hat{L}_x\hat{L}_y = i\hbar[\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y] \tag{247}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Similarly,

$$[\hat{L}_z^2\,,\hat{L}_z] = \hat{L}_z^2\,\hat{L}_z - \hat{L}_z\hat{L}_z^2$$

$$= \hat{L}_z\hat{L}_z\,\hat{L}_z - \hat{L}_z\hat{L}_z\hat{L}_z$$

$$[\hat{L}_z^2\,,\hat{L}_z] = 0 \tag{248}$$

Now putting the value of $\hat{L}_x^2\hat{L}_z$, $\hat{L}_y^2\hat{L}_z$ and $\hat{L}_z^2\hat{L}_z$ in equation (237), we get

$$[\hat{L}^2, \hat{L}_z] = -i\hbar[\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x] + i\hbar[\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y] + 0$$

$$[\hat{L}^2, \hat{L}_z] = 0 \tag{249}$$

Also

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\left[\hat{L}^2, \hat{L}_y\right] = 0; and \left[\hat{L}^2, \hat{L}_x\right] = 0 \tag{250}$$

Hence, the commutation relations of angular momentum operators along two different directions do not commute with each other and hence cannot give eigenvalues simultaneously and accurately. One the other hand, total angular momentum squared and angular momentum along one axis do commute with each other.

The commutation relations between angular momentum operators can be mainly divided into four categories as discussed below.

(a) Orbital angular momentum commutation:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z; \qquad \left[\hat{L}_y, \hat{L}_x\right] = -i\hbar\hat{L}_z \tag{251}$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x; \qquad \left[\hat{L}_z, \hat{L}_y\right] = -i\hbar\hat{L}_x \tag{252}$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y; \qquad \left[\hat{L}_x, \hat{L}_z\right] = -i\hbar\hat{L}_y \tag{253}$$

$$\left[\hat{L}^2, \hat{L}_x\right] = 0; \qquad \left[\hat{L}_x, \hat{L}^2\right] = 0 \tag{254}$$

$$\left[\hat{L}^2, \hat{L}_y\right] = 0; \qquad \left[\hat{L}_y, \hat{L}^2\right] = 0 \tag{255}$$

$$\left[\hat{L}^2, \hat{L}_z\right] = 0; \qquad \left[\hat{L}_z, \hat{L}^2\right] = 0 \tag{256}$$

(b) Spin angular momentum commutation:

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z; \qquad \left[\hat{S}_y, \hat{S}_x\right] = -i\hbar\hat{S}_z \tag{257}$$

$$\left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x; \qquad \left[\hat{S}_z, \hat{S}_y\right] = -i\hbar\hat{S}_x \tag{258}$$

$$\left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y; \qquad \left[\hat{S}_x, \hat{S}_z\right] = -i\hbar\hat{S}_y \tag{259}$$

$$\left[\hat{S}^2, \hat{S}_x\right] = 0; \qquad \left[\hat{S}_x, \hat{S}^2\right] = 0 \tag{260}$$

$$\left[\hat{S}^2, S_y\right] = 0; \qquad \left[\hat{S}_y, \hat{S}^2\right] = 0 \tag{261}$$

$$\left[\hat{S}^2, \hat{S}_z\right] = 0; \qquad \left[\hat{S}_z, \hat{S}^2\right] = 0 \tag{262}$$

(c) Total angular momentum commutation:

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z; \qquad \left[\hat{J}_y, \hat{J}_x\right] = -i\hbar\hat{J}_z \tag{263}$$

$$\left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x; \qquad \left[\hat{J}_z, \hat{J}_y\right] = -i\hbar\hat{J}_x \tag{264}$$

$$\left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y; \qquad \left[\hat{J}_x, \hat{J}_z\right] = -i\hbar\hat{J}_y \tag{265}$$

$$\left[\hat{J}^2, \hat{J}_x\right] = 0; \qquad \left[\hat{J}_x, \hat{J}^2\right] = 0 \tag{266}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$[\hat{J}^2, J_y] = 0; \qquad [\hat{J}_y, \hat{J}^2] = 0 \tag{267}$$

$$[\hat{J}^2, \hat{J}_z] = 0; \qquad [\hat{J}_z, \hat{J}^2] = 0 \tag{268}$$

(d) Total angular momentum commutation:

$$[\hat{L}_x, \hat{S}_x] = 0; \qquad [\hat{S}_x, \hat{L}_x] = 0 \tag{263}$$

$$[\hat{L}_x, \hat{S}_y] = 0; \qquad [\hat{S}_y, \hat{L}_x] = 0 \tag{264}$$

$$[\hat{L}_x, \hat{S}_z] = 0; \qquad [\hat{S}_z, \hat{L}_x] = 0 \tag{265}$$

$$[\hat{L}_y, \hat{S}_x] = 0; \qquad [\hat{S}_x, \hat{L}_y] = 0 \tag{266}$$

$$[\hat{L}_y, \hat{S}_y] = 0; \qquad [\hat{S}_y, \hat{L}_y] = 0 \tag{267}$$

$$[\hat{L}_y, \hat{S}_z] = 0; \qquad [\hat{S}_z, \hat{L}_y] = 0 \tag{268}$$

$$[\hat{L}_z, \hat{S}_x] = 0; \qquad [\hat{S}_x, \hat{L}_z] = 0 \tag{269}$$

$$[\hat{L}_z, \hat{S}_y] = 0; \qquad [\hat{S}_y, \hat{L}_z] = 0 \tag{270}$$

$$[\hat{L}_z, \hat{S}_z] = 0; \qquad [\hat{S}_z, \hat{L}_z] = 0 \tag{271}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

4. Commutators of Ladder operators:

i) Find the commutator of the following

$$[\hat{J}^2, \hat{J}_+] \tag{272}$$

Let

$$[\hat{J}^2, \hat{J}_+] = [\hat{J}^2, \hat{J}_x + i\hat{J}_y] \tag{273}$$

$$= \hat{J}^2(\hat{J}_x + i\hat{J}_y) - (\hat{J}_x + i\hat{J}_y)\hat{J}^2 \tag{274}$$

$$= \hat{J}^2\hat{J}_x + i\hat{J}^2\hat{J}_y - \hat{J}_x\hat{J}^2 - i\hat{J}_y\hat{J}^2 \tag{275}$$

$$= [\hat{J}^2\hat{J}_x - \hat{J}_x\hat{J}^2] + i[\hat{J}^2\hat{J}_y - \hat{J}_y\hat{J}^2] \tag{276}$$

$$= [\hat{J}^2, \hat{J}_x] + i[\hat{J}^2, \hat{J}_y] \tag{277}$$

$$= 0 + i(0) = 0 \tag{278}$$

Hence

$$[\hat{J}^2, \hat{J}_+] = 0 \tag{279}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

Similarly

$$[\hat{J}^2,\hat{J}_-] = 0 \tag{280}$$

ii) Find the commutator of the following

$$[\hat{J}_+,\hat{J}_z\,] \tag{281}$$

Let

$$[\hat{J}_+,\hat{J}_z\,] = [\,\hat{J}_x + i\hat{J}_y,\hat{J}_z] \tag{282}$$

$$= (\hat{J}_x + i\hat{J}_y)\hat{J}_z - \hat{J}_z(\hat{J}_x + i\hat{J}_y) \tag{283}$$

$$= \hat{J}_x\hat{J}_z + i\hat{J}_y\hat{J}_z - \hat{J}_z\hat{J}_x - \hat{J}_z i\hat{J}_y \tag{284}$$

$$= \hat{J}_x\hat{J}_z - \hat{J}_z\hat{J}_x + i\hat{J}_y\hat{J}_z - i\hat{J}_z\hat{J}_y \tag{285}$$

$$= [\hat{J}_x\hat{J}_z - \hat{J}_z\hat{J}_x] + i[\hat{J}_y\hat{J}_z - \hat{J}_z\hat{J}_y] \tag{286}$$

$$= [\hat{J}_x,\hat{J}_z] + i[\hat{J}_y,\hat{J}_z] \tag{287}$$

$$= -i\hbar\hat{J}_y + i\big(i\hbar\hat{J}_x\big) = -i\hbar\hat{J}_y - \hbar\hat{J}_x \tag{288}$$

$$= -\hbar(\hat{J}_x + i\hat{J}_y) = -\hbar\hat{J}_+ \tag{289}$$

$$[\hat{J}_+,\hat{J}_z] = -\hbar\hat{J}_+ \tag{290}$$

Similarly

$$[\hat{J}_-,\hat{J}_z] = \hbar\hat{J}_- \tag{291}$$

iii) Find the commutator of the following

$$[\hat{J}_+,\hat{J}_-\,] \tag{292}$$

Let

$$[\hat{J}_+,\hat{J}_-\,] = (\hat{J}_x + i\hat{J}_y)(\hat{J}_x - i\hat{J}_y) - (\hat{J}_x - i\hat{J}_y)(\hat{J}_x + i\hat{J}_y) \tag{293}$$

$$= \hat{J}_x\hat{J}_x - i\hat{J}_x\hat{J}_y + i\hat{J}_y\hat{J}_x + \hat{J}_y\hat{J}_y - (\hat{J}_x\hat{J}_x + i\hat{J}_x\hat{J}_y - i\hat{J}_y\hat{J}_x + \hat{J}_y\hat{J}_y) \tag{294}$$

$$= \hat{J}_x\hat{J}_x - i\hat{J}_x\hat{J}_y + i\hat{J}_y\hat{J}_x + \hat{J}_y\hat{J}_y - \hat{J}_x\hat{J}_x - i\hat{J}_x\hat{J}_y + i\hat{J}_y\hat{J}_x - \hat{J}_y\hat{J}_y \tag{295}$$

$$= -i\hat{J}_x\hat{J}_y + i\hat{J}_y\hat{J}_x - i\hat{J}_x\hat{J}_y + i\hat{J}_y\hat{J}_x \tag{296}$$

$$= -i[\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x] + i[\hat{J}_y\hat{J}_x - \hat{J}_x\hat{J}_y] \tag{297}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$= -i[\hat{J}_x,\hat{J}_y] + i[\hat{J}_y,\hat{J}_x] \tag{298}$$

$$= -i[i\hbar\hat{J}_z] + i[-i\hbar\hat{J}_z] \tag{299}$$

$$= \hbar\hat{J}_z + \hbar\hat{J}_z = 2\hbar\hat{J}_z \tag{300}$$

The commutation relations between angular-momentum and Ladder operators can be mainly divided into three categories as discussed below.

