

QUANTUM MECHANICS

Quantum Mechanics

Up to 19th century, classical mechanics proposed by Newton was enough to explain all types of motion. But to understand and deal the laws of particles or bodies on the atomic and subatomic scale, a new branch was introduced called quantum mechanics.

Classical Mechanics failed to explain photoelectric effect, atomic structure, optical spectra, black body radiation. But after the introduction of Planck's quantum theory, all these are successfully explained.

Quantum theory: According to Quantum theory, energy or radiation is emitted or absorbed by matter in discrete packets called **quanta**. Each quanta of energy is called **photon**.

It can be represented as $E = h\nu$. where $h = 6.626 \times 10^{-34}$ Js (Planck's Constant)

Matter waves: De Broglie concept

According to De Broglie, a wave is associated with a particle in motion and is called matter waves or De Broglie waves. Its wavelength is $\lambda = \frac{h}{p} = \frac{h}{mv}$ where m is the mass of the particle and p is its momentum.

- If KE of moving particle is given by $E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$ or $P = \sqrt{2mE}$

Then De Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$

- If an electron is accelerated by a potential V ,
then De Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}}$ (since $E = eV$)

Putting the values of $h = 6.626 \times 10^{-34}$ Js, mass of electron, $m = 9.1 \times 10^{-31}$ kg

and charge of electron , $e = 1.6 \times 10^{-19}$ C, we have $\lambda = \frac{12.3}{\sqrt{V}} \text{ \AA}^\circ$ or $\lambda = \sqrt{\frac{150}{V}} \text{ \AA}^\circ$

Heisenberg's Uncertainty Principle

(i) Uncertainty in position and momentum

According to Heisenberg's Uncertainty principle, it is impossible to measure both the position and momentum of an object precisely at same time.

If Δx is the uncertainty in position and Δp is the uncertainty in momentum, then

$$\Delta x \Delta p \geq \frac{\hbar}{2} \text{ where } \hbar = \frac{h}{2\pi} \text{ i.e., } \Delta x \Delta p \geq \frac{h}{4\pi}$$

(ii) Uncertainty in energy and time

According to energy-time uncertainty principle, the energy of an object can be uncertain by an amount ΔE for a time Δt . i.e., $\Delta E \Delta t \geq \frac{\hbar}{2}$

(iii) Uncertainty in angular displacement and angular momentum: $\Delta J_x \cdot \Delta \theta \geq \frac{\hbar}{2}$

Applications of Uncertainty Principle

Some atomic phenomena can be explained using uncertainty principle.

(i) Non existence of electron in the nucleus:

The nucleus of the diameter is in the order of 10^{-15} m. If an electron exists in the nucleus, it can be anywhere within the diameter of the nucleus. Then the uncertainty in position, $\Delta x = 10^{-15}$ m.

By Uncertainty principle, $\Delta x \Delta p \geq \frac{\hbar}{2}$ or $\Delta p = \frac{\hbar}{2\Delta x} = \frac{\hbar}{4\pi\Delta x} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-15}} = 5.27 \times 10^{-20}$ kgm/s

i.e., the momentum of the electron p must be the order of 5.27×10^{-20} kgm/s

We have $E = pc = 5.27 \times 10^{-20} \times 3 \times 10^8 = 15.81 \times 10^{-12}$ J

$$E = \frac{15.81 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV} = 98.8 \text{ MeV}$$

For an electron to exist in the nucleus, it must have an energy of this order. However, the energy of electron is of order of few MeV. So electrons cannot present within the nucleus.

(ii) Uncertainty in frequency of light emitted by an atom (spectral lines have a finite width or natural line broadening)

If an atom is in the excited state, it undergoes a transition to the lower energy state. Such an atom remains in the excited state for about 10^{-8} second. i.e., $\Delta t = 10^{-8}$ s

We have $\Delta E \Delta t \geq \frac{\hbar}{2}$

$$\Delta \nu = \frac{\hbar}{4\pi \times \hbar \times \Delta t} = \frac{1}{4 \times 3.14 \times 10^{-8}} = 0.7 \times 10^7 \text{ Hz} = 7 \text{ MHz.}$$

Here the uncertainty in frequency is of the order of MHz. So this width $\Delta \nu$ of the emitted line is experimentally observed. That means the emitted spectral line is not sharp. This broadening of spectral line which cannot be reduced further is known as natural line broadening.