(a) Ladder operator and total angular momentum commutation:

$$[\hat{J}^2,\hat{J}_+] = 0; \qquad [\hat{J}_+,\hat{J}^2] = 0 \tag{301}$$

$$[\hat{J}^2,\hat{J}_-] = 0; \qquad [\hat{J}_-,\hat{J}^2] = 0 \tag{302}$$

$$[\hat{J}_+,\hat{J}_z] = -\hbar\hat{J}_+; \qquad [\hat{J}_z,\hat{J}_+] = \hbar\hat{J}_+ \tag{303}$$

$$[\hat{J}_-,\hat{J}_z] = \hbar\hat{J}_-; \qquad [\hat{J}_z,\hat{J}_-] = -\hbar\hat{J}_- \tag{304}$$

$$[\hat{J}_+,\hat{J}_-] = 2\hbar\hat{J}_z; \qquad [\hat{J}_-,\hat{J}_+] = -2\hbar\hat{J}_z \tag{305}$$

(b) Ladder operator and orbital angular momentum commutation:

$$[\hat{L}^2,\hat{L}_+] = 0; \qquad [\hat{L}_+,\hat{L}^2] = 0 \tag{306}$$

$$[\hat{L}^2,\hat{L}_-] = 0; \qquad [\hat{L}_-,\hat{L}^2] = 0 \tag{307}$$

$$[\hat{L}_+,\hat{L}_z] = -\hbar\hat{L}_+; \qquad [\hat{L}_z,\hat{L}_+] = \hbar\hat{L}_+ \tag{308}$$

$$[\hat{L}_-,\hat{L}_z] = \hbar\hat{L}_-; \qquad [\hat{L}_z,\hat{L}_-] = -\hbar\hat{L}_- \tag{309}$$

$$[\hat{L}_+,\hat{L}_-] = 2\hbar\hat{L}_z; \qquad [\hat{L}_-,\hat{L}_+] = -2\hbar\hat{L}_z \tag{310}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

(b) Ladder operator and spin angular momentum commutation:

$$[\hat{S}^2,\hat{S}_+] = 0; \qquad [\hat{S}_+,\hat{S}^2] = 0 \tag{311}$$

$$[\hat{S}^2,\hat{S}_-] = 0; \qquad [\hat{S}_-,\hat{S}^2] = 0 \tag{312}$$

$$[\hat{S}_+,\hat{S}_z] = -\hbar\hat{S}_+; \qquad [\hat{S}_z,\hat{S}_+] = \hbar\hat{S}_+ \tag{313}$$

$$[\hat{S}_-,\hat{S}_z] = \hbar\hat{S}_-; \qquad [\hat{S}_z,\hat{S}_-] = -\hbar\hat{S}_- \tag{314}$$

$$[\hat{S}_+,\hat{S}_-] = 2\hbar\hat{S}_z; \qquad [\hat{S}_-,\hat{S}_+] = -2\hbar\hat{S}_z \tag{315}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

❖ Hermitian Operators – Elementary Ideas, Quantum Mechanical Operator for Linear Momentum, Angular Momentum and Energy as Hermitian Operator

It is a quite well-known fact that all the physical properties are actually real quantities, and therefore are bound to have real values. It means that any operator which is used to represent a physical property must yield real values. In this section, we will discuss the elementary idea of Hermitian operators (named in honor of a great mathematician Charles Hermite), and will also prove that many important operators in quantum mechanics like linear momentum, angular momentum and Hamiltonian are Hermitian in nature.

➢ *Elementary Idea of Hermitian Operator*

Every physical property must have real eigen or expectation values, which therefore implies that the corresponding operators should have some special characteristics. One of the most important special characteristics includes a feature that the Hermitian conjugate of such an operator should be itself. In other words, if the Hermitian conjugate of an operator is itself, the operator is called as Hermitian; however, if the Hermitian conjugate of an operator is equal to its negative expression, the operator is called as anti-Hermitian or skew-Hermitian. Mathematically, we can say that

$$if\ A^{\dagger} = A; \qquad A\ is\ Hermitian \tag{316}$$

$$if\ A^{\dagger} = -A; \qquad A\ is\ anti\text{–}\ Hermitian \tag{317}$$

Where A is an operator whose Hermitian conjugate is represented by $A^{\dagger}$.

However, the obvious question regarding the aforementioned definition would be "what is a Hermitian conjugate and how is it obtained". The answer is "the operator $A^{\dagger}$ will be called as the Hermitian conjugate (or adjoint) of operator A if the operation of $A^{\dagger}$ on the complex conjugate of function ψ gives the same result as when the A is operated over ψ". Mathematically, we can say that

$$\langle\psi|A|\psi\rangle = \int_{-\infty}^{+\infty} \psi^{*}(x)A\psi(x)dx = \langle\psi|A\psi\rangle = \langle A^{\dagger}\psi|\psi\rangle \tag{318}$$

or

$$\langle A^{\dagger}\varphi|\psi\rangle = \langle\varphi|A\psi\rangle \tag{319}$$

1. Hermitian conjugates of different operators: The Hermitian conjugates of different operators can be studied in three different categories.

i) Hermitian conjugates of quantum mechanical operators:

Let Q be any quantum mechanical operator, then by the definition of Hermitian conjugates operator, we have the following condition.

$$\langle \varphi | Q\psi \rangle = \langle Q^{\dagger}\varphi | \psi \rangle \tag{320}$$

If Q is the momentum operator, then we can proceed as discussed below.

$$\int \psi^{*}\hat{p}_{x}\psi dx = \int \psi\hat{p}_{x}\psi^{*}dx \tag{321}$$

$$\int \psi^{*}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\psi dx = \int \psi\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^{\dagger}\psi^{*}dx \tag{322}$$

$$\int \psi\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^{\dagger}\psi^{*}dx = \int \psi\left(\frac{h}{2\pi i}\right)^{\dagger}\left(\frac{\partial}{\partial x}\right)^{\dagger}\psi^{*}dx \tag{323}$$

$$\int \psi\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^{\dagger}\psi^{*}dx = \int \psi\left(-\frac{h}{2\pi i}\right)\left(-\frac{\partial}{\partial x}\right)\psi^{*}dx \tag{324}$$

$$\int \psi\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^{\dagger}\psi^{*}dx = \int \psi\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\psi^{*}dx \tag{325}$$

Therefore, we can say that the Hermitian conjugate of the linear momentum operator is itself, and hence it is a Hermitian operator. Now from the most primitive definition of Hermitian operators, that all operators which correspond to observable quantities, we can say that the Hermitian conjugates of the following operator are themselves.

CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Operator	Hermitian conjugate
$\hat{x}$	$\hat{x}$
$\hat{x}^{2}$	$\hat{x}^{2}$
$\hat{p}_{x}$	$\hat{p}_{x}$
$\hat{p}_{x}^{2}$	$\hat{p}_{x}^{2}$
$\hat{T}_{x}$	$\hat{T}_{x}$
$\hat{V}(x)$	$\hat{V}(x)$
$\hat{H}$	$\hat{H}$

ii) Hermitian conjugates of a constant operator:

There are some operators which are complex numbers. The Hermitian conjugates of such operators are actually their complex conjugates. Let we have the operator *A*

$$\hat{A} = a + ib \tag{326}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

and since the definition of Hermitian operator is

$$\langle \varphi | A\psi \rangle = \langle A^{\dagger}\varphi | \psi \rangle \tag{327}$$

gives the integer as

$$\langle \varphi | (a+ib)\psi \rangle = \langle (a-ib)\varphi | \psi \rangle = (a+ib)\langle \varphi | \psi \rangle \tag{328}$$

Hence, the Hermitian conjugates of constant operators are their complex conjugates. The Hermitian conjugates of some operators are given below.

Operator	Hermitian conjugate
$(a+ib)$	$(a+ib)^{\dagger} = (a-ib)$
$(+ib)$	$(+ib)^{\dagger} = (-ib)$
$\left(+\frac{i}{4}\right)$	$\left(+\frac{i}{4}\right)^{\dagger} = \left(-\frac{i}{4}\right)$

iii) Hermitian conjugates of a mathematical operator:

The Hermitian conjugates of mathematical operators can be obtained by obtaining their respective integrals as discussed below. Let we have a mathematical operator *A*

$$\hat{A} = \frac{d}{dx} \tag{326}$$

We use the following integral to derive the result

$$\left\langle \varphi \middle| \frac{d}{dx}\psi \right\rangle = \int_{-\infty}^{+\infty} \varphi^{*}(x)\frac{d\psi(x)}{dx}\,dx \tag{327}$$

Integrating the above equation by part, we get

$$\left\langle \varphi \middle| \frac{d}{dx}\psi \right\rangle = [\varphi^{*}(x)\psi(x)] - \int_{-\infty}^{+\infty} \frac{d\varphi^{*}(x)}{dx}\psi(x)\,dx \tag{328}$$

$$= 0 - \left\langle \frac{d}{dx}\varphi \middle| \psi \right\rangle \tag{329}$$

$$= -\left\langle \frac{d}{dx}\varphi \middle| \psi \right\rangle \tag{330}$$

Hence, the Hermitian conjugate of *d*/*dx* operator is −*d*/*dx*. Similarly, we can prove that the Hermitian conjugate of d^2/dx^2 is d^2/dx^2.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

2. Properties of Hermitian conjugates: From the definition and properties of scalar product, adjoints or Hermitian conjugate show the following properties.

i) Let C a constant and A as an operator.

$$(CA)^{\dagger} = C^{*}A^{\dagger} \tag{331}$$

For example

$$\left(\frac{i}{4}\frac{\partial}{\partial x}\right)^{\dagger} = \left(\frac{i}{4}\right)^{\dagger}\left(\frac{\partial}{\partial x}\right)^{\dagger} \tag{332}$$

$$\left(\frac{i}{4}\frac{\partial}{\partial x}\right)^{\dagger} = \left(-\frac{i}{4}\right)\left(-\frac{\partial}{\partial x}\right) \tag{333}$$

$$\left(\frac{i}{4}\frac{\partial}{\partial x}\right)^{\dagger} = \frac{i}{4}\frac{\partial}{\partial x} \tag{334}$$

ii) Let A and B as two operators.

$$(A+B)^{\dagger} = A^{\dagger} + B^{\dagger} \tag{335}$$

For example

$$\left(\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}\right)^{\dagger} = \left(\frac{\partial}{\partial x}\right)^{\dagger} + \left(\frac{\partial^2}{\partial x^2}\right)^{\dagger} \tag{336}$$

$$\left(\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}\right)^{\dagger} = \left(-\frac{\partial}{\partial x}\right) + \left(\frac{\partial^2}{\partial x^2}\right) \tag{337}$$

$$\left(\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}\right)^{\dagger} = \left(-\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}\right) \tag{338}$$

iii) Let A and B as two operators, then

$$(AB)^{\dagger} = A^{\dagger}B^{\dagger} \tag{339}$$

For example

$$\left(\frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2}\right)^{\dagger} = \left(\frac{\partial}{\partial x}\right)^{\dagger}\left(\frac{\partial^2}{\partial x^2}\right)^{\dagger} \tag{340}$$

$$\left(\frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2}\right)^{\dagger} = \left(-\frac{\partial}{\partial x}\right)\left(\frac{\partial^2}{\partial x^2}\right) \tag{341}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\left(\frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2}\right)^\dagger = \left(-\frac{\partial^3}{\partial x^3}\right) \tag{342}$$

iv) Let A be the operators, then

$$\left(A^\dagger\right)^\dagger = A \tag{343}$$

For example

$$\left[\left(\frac{\partial}{\partial x}\right)^\dagger\right]^\dagger = \left(\frac{\partial}{\partial x}\right) \tag{344}$$

It should also be noted that the multiplication to an anti-hermitian operator by i makes it Hermitian, while the vice-versa is also equally true for adjoints.

v) For any operator A and its adjoint, the product $(AA^\dagger)$ is Hermitian. For instance

$$\left(\frac{\partial}{\partial x}\right)\left(-\frac{\partial}{\partial x}\right) = -\frac{\partial^2}{\partial x^2} \tag{343}$$

vi) For any operator A and its adjoint, the sum $(A+A^\dagger)$ is Hermitian. For instance

$$\left(x + x^\dagger\right) = 2x \tag{343}$$

vii) For any operator A and its adjoint, then $AA^\dagger+A^\dagger A$ is Hermitian. For instance

$$(i3)(i3)^\dagger + (i3)^\dagger(i3) = (i3)(-i3) + (-i3)(i3) = 9 + 9 = 18 \tag{343}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

3. Characterization of Hermitian operator: We know that the average value of any operator (say $\hat{A}$) in quantum mechanics is calculated by the equation given below.

$$\bar{A} = \int \psi^* \hat{A} \psi dx \tag{344}$$

Where ψ is the wave function representing any quantum mechanical state and ψ^* is its complexes conjugate. Now because of the fact that the average value of any physical observable must be a real value, we can say that the operator used in equation (344) must follow the following condition.

$$\bar{A} = \bar{A}^* \tag{345}$$

$$\int \psi^* \hat{A} \psi dx = \left[\int \psi^* \hat{A} \psi dx\right]^* \tag{346}$$

$$\int \psi^* \hat{A} \psi dx = \int (\psi^*)^* \left(\hat{A}\psi\right)^* dx \tag{347}$$

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\int \psi^* \hat{A}\psi dx = \int \psi(\hat{A}\psi)^* dx \tag{348}$$

Every linear operator that satisfies the equation (348) for all quantum-mechanically acceptable wave functions is called the Hermitian operator.