Schrodinger Wave Equation – Time Dependent Equation

In quantum mechanics, the state of a particle is described by the wave function Ψ . Schrodinger wave equations are the equation of motion which governs the propagation of matter waves.

Consider a particle moving forward along the x-direction with momentum P. The wave function of the particle is $\Psi_{(x,t)} = Ae^{i(kx - \omega t)} \rightarrow (1)$

Substituting for ω and k in equation (1), we get,

$$\Psi_{(x,t)} = Ae^{\frac{i}{\hbar}(px - Et)} \rightarrow (2)$$

$$\text{Since } \omega = 2\pi\nu = 2\pi \frac{h\nu}{h} = \frac{E}{\hbar}$$

$$\text{We have } \lambda = \frac{h}{p}$$

$$\text{Also, } k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \text{ or } k = \frac{p}{\hbar}$$

Total energy of a particle is the sum of kinetic energy and potential energy. i.e., $E = \frac{1}{2}mv^2 + V$

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

Multiplying both sides by Ψ , we get, $E\Psi = \frac{p^2}{2m}\Psi + V\Psi \rightarrow (3)$

Differentiating equation (2) w.r.t x , $\frac{\partial \Psi}{\partial x} = A e^{\frac{i}{\hbar}(px-Et)} \times \frac{i}{\hbar} p \rightarrow (4)$

Again differentiating eqn (2) w.r.t x , $\frac{\partial^2 \Psi}{\partial x^2} = A e^{\frac{i}{\hbar}(px-Et)} \times \frac{i^2}{\hbar^2} p^2$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \times \Psi$$

$$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \rightarrow (5)$$

Differentiating eqn (2) w.r.t time, $\frac{\partial \Psi}{\partial t} = A e^{\frac{i}{\hbar}(px-Et)} \times \frac{-i}{\hbar} E = \frac{-i}{\hbar} E \Psi$

$$\text{i.e., } E \Psi = i \hbar \frac{\partial \Psi}{\partial t} \rightarrow (6)$$

Substituting, $p^2 \Psi$ and $E \Psi$ in eqn (3), we get, $i \hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi$

This is Schrodinger's time dependent equation in one dimension.

In three dimensions, $i \hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi + V \Psi$ where $\nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}$

Here we have, $i \hbar \frac{\partial \Psi}{\partial t} = \left(\frac{-\hbar^2}{2m} \nabla^2 + V \right) \Psi$

or $i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$ where \hat{H} is the Hamiltonian operator.

For free particle, $PE = V = 0$, then $i \hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi$

Time independent Schrodinger Equation

In some cases, potential energy V of a particle does not depend on time, it varies with the position of the particle only and then the field is said to be stationary. In such stationary problems, Schrodinger equation can be simplified by separating out time- dependent and position – dependent parts. Accordingly, we write the wave function as a product of a function of position x (ϕ_x) and a function of time t (ϕ_t)

Thus $\Psi_{(x,t)} = \phi_x \phi_t \rightarrow (1)$

Differentiating (1) w.r.t x twice, $\frac{\partial^2 \Psi}{\partial x^2} = \phi_t \frac{\partial^2 \phi_x}{\partial x^2} \rightarrow (2)$

Differentiating (1) w.r.t t , we get $\frac{\partial \Psi}{\partial t} = \phi_x \frac{\partial \phi_t}{\partial t} \rightarrow (3)$

Time dependent Schrodinger equation is $i \hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi \rightarrow (4)$

Substituting (2) and (3) in (4),

$$i \hbar \phi_x \frac{\partial \phi}{\partial t} = \frac{-\hbar^2}{2m} \phi_t \frac{\partial^2 \phi}{\partial x^2} + V \phi_x \phi_t$$

Dividing throughout by $\phi_x \phi_t$,

$$i \hbar \frac{1}{\phi_t} \frac{\partial \phi}{\partial t} = \frac{-\hbar^2}{2m} \frac{1}{\phi_x} \frac{\partial^2 \phi}{\partial x^2} + V$$