Besides the form given by equation (348), one more popular definition of a Hermitian operator is also given below.

$$\int f^* \hat{A} g dx = \int g(\hat{A} f)^* dx \tag{349}$$

From the equation, we can state that a Hermitian operator must fulfill the condition for the well-behaved functions *f* and *g*. It can be clearly seen that on the left side of the equation (349), $\hat{A}$ is operated over the function *g*; while on the right side, the $\hat{A}$ is operated over the function *f*. However, if we put *f* = *g*, the equation (349) is also reduced to equation (348); indicating that both definitions are correct.

4. Properties of Hermitian operators: The important properties of Hermitian operators are discussed below.

i) The eigenvalues of Hermitian operators are always real:

Let $\hat{A}$ be a Hermitian operator with a well-behaved wavefunction ψ representing a quantum mechanical state, then we can say that

$$\hat{A}\psi = a\psi \tag{350}$$

Each side of equation (350) can be expressed as an imaginary and a real part as well; with left-hand real part equal to the right-hand real part, while left side imaginary part equal to right imaginary one. After taking the complex conjugate of equation (350), the imaginary parts would reverse sign but still holding the condition of equivalence.

$$\hat{A}^*\psi^* = a^*\psi^* \tag{351}$$

Multiplying the equation (350) by ψ^* and integrating over the whole configurational space, we get

$$\int \psi^* \hat{A}\psi dx = a \int \psi^* \psi dx \tag{352}$$

Similarly, multiplying the equation (351) by ψ and integrating over the whole configurational space, we get

$$\int \psi \hat{A}^* \psi^* dx = a^* \int \psi \psi^* dx \tag{353}$$

Now because left-hand sides of equation (352) and (353) are equal to each other (owing to the Hermitian nature of the operator), the right-hand sides are also equivalent; therefore, we can say that

$$a^* \int \psi \psi^* dx = a \int \psi^* \psi dx \tag{354}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$0 = (a - a^*) \int \psi^* \psi dx \tag{355}$$

Since the wave function is a square-integrable, the integral part of the equation (355) cannot be zero and left us with the only possibility given blow.

$$(a - a^*) = 0 \tag{356}$$

$$a = a^* \tag{357}$$

The physical interpretation of the result given by equation (357) is that *a* must be real in order to yield zero from equation (356).

ii) *Non-degenerate eigenfunctions of Hermitian operators are always orthogonal to each other:*

Let ψ_m and ψ_n be two square-integrable eigenfunctions of a Hermitian operator $\hat{A}$; therefore, we say

$$\hat{A}\psi_m = a_1\psi_m \tag{358}$$

also

$$\hat{A}^*\psi_n^* = a_2\psi_n^* \tag{359}$$

Multiplying the equation (358) by ψ_n^* and integrating over the whole configurational space, we get

$$\int \psi_n^* \hat{A} \psi_m dx = a_1 \int \psi_n^* \psi_m dx \tag{360}$$

Similarly, multiplying the equation (359) by ψ_m and integrating over the whole configurational space, we get

$$\int \psi_m \hat{A}^* \psi_n^* dx = a_2 \int \psi_m \psi_n^* dx \tag{361}$$

Now because left-hand sides of equation (360) and (361) are equal to each other (owing to the Hermitian nature of the operator), the right-hand sides are also equivalent; therefore, we can say that

$$a_1 \int \psi_n^* \psi_m dx = a_2 \int \psi_m \psi_n^* dx \tag{362}$$

$$(a_1 - a_2) \int \psi_m \psi_n^* dx = 0 \tag{363}$$

Since the wave functions used are non-degenerate i.e. $a_1 \neq a_2$; the only possibility we are left with for the equation to be true is given below.

$$\int \psi_m \psi_n^* dx = 0 \tag{364}$$

Hence, we can say that ψ_m and ψ_n are definitely orthogonal to each other.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

iii) *If two Hermitian operators commute, their product is also a Hermitian operator:*

Let ψ_1 and ψ_2 be two well-behaved functions; while $\hat{A}$ and $\hat{B}$ as two Hermitian operators. Therefore, we can say that

$$\int \psi_1^* \hat{A}\hat{B}\psi_2 dx \tag{365}$$

Since $\hat{A}$ is Hermitian, we can say that

$$\int \psi_1^* \hat{A}\hat{B}\psi_2 dx = \int \psi_1^* \hat{A}(\hat{B}\psi_2) dx \tag{366}$$

$$\int \hat{A}^* \psi_1^* \hat{B}\psi_2 dx = \int \psi_1^* \hat{A}(\hat{B}\psi_2) dx \tag{367}$$

Since $\hat{B}$ is also Hermitian, therefore

$$\int (\hat{A}^* \psi_1^*) \hat{B}\psi_2 dx = \int \hat{B}^* \hat{A}^* \psi_1^* \psi_2 dx \tag{368}$$

From equation (366) and (368), we get

$$\int \psi_1^* \hat{A}\hat{B}\psi_2 dx = \int \hat{B}^* \hat{A}^* \psi_1^* \psi_2 dx \tag{369}$$

If the operator $\hat{A}$ and $\hat{B}$ commute with each other, we have

$$\hat{A}\hat{B} = \hat{B}\hat{A} \quad or \quad \hat{A}^*\hat{B}^* = \hat{B}^*\hat{A}^* \tag{370}$$

Therefore, equation (369) becomes

$$\int \psi_1^* \hat{A}\hat{B}\psi_2 dx = \int \hat{A}^* \hat{B}^* \psi_1^* \psi_2 dx \tag{371}$$

Which is the condition for the product operator to act as Hermitian.

iv) *If two Hermitian operators do not commute, their commutator operator is anti-Hermitian in nature:*

Let $\hat{A}$ and $\hat{B}$ as two Hermitian operators; therefore, we can say that their commutation must follow the following condition.

$$[\hat{A}, \hat{B}]^* = (\hat{A}\hat{B})^* - (\hat{B}\hat{A})^* \tag{372}$$

or

$$[\hat{A}, \hat{B}]^* = \hat{A}^*\hat{B}^* - \hat{B}^*\hat{A}^* = -(\hat{B}^*\hat{A}^* - \hat{A}^*\hat{B}^*) \tag{373}$$

or

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$[\hat{A},\hat{B}]^* = -[\hat{B},\hat{A}]^* \tag{374}$$

$$[\hat{A},\hat{B}]^* = -[\hat{B},\hat{A}]^* \tag{375}$$

For instance, consider the commutator of position and momentum operator

$$[\hat{x},\hat{p}_x] = i\frac{h}{2\pi} \tag{376}$$

The commutator $i\hbar$ is antihermitian in nature.

➢ *The Linear Momentum Operator as Hermitian*

In order to prove the linear momentum operator as the Hermitian, we must find its Hermitian conjugate first. The general expression of linear momentum operator is

$$\hat{p}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x} \tag{377}$$

Let $\hat{p}_x^\dagger$ be the Hermitian conjugate which can be calculated as follows:

$$\hat{p}_x^\dagger = \left(\frac{h}{2\pi i}\right)^\dagger \left(\frac{\partial}{\partial x}\right)^\dagger \tag{378}$$

or

$$\hat{p}_x^\dagger = \left(-\frac{h}{2\pi i}\right)\left(-\frac{\partial}{\partial x}\right) \tag{379}$$

or

$$\hat{p}_x^\dagger = \left(\frac{h}{2\pi i}\right)\left(\frac{\partial}{\partial x}\right) \tag{380}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Comparing equation (377) and (380), we can see that the Hermitian conjugate of linear momentum operator is exactly equal to the linear momentum operator i.e. $\hat{p}_x^\dagger = \hat{p}_x$; proving that it is defiantly a Hermitian operator.

➢ *The Angular Momentum Operator as Hermitian*

In order to prove the angular momentum operator as Hermitian, we must find its Hermitian conjugate first. The general expression of the angular momentum operator is

$$\hat{L} = \frac{h}{2\pi i}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{381}$$

Let $\hat{L}_x^\dagger$ be the Hermitian conjugate which can be calculated as follows:

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\hat{L}_x^\dagger = \left[\frac{h}{2\pi i}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\right]^\dagger \tag{382}$$

$$= \left[\frac{h}{2\pi i}y\frac{\partial}{\partial z} - \frac{h}{2\pi i}z\frac{\partial}{\partial y} + \frac{h}{2\pi i}z\frac{\partial}{\partial x} - \frac{h}{2\pi i}x\frac{\partial}{\partial z} + \frac{h}{2\pi i}x\frac{\partial}{\partial y} - \frac{h}{2\pi i}y\frac{\partial}{\partial x}\right]^\dagger$$

or

$$\begin{aligned}\hat{L}_x^\dagger = {} & \left(\frac{h}{2\pi i}\right)^\dagger (y)^\dagger \left(\frac{\partial}{\partial z}\right)^\dagger - \left(\frac{h}{2\pi i}\right)^\dagger (z)^\dagger \left(\frac{\partial}{\partial y}\right)^\dagger + \left(\frac{h}{2\pi i}\right)^\dagger (z)^\dagger \left(\frac{\partial}{\partial x}\right)^\dagger \\ & - \left(\frac{h}{2\pi i}\right)^\dagger (x)^\dagger \left(\frac{\partial}{\partial z}\right)^\dagger + \left(\frac{h}{2\pi i}\right)^\dagger (x)^\dagger \left(\frac{\partial}{\partial y}\right)^\dagger - \left(\frac{h}{2\pi i}\right)^\dagger (y)^\dagger \left(\frac{\partial}{\partial x}\right)^\dagger\end{aligned} \tag{383}$$

or

$$\begin{aligned}\hat{L}_x^\dagger = {} & \left(-\frac{h}{2\pi i}\right)(y)\left(-\frac{\partial}{\partial z}\right) - \left(-\frac{h}{2\pi i}\right)(z)\left(-\frac{\partial}{\partial y}\right) + \left(-\frac{h}{2\pi i}\right)(z)\left(-\frac{\partial}{\partial x}\right) \\ & - \left(-\frac{h}{2\pi i}\right)(x)\left(-\frac{\partial}{\partial z}\right) + \left(-\frac{h}{2\pi i}\right)(x)\left(-\frac{\partial}{\partial y}\right) \\ & - \left(-\frac{h}{2\pi i}\right)(y)\left(-\frac{\partial}{\partial x}\right)\end{aligned} \tag{384}$$

or

$$\hat{L}^\dagger = \frac{h}{2\pi i}y\frac{\partial}{\partial z} - \frac{h}{2\pi i}z\frac{\partial}{\partial y} + \frac{h}{2\pi i}z\frac{\partial}{\partial x} - \frac{h}{2\pi i}x\frac{\partial}{\partial z} + \frac{h}{2\pi i}x\frac{\partial}{\partial y} - \frac{h}{2\pi i}y\frac{\partial}{\partial x} \tag{385}$$

$$\hat{L}^\dagger = \frac{h}{2\pi i}\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{386}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Comparing equation (381) and (386), we can see that the Hermitian conjugate of the angular momentum operator is exactly equal to the angular momentum operator i.e. $\hat{L}^\dagger = \hat{L}$; proving that it is defiantly a Hermitian operator.