The LHS is a function of t alone while the RHS is a function of x alone. For the equation to be consistent, each side must be equal to same constant K .

$$\frac{\partial \phi}{\phi} = \frac{-i}{\hbar} K \partial t$$

Integrating, $\phi(t) = e^{\frac{-i}{\hbar} K t}$

$$\Psi(x,t) = \phi_x e^{\frac{-i}{\hbar} K t} \rightarrow (5)$$

Differentiating (5) w.r.t t , $\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} K \Psi$ or $K \Psi = i \hbar \frac{\partial \Psi}{\partial t} \rightarrow (6)$

Here we can see that K is identical with E , the total energy.

Then we can write,

$$\frac{-\hbar^2}{2m} \frac{1}{\phi_x} \frac{\partial^2 \phi}{\partial x^2} + V = E \Psi$$

$$\text{Or } \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + (E - V) \Psi = 0$$

$$\text{Or, } \frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \Psi = 0$$

This is Schrodinger's time-independent equation in one dimension or also called as **steady state** form of Schrodinger equation.

For free particle, $PE = V = 0$, then one dimensional time independent Schrodinger eqn becomes

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} E \Psi = 0$$

In three dimensional, $\nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V) \Psi = 0$

Wave function (Ψ)

It is a mathematical function which describes the state of a particle or a system. It is a function of position coordinates and time. $\Psi = \Psi(x,y,z,t)$. Wave function Ψ is a complex quantity. Wave function Ψ describes the behavior of a single particle.

* **Probability density:** The wave function Ψ itself has no physical meaning, but the square of absolute magnitude $|\Psi|^2$ or $\Psi \Psi^*$ gives the probability of finding the particle in unit volume (probability density), where Ψ^* is the complex conjugate of Ψ . i.e., $P(x) = \Psi \Psi^* = |\Psi|^2$

Ψ , as such, is not an observable (physically measurable quantity). But $\Psi\Psi^*$ is an observable. This is the statistical interpretation of Ψ .

* **Normalization:** Since the square of modulus of a complex valued function is non negative, so is $\Psi\Psi^* = |\Psi|^2$. A wave function that satisfies the condition $\int_{-\infty}^{\infty} \Psi\Psi^* dx dy dz = 1 \rightarrow (1)$ is called a normalized wave function and is called normalization condition. This condition means that the probability to find the particle somewhere in the whole region where the particle is trapped is unity. The solution of Schrodinger equation need not satisfy this above condition directly. But we can normalize it by multiplying the function by a suitable constant called normalization constant. Essential requisites for a well behaved wave function (constraints on wave function) for a given system are

- * Wave function Ψ should be single valued.
- * Wave function Ψ should be finite.
- * Wave function and its derivatives $\frac{\partial\Psi}{\partial x}$, $\frac{\partial^2\Psi}{\partial x^2}$ etc must be continuous .
- * Ψ must be a normalized function.

Operators

In quantum mechanics, every observable quantity of classical mechanics like position, momentum, energy etc are represented by a linear operator.

Operator transform one function to another.

- **Energy Operator:**

$$\text{We have } \Psi_{(x,t)} = Ae^{i/\hbar(Px-Et)}$$

$$\text{Differentiating w.r.t time t, } \frac{\partial\Psi}{\partial t} = Ae^{i/\hbar(Px-Et)} \times \frac{-i}{\hbar} E = \frac{-i}{\hbar} E\Psi$$

$$\text{i.e., } E\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

Here the energy operator is $\mathbf{E} = i\hbar \frac{\partial}{\partial t}$

- **Momentum Operator:**

$$\text{We have } \Psi_{(x,t)} = Ae^{i/\hbar(Px-Et)}$$

$$\text{Differentiating w.r.t x, } \frac{\partial\Psi}{\partial x} = Ae^{i/\hbar(Px-Et)} \times \frac{i}{\hbar} P = \frac{i}{\hbar} P\Psi$$

$$P\Psi = -i\hbar \frac{\partial\Psi}{\partial x}$$

Here the momentum operator is $\mathbf{P} = -i\hbar \frac{\partial}{\partial x}$

In 3D, momentum operator is $\mathbf{P} = -i\hbar \nabla$

- **Kinetic Energy Operator:**

$$\text{We have, KE} = \frac{1}{2} m v^2 = \frac{P^2}{2m} \text{ where m is the mass of the particle.}$$