- ***The Hamiltonian or Energy Operator as Hermitian***

In order to prove the energy operator as Hermitian, we must find its Hermitian conjugate first. The general expression of the energy operator is

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x) \tag{387}$$

Let $\hat{H}^\dagger$ be the Hermitian conjugate which can be calculated as follows:

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$\hat{H}^{\dagger} = \left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)\right]^{\dagger} \tag{388}$$

or

$$\hat{H}^{\dagger} = \left[\frac{-h^2}{8\pi^2 m}\frac{\partial}{\partial x}\frac{\partial}{\partial x} + V(x)\right]^{\dagger} \tag{389}$$

$$\hat{H}^{\dagger} = \left(\frac{-h^2}{8\pi^2 m}\right)^{\dagger}\left(\frac{\partial}{\partial x}\right)^{\dagger}\left(\frac{\partial}{\partial x}\right)^{\dagger} + (V(x))^{\dagger} \tag{390}$$

or

$$\hat{H}^{\dagger} = \left(\frac{-h^2}{8\pi^2 m}\right)\left(-\frac{\partial}{\partial x}\right)\left(-\frac{\partial}{\partial x}\right) + (V(x)) \tag{391}$$

$$\hat{H}^{\dagger} = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x) \tag{392}$$

Comparing equation (387) and (392), we can see that the Hermitian conjugate of energy operator is exactly equal to the energy operator i.e. $\hat{H}^{\dagger} = \hat{H}$; proving that it is defiantly a Hermitian operator.

❖ The Average Value of the Square of Hermitian Operators

The expectation value of the square of every Hermitian operator is always positive. In other words, we can say that if *A* is a Hermitian operator, then

$$\langle A^2 \rangle > 0 \tag{393}$$

This can be proved by taking a well-behaved function ψ as discussed below.

$$\langle A^2 \rangle = \frac{\int \psi^* A^2\, \psi d\tau}{\int \psi^* \psi d\tau} \tag{394}$$

The right-hand side of equation (394) will be positive only if the numerator as well as denominator, both are either positive or negative. Since the wave-function is well-behaved (normalized), the value of denominator is

$$\int \psi^*\, \psi d\tau = 1 \tag{395}$$

Since the denominator is positive, the numerator must also be positive. Now owing to the Hermitian nature of operator *A,* we can evaluate the numerator as given below.

$$\int \psi^* A^2\, \psi d\tau = \int \psi^* A A^* \psi\, d\tau \tag{396}$$

$$= \int (\psi^* A^*) A\psi\, d\tau \tag{397}$$

or

$$= \int |A\psi|^2\, d\tau \tag{398}$$

Hence, the value of numerator given by equation (398) is greater than zero i.e. positive, making the average value of the square of the Hermitian operator (*A*) also positive.

❖ Commuting Operators and Uncertainty Principle (*x* & *p*; *E* & *t*)

One of the most important properties of operator multiplication is the commutation relation or the commutation rule. Two operators, A and B, are said to be commutating or non-commutating depending upon the magnitude of their commutator.

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \ \rightarrow Commutating \tag{399}$$

and

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0 \ \rightarrow Non\text{-}commutating \tag{400}$$

The physical significance of the commutation relations implies in the fact that when two operators commute, they possess simultaneous set of eigenfunctions; and their respective physical properties can be evaluated simultaneously and accurately. However, if the commutator is non-zero, the respective physical properties cannot be obtained simultaneously and accurately; which is actually the popular uncertainty principal. Two of the most common uncertainty systems; position-momentum and energy-time; can also be proved from commutation relations.

➢ *Position-Momentum Uncertainty (x & p)*

The position-momentum uncertainty can be justified only if the commutation of their operators is non-zero. Therefore, we need to find the following.

$$[\hat{x}, \hat{p}_x] \tag{401}$$

Let it be operated over a function ψ. We have

$$[\hat{x}, \hat{p}_x\,]\psi = \hat{x}\,\hat{p}_x\,\psi - \hat{p}_x\,\hat{x}\ \psi \tag{402}$$

or

$$[\hat{x},\hat{p}_x\,]\psi = x\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi - \frac{h}{2\pi i}\frac{\partial}{\partial x}x\,\psi \tag{403}$$

$$[\hat{x},\hat{p}_x\,]\psi = \frac{h}{2\pi i}x\frac{\partial \psi}{\partial x} - \frac{h}{2\pi i}x\frac{\partial \psi}{\partial x} - \frac{h}{2\pi i}\psi\frac{\partial x}{\partial x} \tag{404}$$

$$[\hat{x},\hat{p}_x\,]\psi = -\frac{h}{2\pi i}\psi \tag{405}$$

$$[\hat{x},\hat{p}_x\,] = -\frac{h}{2\pi i} = \frac{hi}{2\pi} = i\hbar \tag{406}$$

Equation (406) proves that we cannot determine the position and momentum of a particle along one axis simultaneously and accurately.

- ***Energy-Time Uncertainty (E & t)***

The energy-time uncertainty can be justified only if the commutation of their operators is non-zero. Therefore, we need to find the following.

$$[\hat{t},\hat{E}\,] \tag{407}$$

Let it be operated over a function ψ(*t*). We have

$$[\hat{t},\hat{E}\,]\psi = \hat{t}\,\hat{E}\,\psi - \hat{E}\hat{t}\,\psi \tag{408}$$

or

$$[\hat{t},\hat{E}\,]\psi = t\frac{h}{2\pi i}\frac{\partial}{\partial t}\psi - \frac{h}{2\pi i}\frac{\partial}{\partial t}t\,\psi \tag{409}$$

$$[\hat{t},\hat{E}\,]\psi = \frac{h}{2\pi i}t\frac{\partial \psi}{\partial t} - \frac{h}{2\pi i}t\frac{\partial \psi}{\partial t} - \frac{h}{2\pi i}\psi\frac{\partial t}{\partial t} \tag{410}$$

$$[\hat{t},\hat{E}\,]\psi = -\frac{h}{2\pi i}\psi \tag{411}$$

$$[\hat{t},\hat{E}\,] = -\frac{h}{2\pi i} \tag{412}$$

$$[\hat{t},\hat{E}\,] = \frac{hi}{2\pi} \tag{413}$$

$$[\hat{t},\hat{E}\,] = i\hbar \tag{414}$$

The equation (412) proves that higher the lifetime of the state lower will be energy fluctuation i.e. uncertainty ΔE, and the vice-versa is also true.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

❖ Schrodinger Wave Equation for a Particle in One Dimensional Box

In the first section of this chapter, we discussed the postulates of quantum mechanics i.e. the step-by-step procedure to solve a quantum mechanical problem. Now it's the time to implement those rules to the simplest quantum mechanical problem i.e. particle in a one-dimensional box. Consider a particle trapped in a one-dimensional box of length "*a*", which means that this particle can travel in only one direction only, say along *x*-axis. The potential inside the box is V, while outside to the box it is infinite.

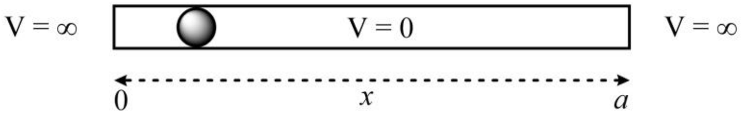


Figure 7. The particle in a one-dimensional box.

One other popular depiction of the particle in a one-dimensional box is also given in which the potential is shown vertically while the displacement is projected along the horizontal line.

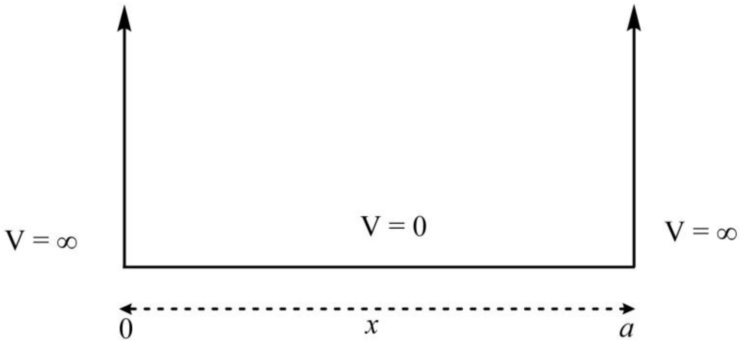


Figure 8. The second representation particle in a one-dimensional box.

So far we have considered a quantum mechanical system of a particle trapped in a one-dimensional box. Now suppose that we need to find various physical properties associated with different states of this system. Had it been a classical system, we would use simple formulas from classical mechanics to determine the value of different physical properties. However, being a quantum mechanical system, we cannot use those expressions because they would give irrational results. Therefore, we need to use the postulates of quantum mechanics to evaluate various physical properties.

Let ψ be the function that describes all the states of the particle in a one-dimensional box. At this point we have no information about the exact mathematical expression of ψ; nevertheless, we know that there is one operator that does not need the absolute expression of wave function but uses the symbolic form only, the Hamiltonian operator. The operation of Hamiltonian operator over this symbolic form can be rearranged to give to construct the Schrodinger wave equation; and we all know that the wave function as well the energy, both are the obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \tag{415}$$

After putting the value of one-dimensional Hamiltonian in equation (415), we get

$$\left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V\right]\psi = E\psi \tag{416}$$

or

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi \tag{417}$$

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + V\psi - E\psi = 0 \tag{418}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}E\psi - \frac{8\pi^2 m}{h^2}V\psi = 0 \tag{419}$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{420}$$

The above-mentioned second order differential equation is the Schrodinger wave equation for a particle moving along one dimension only. Since the conditions outside and inside the box are different, the equation (420) must be solved separately for both cases.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

1. The solution of Schrodinger wave equation for outside the box: After putting the value of potential outside the box in equation (420) i.e. V = ∞, we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0 \tag{421}$$

Since E is negligible in comparison to the ∞, the above equation becomes

$$\frac{\partial^2\psi}{\partial x^2} - \infty\psi = 0 \tag{422}$$

$$\infty\psi = \frac{\partial^2\psi}{\partial x^2} \tag{423}$$

$$\psi = \frac{1}{\infty}\frac{\partial^2\psi}{\partial x^2} = 0 \tag{424}$$

The physical significance of the equation (424) is that the particle cannot go outside the box, and is always reflected back when it strikes the boundaries. In other words, as the function describing the existence of particles is zero outside the box, the particle cannot exist outside the box.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

2. Solution of Schrodinger wave equation for inside the box: After putting the value of potential inside the box in equation (420) i.e. V = 0, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0 \tag{425}$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \tag{426}$$