So, KE operator $E_k = \frac{P^2}{2m} = \frac{1}{2m} \left(-i \hbar \frac{\partial}{\partial x} \right)^2$

$$E_k = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

In 3D, kinetic energy operator is $E_k = -\frac{\hbar^2}{2m} \nabla^2$

• **Hamiltonian Operator/ Total Energy Operator:**

TE = $\frac{P^2}{2m} + V$ Here TE is equal to the Hamiltonian function.

$$H_{(x,p_x)} = \frac{P^2}{2m} + V$$

$$H_{(x,p_x)} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

In 3D, Hamiltonian operator, $H_{(x,p_x)} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)$

Eigen value and Eigen function

An equation of the form $\hat{A} \Psi = a \Psi$ is called eigen value equation where \hat{A} is an operator and a is a scalar called an eigen value. The function Ψ is called an eigen function of the operator \hat{A} . In an eigen value equation, the operator transforms the function Ψ with a number a multiplied to it.

In quantum mechanics, a dynamical variable is represented by a linear operator. The state of a physical system corresponding to an eigen value is called an eigen state. It is represented by eigen function of the operator having the particular eigen value. **Eigen values represent the only possible value of that property of the system in that state.**

* Schrodinger equation is an eigen value function.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi = E \Psi$$

$\hat{H} \Psi = E \Psi$ where $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$ is Hamiltonian operator.

Here E is the eigen value and Ψ is the eigen function.

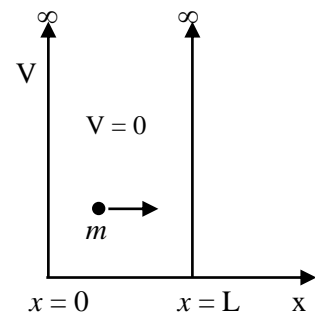
Particle in a one dimensional infinite square well potential

Consider the motion of a particle of mass m confined to move between two walls of infinite height at $x = 0$ and $x = L$.

The width of the box is L. Let this is moving along x - direction.

The particle is bouncing back and forth between the walls of the box.

Potential energy is $V = 0$, everywhere within the walls and $V = \infty$ outside the wall.



$V = 0$ for $0 < x < L$
 $V = \infty$ for $x \leq 0$ and $x \geq L$

One dimensional Schrodinger equation is $\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \Psi = 0$

Inside the box, $V = 0$, then 1D Schrodinger equation becomes,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} E \Psi = 0 \rightarrow (1)$$

Putting $\frac{2mE}{\hbar^2} = k^2$, then eqn (1) becomes, $\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi = 0 \rightarrow (2)$

The general solution of the equation is $\Psi = A \sin kx + B \cos kx \rightarrow (3)$

Now we apply the continuity condition on Ψ . Since it is impossible to find the particle outside the box, Ψ must be zero for all points outside the box.

ie, $\Psi = 0$ for $x \leq 0$

$\Psi = 0$ for $x \geq L$

Applying first condition at $x = 0$ on eqn (3), $0 = A \sin 0 + B \cos 0$.

Then $B = 0$

Then eqn (3) becomes $\Psi = A \sin kx \rightarrow (4)$

Using the condition at $x = L$ on eqn (3), we get $0 = A \sin kL$

Since $A \neq 0$, $\sin kL$ must be equal to 0. Hence $\sin kL = 0$

Or $kL = n\pi$ where n is the integer or $k = \frac{n\pi}{L} \rightarrow (5)$

Hence the eqn (4) becomes $\Psi_n = A \sin\left(\frac{n\pi}{L}x\right) \rightarrow (6)$

To find A , apply the normalization condition, $\int_0^L |\Psi|^2 dx = 1$

i.e., $\int_0^L A \sin\left(\frac{n\pi}{L}x\right) \cdot A \sin\left(\frac{n\pi}{L}x\right) dx = 1$