Now consider

$$k^2=\frac{8\pi^2 mE}{h^2} \tag{427}$$

After using the value from equation (427) in equation (426), we get

$$\frac{\partial^2\psi}{\partial x^2}+k^2\psi=0 \tag{428}$$

The general solution of the above equation is

$$\psi=A\,Sin\,kx+B\,Cos\,kx \tag{429}$$

Hence, from just the symbolic form we have obtained some kind of expression for the wave function defining quantum mechanical states. However, the function given by equation (429) cannot be used to find different physical properties or the nature of corresponding quantum mechanical states. The reason is that this expression does have some unknown parameters like *A*, *B* and *k*. Since the function describing any quantum mechanical state must be single-valued, finite and continuous; the function ψ must also follow these conditions to become a "wave-function". Therefore, these boundary conditions are fulfilled only if the magnitude of ψ is zero at the start and at the end of the box (function outside is zero).

i) The first boundary condition: ψ must vanish when *x* = 0 i.e.

$$0=A\,Sin\,k(0)+B\,Cos\,k(0) \tag{430}$$

$$0=0+B\,Cos\,k(0) \tag{431}$$

$$B=0 \tag{432}$$

So, the function ψ is acceptable only if the value of the constant *B* is zero. After putting the value of *B* in equation (429), we get

$$\psi=A\,Sin\,kx+(0)\,Cos\,kx \tag{433}$$

$$\psi=A\,Sin\,kx \tag{434}$$

Buy the complete book with TOC navigation, high resolution images and no watermark.

ii) The second boundary condition: ψ must vanish when $x = a$, i.e.,

$$0 = A\,Sin\,ka \tag{435}$$

$$Sin\,ka = 0 \tag{436}$$

Moreover, as we know that

$$Sin\,0 = 0 \quad or \quad Sin\,0\pi = 0 \tag{437}$$

$$Sin\,180 = 0 \quad or \quad Sin\,1\pi = 0 \tag{438}$$

$$Sin\,360 = 0 \quad or \quad Sin\,2\pi = 0 \tag{439}$$

$$Sin\,540 = 0 \quad or \quad Sin\,3\pi = 0 \tag{440}$$

or

$$Sin\,n\pi = 0 \tag{441}$$

Where n = 0, 1, 2, 3, 4, 5 …. ∞. Comparing equation (436) and equation (441), we conclude that

$$Sin\,ka = Sin\,n\pi = 0 \tag{442}$$

Which eventually means that

$$ka = n\pi \tag{443}$$

$$k = \frac{n\pi}{a} \tag{444}$$

After putting the value of k in equation (434), we get

$$\psi = A\,Sin\frac{n\pi x}{a} \tag{445}$$

The only parameters that is still unknown in equation (445) is A, which can also be obtained by the condition of normalization i.e. the function must define the state completely. Therefore, we can say that

$$\int_0^a \psi^2 = A^2 \int_0^a Sin^2\left(\frac{n\pi x}{a}\right) = 1 \tag{446}$$

$$A^2.\frac{a}{2} = 1 \tag{447}$$

$$A^2 = \frac{2}{a} \quad or \quad A = \sqrt{\frac{2}{a}} \tag{448}$$

After putting the value of A in equation (445), we get

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM CHEMISTRY DALAL INSTITUTE (info@dalalinstitute.com, +91-9802825820) www.dalalinstitute.com SINCE 2012 Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\psi = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \tag{449}$$

Since the function ψ also depends upon the discrete variable *n*, it is better to write the above equation given as

$$\psi_n = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \tag{450}$$

The equation (450) represents all the quantum mechanical states of a particle in one-dimensional box. We can obtain functions for individual states just by putting different values of "*n*" allowed by the boundary conditions.

For first quantum mechanical state i.e *n* = 1

$$\psi_1 = \sqrt{\frac{2}{a}}\, Sin\frac{\pi x}{a} \tag{451}$$

For second quantum mechanical state i.e *n* = 2

$$\psi_2 = \sqrt{\frac{2}{a}}\, Sin\frac{2\pi x}{a} \tag{452}$$

For third quantum mechanical state i.e *n* = 3

$$\psi_3 = \sqrt{\frac{2}{a}}\, Sin\frac{3\pi x}{a} \tag{453}$$

Similarly, we can write the expression for ψ_4, ψ_5, ψ_6 and so on. It is also worthy to note that even though the *n* = 0 is permitted by the boundary condition, we still didn't use it in equation (450); which is obviously because it makes the whole function to collapse to zero.

One of the most remarkable results of this procedure that we have not discussed yet is the correlation of equation (427) and equation (444).

$$k^2 = \frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{a^2} \tag{454}$$

$$E_n = \frac{n^2h^2}{8ma^2} \tag{455}$$

The energy of different quantum mechanical states can be obtained by putting n = 1, 2, 3.... ∞ in equation (455). Hence, we have obtained the wave-function as well as the energy for a particle in one-dimensional box.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

❖ Evaluation of Average Position, Average Momentum and Determination of Uncertainty in Position and Momentum and Hence Heisenberg's Uncertainty Principle

The third postulate of quantum mechanics states that when the wave-function of a particular quantum mechanical state is multiplied by the operator of an observable quantity, we get a real value multiplied by the wave function itself. However, the value obtained this way can be constant or variable. Mathematically, the constant value of the observable quantity can be reported directly, and the function is called an eigenfunction of the operator under consideration. If the value of the physical property obtained after multiplying the wave function by the corresponding operator is variable i.e. non-eigen, the value can be reported only after averaging it over the whole configurational space.

$$< a > = \frac{\oint \psi^* \hat{O} \psi \, d\tau}{\oint \psi^* \psi \, d\tau} \tag{456}$$

Since the wave function ψ is normalized, the denominator becomes unity; therefore, equation (456) is reduced to the following

$$< a > = \oint \psi^* \hat{O} \psi \, d\tau \tag{457}$$

Since the operation by the Hamiltonian over the symbolic form has already given the absolute expressions for different quantum mechanical states, now we can operate other operators to evaluate their average values. In this section, we will determine the average values of position, position-squared, momentum and momentum-squared; which in turn will be used to prove the Heisenberg's uncertainty finally.

➢ *Evaluation of Average Position*

The quantum mechanical operator for the position of a particle in one-dimensional is $\hat{x}$; while the general form of wave function is

$$\psi_n = \sqrt{\frac{2}{a}} \, Sin \frac{n\pi x}{a} \tag{458}$$

Using this in equation (457), we get

$$< x > = \oint \psi^* x \, \psi \, d\tau \tag{459}$$

or

$$< x > = \oint x \, \psi^2 \, dx \tag{460}$$

$$< x > = \int_0^a x.\ \frac{2}{a} Sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a}\int_0^a x\ Sin^2\left(\frac{n\pi x}{a}\right) dx \tag{461}$$

$$= \frac{2}{a}\int_0^a x \left[\frac{1 - Cos\left(\frac{2n\pi x}{a}\right)}{2}\right] dx \tag{462}$$

$$= \frac{1}{a}\int_0^a \left(x - x\ Cos\frac{2n\pi x}{a}\right) dx \tag{463}$$

$$= \frac{1}{a}\left[\int_0^a x\ dx - \int_0^a x\ Cos\left(\frac{2n\pi x}{a}\right) dx\right] \tag{464}$$

$$= \frac{1}{a}\left[\frac{a^2}{2} - 0\right] = \frac{a}{2} \tag{465}$$

- ***Evaluation of Average Position-Squared***

The quantum mechanical operator for the position-squared of a particle in one-dimensional is $\hat{x}^2$; Using this in equation (457), we get

$$< x^2 > = \oint \psi^*\, x^2\, \psi\, dx \tag{466}$$

$$< x^2 > = \int_0^a x^2.\ \frac{2}{a} Sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a}\int_0^a x^2\ Sin^2\left(\frac{n\pi x}{a}\right) dx \tag{467}$$

$$= \frac{2}{a}\int_0^a x^2 \left[\frac{1 - Cos\left(\frac{2n\pi x}{a}\right)}{2}\right] dx \tag{468}$$

$$= \frac{2}{a}\left[\frac{a^3}{6} - \frac{a^3}{4n^2\pi^2}\right] = \frac{1}{a}\left[\frac{a^3}{3} - \frac{a^3}{2n^2\pi^2}\right] \tag{469}$$

$$= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} \tag{470}$$

- ***Evaluation of Average Momentum***

The quantum mechanical operator for the position-squared of a particle in one-dimensional is $\hat{p}_x$; Using this in equation (457), we get

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

$$< \hat{p}_x > = \oint \psi^* \, \frac{h}{2\pi i}\frac{\partial}{\partial x} \, \psi \, dx \tag{471}$$

$$< \hat{p}_x > = \int_0^a \left[\sqrt{\frac{2}{a}} Sin\left(\frac{n\pi x}{a}\right)\right] \frac{h}{2\pi i}\frac{\partial}{\partial x} \left[\sqrt{\frac{2}{a}} Sin\left(\frac{n\pi x}{a}\right)\right] dx \tag{472}$$

$$= \frac{h}{2\pi i}\left[\frac{2}{a}\right] \int_0^a Sin\left(\frac{n\pi x}{a}\right)\left(\frac{n\pi}{a}\right) \, Cos\left(\frac{n\pi x}{a}\right) dx \tag{473}$$

$$= \frac{h}{2\pi i}\left[\frac{2}{a}\right]\left(\frac{n\pi}{a}\right) \int_0^a Sin\left(\frac{n\pi x}{a}\right) \, Cos\left(\frac{n\pi x}{a}\right) dx \tag{474}$$

$$< \hat{p}_x > = 0 \tag{475}$$

➢ ***Evaluation of Average Momentum-Squared***

The quantum mechanical operator for the position-squared of particle in one-dimensional is $\hat{p}_x^2$; Using this in equation (457), we get

$$< \hat{p}_x^2 > = \oint \psi^* \left(-\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}\right) \psi \, dx \tag{476}$$

$$< \hat{p}_x^2 > = \int_0^a \left[\sqrt{\frac{2}{a}} Sin\left(\frac{n\pi x}{a}\right)\right] \left(-\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}\right) \left[\sqrt{\frac{2}{a}} Sin\left(\frac{n\pi x}{a}\right)\right] dx \tag{477}$$

$$= -\frac{h^2}{4\pi^2}\left(\frac{2}{a}\right) \int_0^a Sin\left(\frac{n\pi x}{a}\right)\left[(-)\left(\frac{n\pi}{a}\right)^2 Sin\left(\frac{n\pi x}{a}\right)\right] dx \tag{478}$$

$$= \frac{h^2}{4\pi^2}\left(\frac{2}{a}\right)\left(\frac{n\pi}{a}\right)^2 \int_0^a Sin^2\left(\frac{n\pi x}{a}\right) dx \tag{479}$$

$$= \frac{n^2 h^2}{2a^3} \int_0^a Sin^2\left(\frac{n\pi x}{a}\right) dx \tag{480}$$

$$= \frac{n^2 h^2}{2a^3} \int_0^a \left[\frac{1 - Cos\left(\frac{2n\pi x}{a}\right)}{2}\right] dx \tag{481}$$

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector-14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

DALAL INSTITUTE

$$= \frac{n^2h^2}{2a^3}\left[\frac{x - Sin\left(\frac{2n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_0^a \tag*{(482)}$$

or

$$= \frac{n^2h^2}{2a^3}\left(\frac{a}{2}\right) \tag*{(483)}$$

or

$$< \hat{p}_x^2 > = \frac{n^2h^2}{4a^2} \tag*{(484)}$$

- ***The Heisenberg's Uncertainty***

In order to prove the Heisenberg's uncertainty principle from for the quantum mechanical system of a particle in one-dimensional box, we first need to find the uncertainties in position and momentum. Once both uncertainties are known, we can simply multiply both to yield final result.