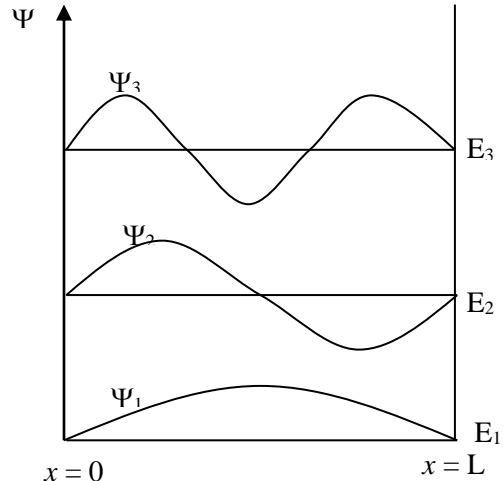
$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = 1$$

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

$$\frac{A^2}{2} \left[x - \frac{\sin \frac{2n\pi x}{L}}{\frac{2n\pi}{L}} \right]_0^L = 1 \quad \text{or} \quad \frac{A^2}{2} \left[L - \frac{\sin \frac{2n\pi L}{L}}{\frac{2n\pi}{L}} \right] = 1$$

Since $\sin 2n\pi = 0$, $\frac{A^2}{2} \times L = 1$ Or $A = \sqrt{\frac{2}{L}} \rightarrow (7)$

Thus eqn (6) becomes $\Psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$. This is the normalized wave function of particle in a potential box of length L.



Wave function of first three energy level

Energy eigen values

We have $\frac{2mE}{\hbar^2} = k^2$.

Then $E = \frac{k^2\hbar^2}{2m} = \left(\frac{n\pi}{L}\right)^2 \left(\frac{\hbar^2}{2m}\right) = \frac{n^2\pi^2\hbar^2}{2mL^2}$

i.e., $E = \frac{n^2\pi^2\hbar^2}{2mL^2}$ where $n = 1, 2, 3, \dots$

For ground state, $n = 1, E_1 = \frac{\pi^2\hbar^2}{2mL^2}$

For $n = 2, E_2 = \frac{(2)^2\pi^2\hbar^2}{2mL^2} = 4E_1$

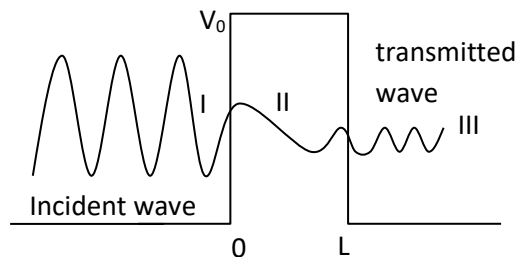
For $n = 3, E_3 = \frac{(3)^2\pi^2\hbar^2}{2mL^2} = 9E_1 \dots\dots\dots$

Different values of energy for n are called **energy eigen values** and $\Psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$ is **eigen function**.

According to quantum mechanics, a system can take only certain specific energies. Such discrete energies are the **energy eigen values** of the Schrodinger equation for the system.

Quantum Mechanical Tunneling

Consider a particle of mass m and energy $E < V_0$ incident on a potential barrier V_0 . Quantum mechanically, there will be a finite probability for the particle to penetrate through a barrier even if $E < V_0$. This phenomenon of tunneling through barriers higher than their own incident energy is known as **tunneling** in quantum mechanics.



The solution of the Schrödinger equation for the particle gives the wave function for the three regions.

The concept of barrier penetration is used to explain a number of phenomenon in physics. Some of them are as follows.

- (i) The emission of α -particles from radioactive nuclei.
- (ii) Barrier penetration in electronic devices such as tunnel diode and Josephson junction.
- (iii) Electron tunneling in scanning tunneling microscope.

NANOTECHNOLOGY

Most of the properties of a solid depends on size of the solid. When size of the material becomes smaller and smaller, the properties of materials change drastically in

Most of the nanomaterials exhibit remarkable variations in physical properties as compared to bulk materials. The cause of variation may be due to following facts.

- (i) Large ratio of surface to volume
- (ii) Quantum confinement
- (iii) Large surface energy
- (iv) Reduced imperfections.