1. Uncertainty in position: The uncertainty in position is simply the difference between the square root of the uncertainty in the position-squared. Mathematically, we can say that

$$\Delta x = (< x^2 > - < x >^2)^{1/2} \tag*{(485)}$$

After putting the values of average position and position-squared from equation (465) and (470) in equation (485), we get

$$\Delta x = \left[\left(\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}\right) - \left(\frac{a}{2}\right)^2\right]^{1/2} \tag*{(486)}$$

or

$$\Delta x = \left[\left(\frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}\right)\right]^{1/2} \tag*{(487}$$

or

$$\Delta x = a\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2} \tag*{(488)}$$

2. Uncertainty in momentum: The uncertainty in momentum is simply the square root of the difference between the uncertainty in momentum and uncertainty in the momentum-squared. Mathematically, we can say that

CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$\Delta p_x = (< p_x^2 > - < p_x >^2)^{1/2} \tag{489}$$

After putting the values of average position and position-squared from equation (475) and (484) in equation (489), we get

$$\Delta p_x = \left[\left(\frac{n^2h^2}{4a^2}\right) - (0)^2\right]^{1/2} \tag{490}$$

or

$$\Delta p_x = \frac{nh}{2a} \tag{491}$$

Now multiplying equation (488) and (491), we get

$$\Delta x.\Delta p_x = \left[a\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2}\right]\left(\frac{nh}{2a}\right) \tag{492}$$

or

$$= \frac{nh}{2}\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2} \tag{493}$$

Multiply and divide the above equation by $2n\pi$

$$\Delta x.\Delta p_x = \frac{nh}{2}.\frac{2n\pi}{2n\pi}\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2} \tag{493}$$

or

$$= \frac{nh}{2}.\frac{1}{2n\pi}\left(\frac{4n^2\pi^2}{12} - \frac{4n^2\pi^2}{2n^2\pi^2}\right)^{1/2} \tag{494}$$

or

$$\Delta x.\Delta p_x = \frac{h}{4\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \tag{495}$$

Since $n^2\pi^2/3$ is always greater than 2, we can conclude that

$$\Delta x.\Delta p_x > \frac{h}{4\pi} \tag{496}$$

Which is the famous Heisenberg's uncertainty principle.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation,
high resolution images and
no watermark.

Copyright © Mandeep Dalal

❖ Pictorial Representation of the Wave Equation of a Particle in One Dimensional Box and Its Influence on the Kinetic Energy of the Particle in Each Successive Quantum Level

The solution of the Schrodinger wave equation for a one-dimensional box gives the wave function as well as the energy of the system. The general form of wave-function representing various quantum mechanical states is given below.

$$\psi_n = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \tag{497}$$

The energy of the system is given by equation (498) as:

$$E_n = \frac{n^2h^2}{8ma^2} \tag{498}$$

The general depiction of a particle trapped in a one-dimensional box with zero potential inside, along with the conditions outside, is shown below.

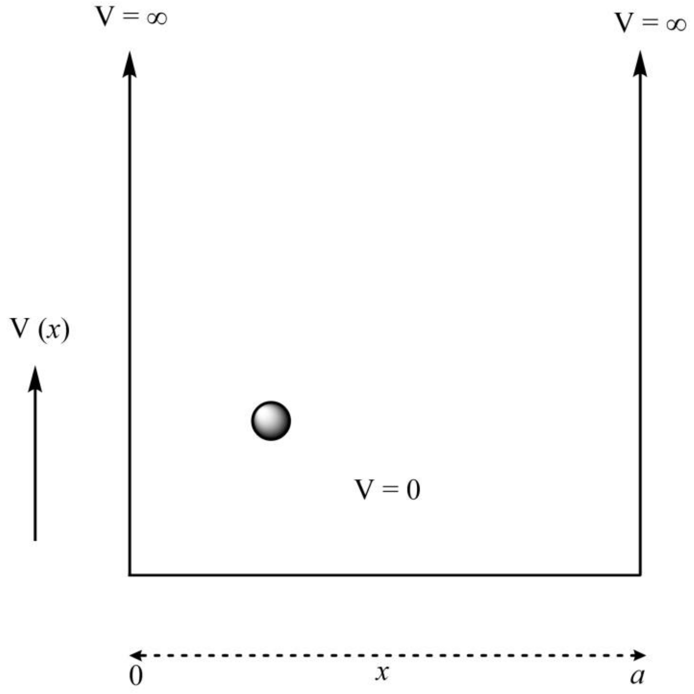
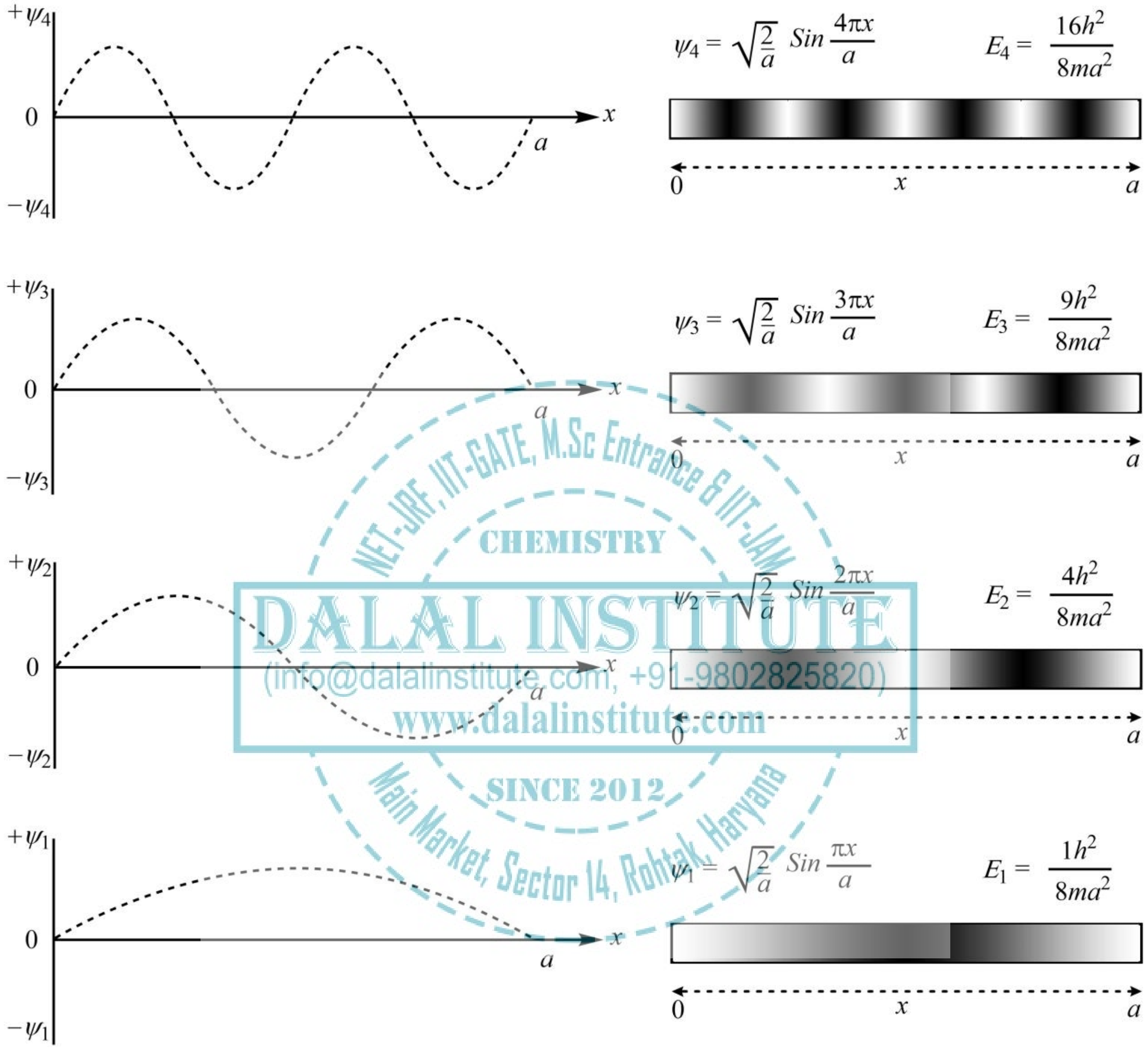


Figure 9. The graphical and pictorial representation of various wave-functions of the particle trapped in a one-dimensional box.

The pictorial representation of the wave-functions in different quantum mechanical states and the corresponding energies are shown below.



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Figure 10. The graphical and pictorial representation of various wave-functions of the particle trapped in a one-dimensional box.

It can be seen clearly from the figure given above that as the number of nodes in wave-function defining a particular quantum mechanical state increases, the energy of the state also increases.

Furthermore, we can also comment on the symmetry of different wave functions w.r.t the center of the box. The symmetry of different states can be classified mainly into two categories as given below.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

$$Symmetric \rightarrow Even\ function \rightarrow \psi_{odd}$$

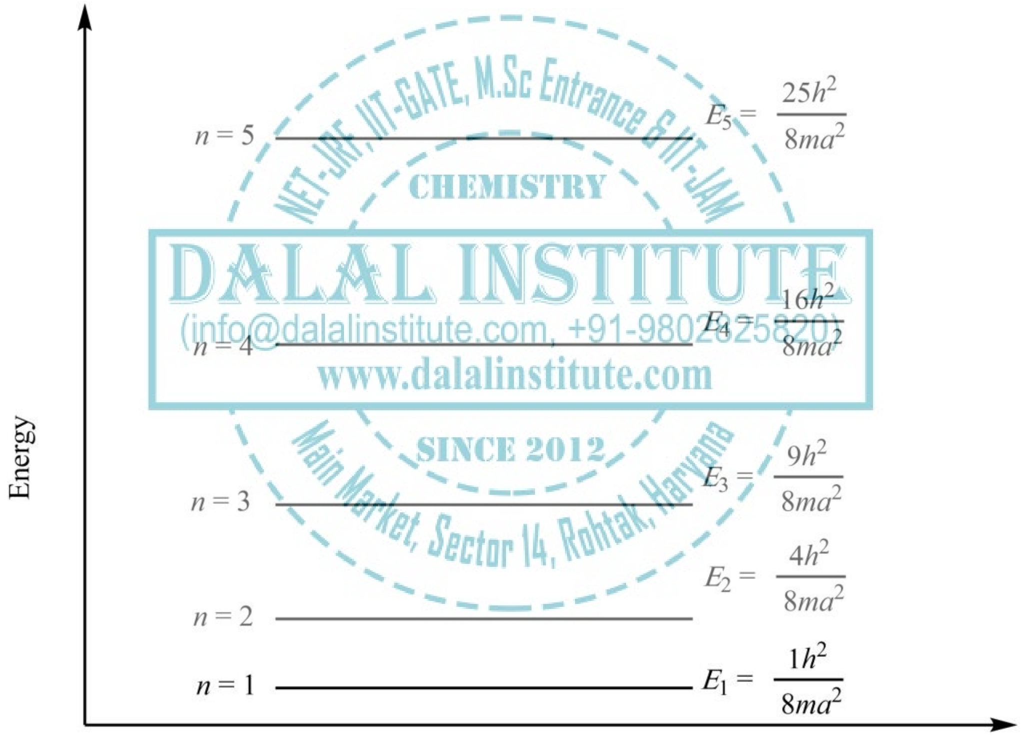
and

$$Antisymmetric \rightarrow Odd\ function \rightarrow \psi_{even}$$

Hence, function like ψ_1, ψ_3, ψ_5 are symmetric while ψ_2, ψ_4, ψ_6 are antisymmetric. Some of the important results wavefunction and energy analysis for the particle in a one-dimensional box are listed below.

- ***Quantization of Energy***

Owing to the discrete domain of n i.e. 1, 2, 3 …. ∞; the kinetic energy associated with the particle, that is trapped in a one-dimensional box, can also have discrete or quantized values only. Therefore, the quantized variable is also popularly called as the "quantum number.



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Figure 11. The quantized or discrete energy levels a particle of mass m, confined in a one-dimensional box of length a.

It is also worthy to note that the energy gap between successive energy levels shows a linear divergence with the increasing value of the quantum number n. Moreover, the energy of particle also depends inversely upon the mass and the box length; which eventually means that the energy levels would become continuous if the mass or length of the box becomes very large, proving the Bohr's correspondence principle.

Buy the complete book with TOC navigation, high resolution images and no watermark.

➢ *Non-Quantization of the Energy of the Particle*

If the walls of the box are removed, the boundary conditions will no longer be applicable, and the particle would become free to move. In other words, the constant A, B and k can have any value; and therefore, states of the particle are not quantized anymore. The general expression for the energy of the particle is

$$E_n = \frac{n^2h^2}{8ma^2} \tag{498}$$

Hence, in such a case, a freely moving particle like an electron has restrictions and gives a continuous energy spectrum.

➢ *Box length and the Wave Function at the Walls*

We have already studied that the magnitude of the wave function at the ends of the box must be equal to zero to maintain its continuity. This is possible only if the length of the box is an integral multiple of half of the wavelength. This can be proved as

$$E_n = \frac{n^2h^2}{8ma^2} \tag{499}$$

Also

$$E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{p^2}{2m} \tag{500}$$

Using the de-Brogli relation ($\lambda = h/p$) in equation (500), we get

$$E = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{501}$$

Now from equation (499) and (501), we conclude

$$\frac{n^2h^2}{8ma^2} = \frac{h^2}{2m\lambda^2} \tag{502}$$

or

$$\frac{n^2}{4a^2} = \frac{1}{\lambda^2} \tag{503}$$

or

$$a = n\left(\frac{\lambda}{2}\right) \tag{504}$$

This result of equation (504) also proves that the number of nodes in nth quantum mechanical state are n–1.

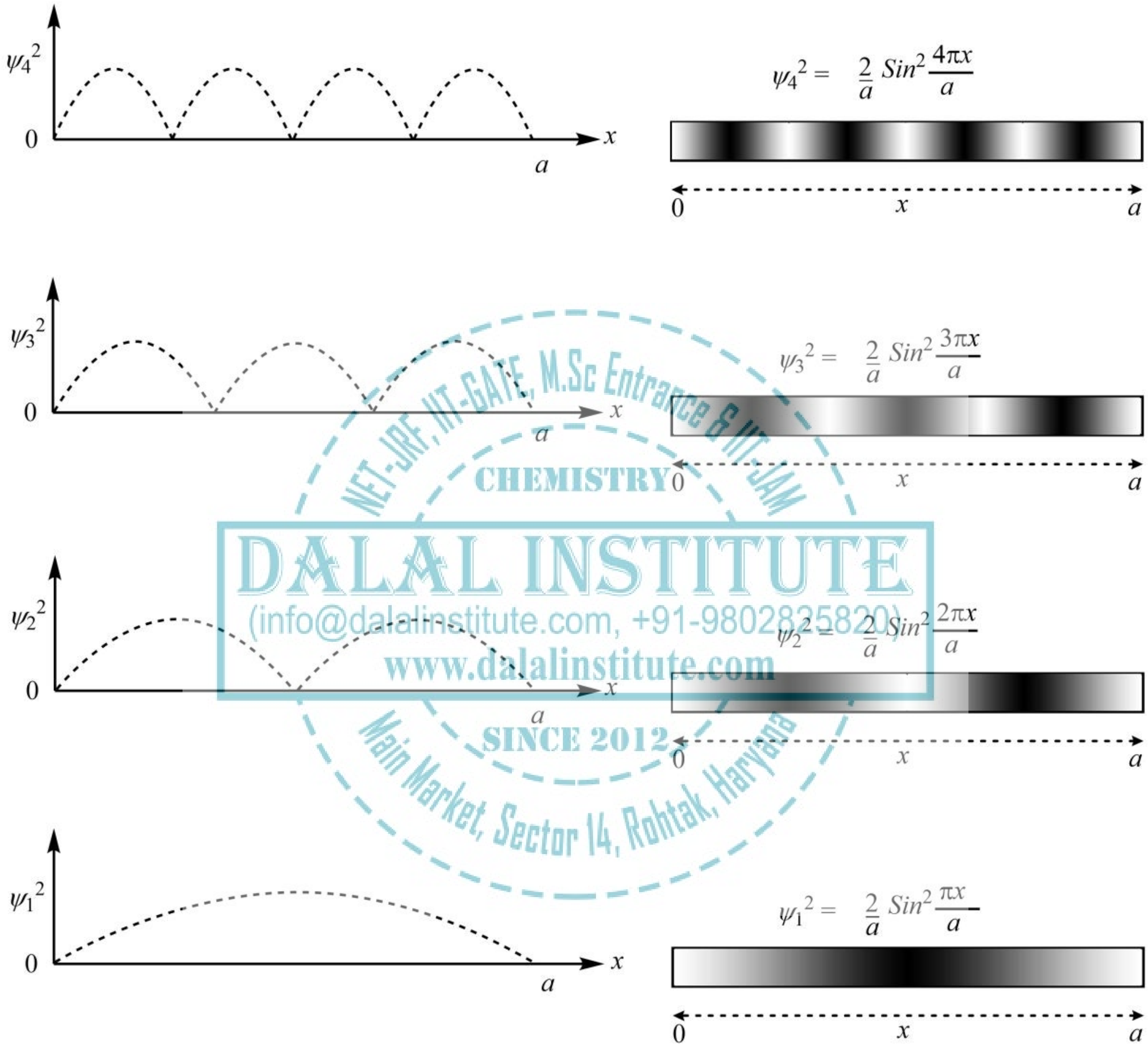
NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

➢ ***The Probability Density***

The wave density of simply the probability density in the one-dimensional box is not the same at all the points. It is more noticeable when the quantum number defining the state is small. However, it becomes more and more uniform as *n* increases.



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Figure 12. The graphical and pictorial representation of the probability density of a particle with mass *m* and confined in a one-dimensional box of length *a*.

The increasing uniformity of with increasing value of *n* is in accordance with the Bohr's correspondence principle which states that the results of quantum mechanics approach classical values at very high quantum numbers.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

❖ Lowest Energy of the Particle

As we have already discussed that the wave function and energy, both are obtained as the solution of the Schrodinger wave equation for a particle in a one-dimensional box. The general forms of wave-function and energy for various quantum mechanical states are given below.

$$\psi_n = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \qquad and \qquad E_n = \frac{n^2h^2}{8ma^2} \tag{505}$$

We can write the expressions for ψ_1, ψ_2, ψ_3, ψ_4, ψ_5, ψ_6 and so on; however, it is also worthy to note that even though the $n = 0$ is permitted by the boundary condition, we cannot use it because this would make the whole function to collapse to zero.

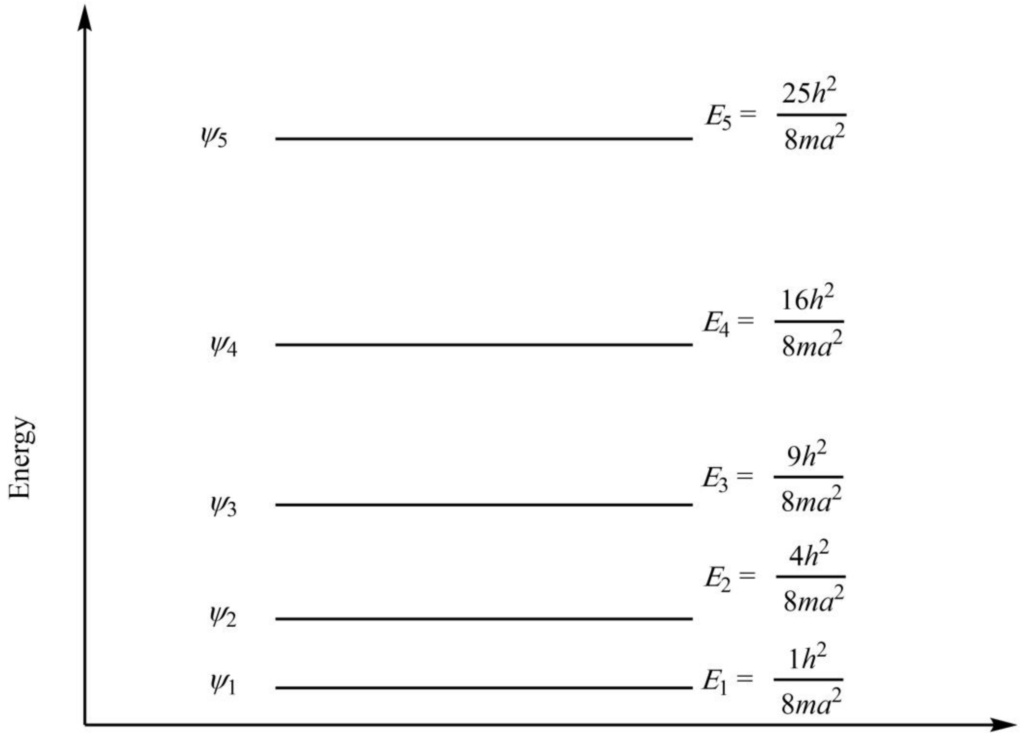


Figure 13. All the energy levels a particle in a one-dimensional box of including the "lowest energy of the particle".

Hence, the minimum acceptable value of the quantum number n is 1 rather than 0; which makes the minimum energy of the particle non-zero.

$$E_1 = \frac{h^2}{8ma^2} \tag{506}$$

This non-zero value is popularly called as the zero-point energy and is a function of the mass of the particle and length of the box.

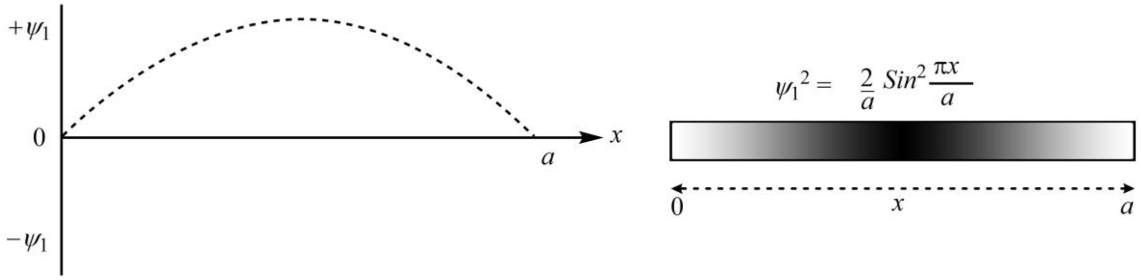


Figure 14. The plot of the wave function (left) and probability for the lowest energy state a particle in one-trapped in dimensional box.

Hence, in order to create the lowest energy, the particle must occupy the whole box without any node, having the highest probability at the center.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

Buy the complete book with TOC navigation, high resolution images and no watermark.

Copyright © Mandeep Dalal

❖ Problems

Q 1. State and explain the third postulate of quantum mechanics.

Q 2. Why should the function representing a quantum mechanical state be continuous, single-valued and finite?

Q 3. Why don't we report non-eigenvalues directly? What is the need for their expectation values?