Surface area to volume ratio

Surface area to volume ratio in nanoparticle have a significant effect on the nanoparticle properties. Nanoparticles have a relatively larger surface area when compared to the same volume of the material.

Let us consider a sphere of radius r , the surface area of the sphere is $4\pi r^2$ and the volume of the sphere is $\frac{4}{3}\pi r^3$.

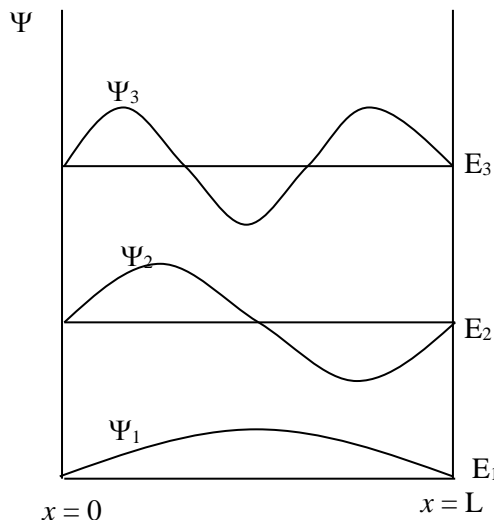
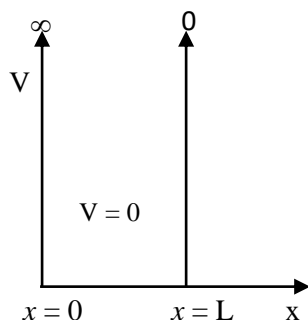
$$\text{The surface area to volume ratio} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

It means that the surface area to volume ratio increases with the decrease in radius of the sphere and vice versa. It can also be concluded here that when given volume is divided into smaller pieces, the surface area increases. So a greater portion of the atoms are found at the surface compared to those inside. Therefore nanoparticles have a much greater surface area per unit volume compared with the larger particles. It leads nanoparticles to become more chemically reactive. As growth and catalytic chemical reaction occurs at surfaces, a given mass of nanomaterials will be much more reactive than the same mass of material made up of large particles.

Quantum confinement

The phenomenon of the nonzero lowest energy and quantization of the allowed energy levels arising from the confinement of electrons within a limited space. The physical properties of semiconducting nanostructures arise from quantum confinement.

Consider the motion of an electron in a small length L, but with two walls of infinite height at the ends. The electron is confined to move in the portion $x = 0$ to $x = L$ only.



Wave functions of first three energy levels

A one dimensional box of width L

Potential energy is zero, since there is no attraction or repulsion. Wave associated with motion of a particle is called de Broglie wave or matter wave. The motion of the particle is such that the width of the one dimensional box must be an integral multiple of $\frac{\lambda}{2}$. This is the formation of standing waves in the width L of the box. i.e., $L = \frac{n\lambda}{2}$ where $n = 1, 2, 3, \dots$

De Broglie wavelength $\lambda = \frac{h}{p}$

$$\text{Kinetic energy } E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m\left(\frac{2L}{n}\right)^2} = \frac{n^2 h^2}{8mL^2}$$

Since potential energy is zero, the above expression gives the total energy.

\therefore Total energy $E = \frac{n^2 h^2}{8mL^2}$ where $n = 1, 2, 3, \dots$ is called the quantum number. The above expression can be derived from Schrodinger's equation in Quantum mechanics. The minimum energy is non zero and is given

$$\text{by } E_1 = \frac{h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

The first excited energy is $E_2 = 4E_1$

Thus the possible energies are $E_1, 4E_1, 9E_1, \dots$ where E_1 is the ground state energy. This shows that particle confined to move in a small space can have only particular energy values. It cannot have any value of energy. Thus the quantum confinement leads to nonzero lowest energy and quantized higher energy values.

Quantum dot – Quantum confinement in 3D

Quantum dots are zero dimensional structures in which the electron is confined in all three dimensions. Their energy states are quantized in all three directions.