Q 4. Derive Schrodinger wave equation from the postulates of quantum mechanics.

Q 5. What is the Max-Born interpretation of "wave function"? Explain in detail by taking the example of one-dimensional systems.

Q 6. What is position-time uncertainty? How would you prove it for the photons passing through a slit of length d?

Q 7. What is operator commutation? Evaluate $[\hat{x}^2, \widehat{p_x}]$.

Q 8. Explain the energy-time uncertainty for a particle traveling along x-axis. Also, support your argument from the results of operator algebra.

Q 9. What are Hermitian operators? Prove that the operators for linear momentum and angular momentum are Hermitian in nature.

Q 10. Can the average value for the square of the Hermitian operator be negative? If not, explain why?

Q 11. Derive and solve the Schrodinger wave equation for a particle moving in a one-dimensional box.

Q 12. Prove the Heisenberg's uncertainty principle for the particle trapped in a one-dimensional box of length a. Also, comment on its validity in other systems.

Q 13. Give the pictorial representation of the first three quantum mechanical states of a particle in a one-dimensional box. Also, formulate the corresponding symmetry and number of nodes.

Q 14. Derive the relation between the box length and the wavelength of the particle in the 1-dimensional box.

Q 15. What is zero-point energy? How is it created by a particle of mass m which is trapped in a one-dimensional box of length a.

Q 16. What is the average position? How is it different from the "most probable position"?

Q 17. State and explain the Bohr's correspondence principle.

Copyright © Mandeep Dalal

❖ Bibliography

[1] B. R. Puri, L. R. Sharma, M.S. Pathania, *Principles of Physical Chemistry*, Vishal Publications, Jalandhar, India, 2018.

[2] I. N. Levine, *Quantum Chemistry*, Pearson Prentice Hall, New Jersey, USA, 2009.

[3] D. A. McQuarrie, *Quantum Chemistry*, University Science Books, California, USA, 2008.

[4] E. Steiner, *The Chemistry Maths Book*, Oxford University Press, Oxford, UK, 2008.

[5] P. Atkins, J. Paula, *Physical Chemistry*, Oxford University Press, Oxford, UK, 2010.

[6] M. Reed, B. Simon *Functional Analysis*, Elsevier, Amsterdam, Netherlands, 2003.

[7] G. E. Bowman, Essential Quantum Mechanics, Oxford University Press, Oxford, UK, 2008.

[8] W. Heisenberg, *Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik*, Zeitschrift für Physik, 1927, 172.

[9] E. Schrödinger, *Die gegenwärtige Situation in der Quantenmechanik*, Naturwissenschaften. 1935, 807.

[10] P. Alberto, C. Fiolhaisdag, V. Gil, *Relativistic particle in a box*, European Journal of Physics, 1996, 17.

[11] R. K. Prasad, *Quantum Chemistry*, New Age International Publishers, New Delhi, India, 2010.

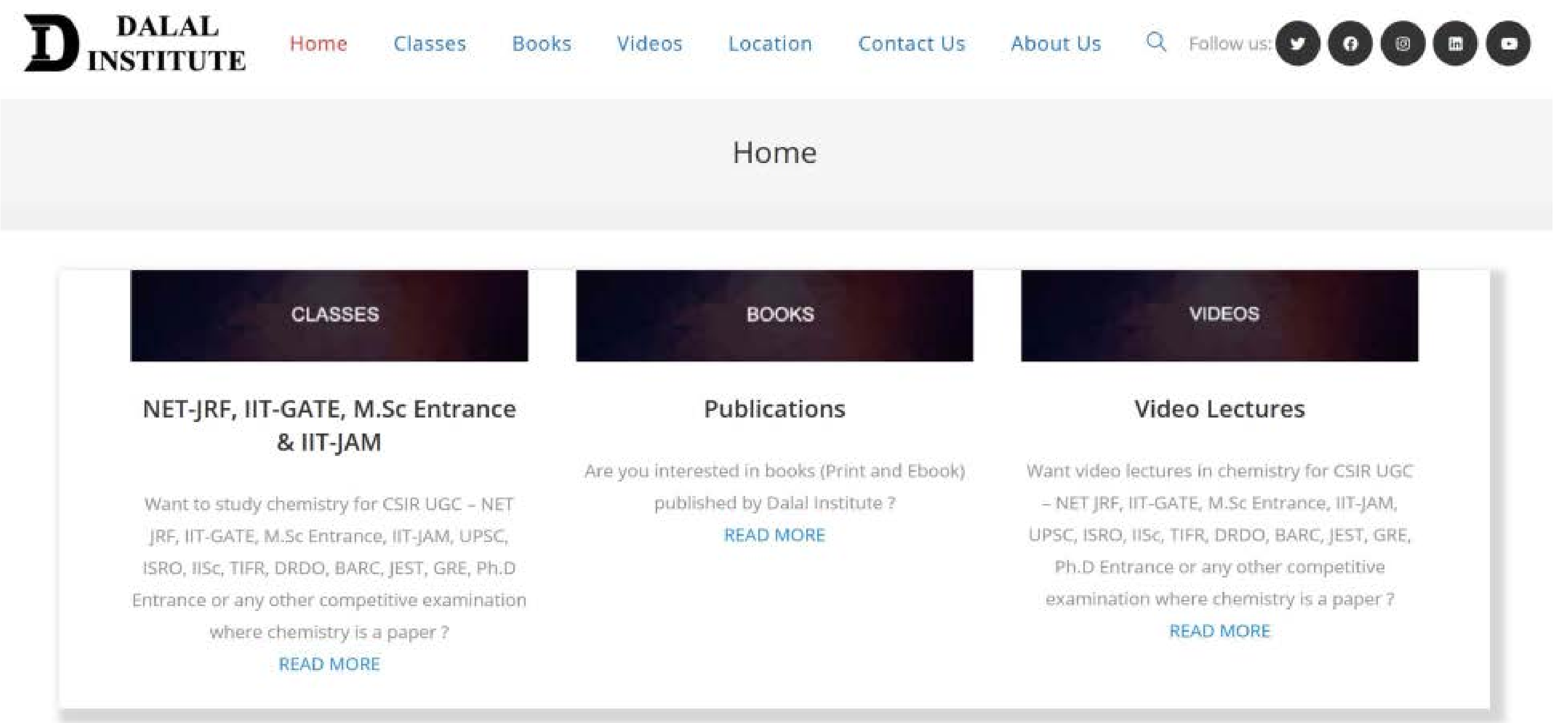
LEGAL NOTICE

This document is an excerpt from the book entitled "A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal", and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher's website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM
CHEMISTRY
DALAL INSTITUTE
(info@dalalinstitute.com, +91-9802825820)
www.dalalinstitute.com
SINCE 2012
Main Market, Sector 14, Rohtak, Haryana

This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

Home: https://www.dalalinstitute.com/
Classes: https://www.dalalinstitute.com/classes/
Books: https://www.dalalinstitute.com/books/
Videos: https://www.dalalinstitute.com/videos/
Location: https://www.dalalinstitute.com/location/
Contact Us: https://www.dalalinstitute.com/contact-us/
About Us: https://www.dalalinstitute.com/about-us/

Postgraduate Level Classes
(NET-JRF & IIT-GATE)
Admission
Regular Program Distance Learning
Test Series Result

Undergraduate Level Classes
(M.Sc Entrance & IIT-JAM)
Admission
Regular Program Distance Learning
Test Series Result

A Textbook of Physical Chemistry – Volume 1

"A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal" is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.
READ MORE

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

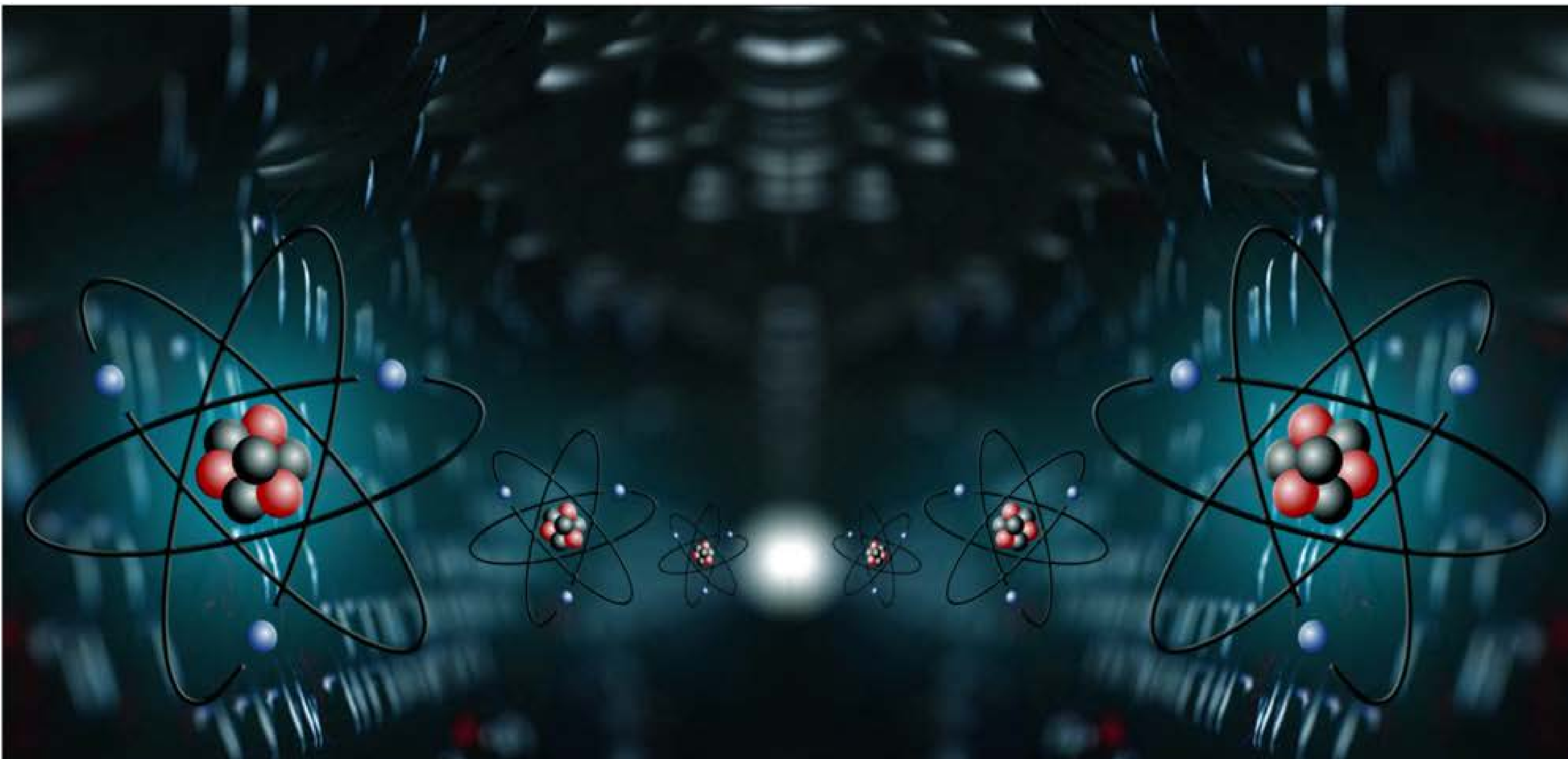
Sign Up

International
Edition

A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-1-7
9 788193 872017
MRP: Rs 800.00

DALAL INSTITUTE
Main Market, Sector-14, Rohtak, Haryana-124001
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com