In this case Schrodinger equation is

$$\nabla^2\Psi(\vec{r}) + \frac{2m}{\hbar^2} (E - V(\vec{r}))\Psi(\vec{r}) = 0$$

$$\Psi_{(x,y,z)} = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_x\pi x}{L_x}\right) \sin\left(\frac{n_y\pi y}{L_y}\right) \sin\left(\frac{n_z\pi z}{L_z}\right)$$

$$\text{Energy values } E_n = \frac{\pi^2\hbar^2}{2m} \left[\frac{n_x^2\pi^2}{L_x^2} + \frac{n_y^2\pi^2}{L_y^2} + \frac{n_z^2\pi^2}{L_z^2} \right]$$

Quantum dots are usually formed by a definite number of atoms. They are represented by atomic clusters or nanocrystallites.

Quantum wire (Nano wires) – Quantum confinement in 2D

A nanowire or quantum wire is a wire of dimensions of the order of nanometers. This is called quantum wire because their properties are governed by the law of quantum mechanics. Nano wire is a one dimensional structure in which the electrons are confined in two dimensions and are allowed to move freely along one dimension.

Suppose the carriers are confined in Y and Z directions to small distances L_y and L_z respectively and free to move in x direction, then we have,

$$\Psi_{(x,y,z)} = \sqrt{\frac{2}{L_y}} \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_y\pi y}{L_y}\right) \sin\left(\frac{n_z\pi z}{L_z}\right) e^{ik_x x}$$

$$\text{Energy values } E_n = \frac{\hbar^2}{2m} \left[\frac{n_y^2\pi^2}{L_y^2} + \frac{n_z^2\pi^2}{L_z^2} \right] + \frac{\hbar^2 K_x^2}{2m}$$

Nanowires can be used to link or connect tiny components in nanocircuits. Their area of applications are electronics, optoelectronics and Micro Electro Mechanical Systems (MEMS).

Nanosheet – Quantum confinement in 1D

In nanosheet confinement is present in only one dimension. That is carriers are allowed to move freely along a two dimensional plane. Suppose the confinement is present along Z direction to a small distance L_z and free to move along x and y directions.

Schrodinger equation in this case is

$$\Psi_{(x,y,z)} = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z\pi z}{L_z}\right) e^{ik_x x} \cdot e^{ik_y y}$$

$$\text{Energy values } E_n = \frac{\hbar^2}{2m} \left[\frac{n_z^2\pi^2}{L_z^2} \right] + \frac{\hbar^2 K_x^2}{2m} + \frac{\hbar^2 K_y^2}{2m}$$

Properties of nanomaterials

Mechanical Properties

* Nanomaterials have lower melting point and reduced lattice constant due to large surface to volume ratio.

It is observed that nanoparticles of metals, semiconductors and molecular crystals have lower melting point as compared to their bulk form, when the particle size is less than 100nm.

For example, melting point of gold decreases rapidly for nanoparticles with diameter below 5nm.

* Smaller structures have less surface defects. Hence, nanowires have mechanical strength much greater than that of thick ones.

For example, copper with an average grain size of 6nm has 5 times higher hardness over a sample size 50micron. Strength of the material increases significantly as the particle size decreases.

* Hardness and yield strength of the material increases as the particle size is decreased.

* Nanostructured materials have high moduli of elasticity and their toughness also increases.

Optical Properties

As we go in nanorange, number of atoms decreases on the surface and hence the band gap is more. Optical properties such as colour and transparency are observed to change at nanoscale level.

For examples,

Bulk gold – appears yellow in colour while nano gold appears red, orange, purple or greenish depends on the size.

Bulk silicon appears grey in colour while nanosized silicon appears red in colour.

Zinc oxide gives white appearance while nanoscale zinc oxide appears transparent.

Optical properties of nanomaterials are due

(i) to increase in energy level spacing- quantum size effect.

(ii) surface plasmon resonance (SPR)

Surface Plasmon Resonance (SPR): SPR is a dipolar excitation of the entire particle between the negatively charged free electrons and its positively charged lattice.

Plasmon is the quantum of oscillation arising as a result of collective excitation in a plasma like system composed of positive ions and free electrons. The Plasmon which is concentrated at surface of the material are referred as Surface Plasmon. When the size of nanocrystal is comparable to the wavelength of incident light, they exhibit different colours.

The electric field of an incoming light induces a polarization of the free electrons with respect to the ionic core of a spherical metal particle. The net charge difference occurs at the nanoparticle surface. It acts as a restoring force. Hence a dipolar oscillation of electrons is created with a certain frequency. Noble metals have the resonance frequency in the visible light range. The surface Plasmon resonance is responsible for colour of gold nanoparticles and silver nanoparticles in solutions. Analysis shows that the Plasmon resonance depends on the particle size.

The colouration of nanoparticles renders practical applications and some of the applications have been explored and practically used.

Electrical Properties

Electrical conductivity of nanomaterials depends on increased perfection, reduced impurity and dislocations. The electrical conductivity decreases with reduced dimensions due to increased surface scattering. As the bulk material reduces its size, continuous energy bands are replaced by discrete energy levels and bandgap increases as the size decreases. As a result, some metal nanowires undergo transition to become semiconductors and semiconductors might become insulators when the diameter changes below a critical value.

Electrical conductivity of nanomaterials may be enhanced due to better ordering in microstructure. Ballistic conduction occurs when the length of the conductor is smaller than the electron mean free path. Tunneling conduction is another charge transport mechanism in nanometer range.

Applications

Nanomaterials have very wide ranging applications.

- * Nanotechnology can play a key role in the improvement of efficiency of fuel cells, storing hydrogen in fuel cells.
- * Nanomaterials are harder than conventional materials. Therefore, cutting tools and drills made of nanocrystalline materials such as titanium carbide, tungsten carbide etc are harder and wear resistant. Nanocrystalline silicon nitride and silicon carbide are extremely useful for the manufacture of high strength springs, ball bearings etc.
- * In new generation batteries, nanomaterials can hold more energy as compared to the conventional plates. Frequent recharging is not needed with nickel metal hydride (Ni-MH) batteries made of nanocrystalline nickel and metal hydrides. The life time of such batteries is also much longer.
- * Carbon nanotubes are used in nanoelectronics, batteries, displays, high strength composites, solar panels etc. CNT are very efficient materials for the manufacturing of low cost solar panels. Composite materials reinforced with CNT fibres are used for space applications. CNT employed solar panels will significantly reduce the cost of solar panels for the conversion of solar energy into electrical energy at affordable cost. CNT are very much stronger than steel and hence used for car bodies, aeroplanes, used as armour on military vehicles etc.
- * Nanomaterials are used in the preparation of cosmetic powder, spray perfumes and deodorants. Finely dispersed pharmaceuticals are good in rapid drug delivery and hence reduced dosage for patients.
- * When nanocrystalline powders compacted and applied as coating, they provide improved strength and ductility to conventional materials like ceramics, composite materials and metal alloys.
- * Nanoshells can be used to destroy cancer cells.
- * Quantum dots may be used in future for locating cancer tumours.

- * Nanoparticle can be used to improve MRI images of cancer tumours.
- * Nanocrystalline silver can be used to treat wounds.
- * Nanotechnology is being used to reduce air pollution and can be used to reduce water pollution.
- * Fabric with nanosized particle or fibres will improve its properties without increase in weight, thickness or stiffness.
- * By using nanomaterials air leakage from tennis balls can be minimized.
- * Nanorods can be used as cleaning agent.
- * TiO nanoparticles in sunscreen film can absorb harmful ultraviolet radiation.
- * Nanoparticle can be used in better packaging of food items.

Excitons

When an atom at a lattice site loses an electron, the atom acquires a positive charge and is called a hole. If the hole remains localized at the lattice site and the detached negative electron remains in its neighbourhood, it will be attracted to the positively charge hole through Coulomb interaction and can bound to form a hydrogen type atom. This bound pair of electron-hole is known as exciton.

Exciton has the properties of a particle, it is mobile and able to move around the lattice. The electron and hole forming a given exciton could be physically close to each other or separated by a few lattice spacing. If 'd' is the dimension of nanoparticle and a_{eff} is the exciton radius, then

$d > a_{eff}$ - weak confinement

$d < a_{eff}$ - strong confinement

$d \gg a_{eff}$ - no confinement