Module –I: Quantum Mechanics

Wave function and its Physical Significance

Wave Function

A **wave function** in quantum mechanics describes the quantum state of an isolated system of one or more particles containing all the information about the entire system. It gives is probabilistic interpretation of amplitude, commonly denoted by the Greek letters ψ or Ψ. It is single valued and continuous function of space and time.

Properties of Wave function

Wave function has the following properties
   (i) It contains all the measurable information about the particle.
   (ii) It basically corresponds to the probability of finding a particle in space (in 3D) that will be one. i.e. $\psi^*\psi = 1$ in all over the space.
   (iii) It is single valued and continuous function of space and time.
   (iv) It allows expectation value or effective average value calculation.
   (v) It allows energy calculation via Schrodinger's equation.
   (vi) It should be sine wave for free particle, implies a preciously determined momentum and a totally uncertain position (uncertainty principle).

Postulates of Quantum Mechanics

Postulate 1. The state of a quantum mechanical system is completely specified by a function $\Psi(r, t)$ that depends upon the coordinates of the particle(s) and on time. This function, called the wavefunction or state function, has the important property that $|\Psi(r, t)|^2$ represents the probability density of the particle located at position r at time t.

The normalization condition is $\int_{-\infty}^{\infty}|\psi(r,t)|^2 dr = 1$. The wavefunction must also be single-valued, continuous, and finite.

Postulate 2. To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

Postulate 3. If a system is in a state described by a normalized wavefunction Ψ, then the average value of the observable corresponding to $\hat{A}$ is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\mathbf{r}$$

Postulate 4. The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi(\mathbf{r},t),$$

where $\hat{H}$ is the Hamiltonian of the system. If Ψ is an eigenstate of $\hat{H}$, it follows that $\Psi(\mathbf{r},t) = \Psi(\mathbf{r},0)e^{-iEt/\hbar}$.

Operators in Quantum Mechanics and Commutation Relations

position operator $\hat{x}$ defined by $\hat{x}\psi(x) = x\psi(x)$

momentum operator $\hat{p}$ defined by $\hat{p}\psi(x) = -i\hbar\dfrac{\partial\psi}{\partial x}$

Linear Operator

An operator $\hat{A}$ is said to be linear if

$$\hat{A}(cf(x)) = c\hat{A}f(x)$$
$$\text{and}$$
$$\hat{A}(f(x) + g(x)) = \hat{A}f(x) + \hat{A}g(x)$$

where $f(x)$ and $g(x)$ are any two appropriate functions and c is a complex constant.
Examples: the operators $\hat{x}$, $\hat{p}$ and $\hat{H}$ are all linear operators. This can be checked by explicit calculation (Exercise!).

Hermitian Operator

The operator $\hat{A}$ is called hermitian if

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

Examples:
(i) the operator $\hat{x}$ is hermitian. Indeed:

$$\int (\hat{x}\psi)^* \psi\, dx = \int (x\psi)^* \psi\, dx = \int \psi^* x\psi\, dx = \int \psi^* \hat{x}\psi\, dx$$

(ii) the operator $\hat{p} = -i\hbar d/dx$ is hermitian:

$$\int (\hat{p}\psi)^* \psi\, dx = \int \left(-i\hbar\frac{d\psi}{dx}\right)^* \psi\, dx$$
$$= i\hbar \int \left(\frac{d\psi}{dx}\right)^* \psi\, dx$$

and after integration by parts, and recognizing that the wfn tends to zero as $x \to \infty$, we get on the right-hand side

$$-i\hbar \int \psi^* \frac{d\psi}{dx}\, dx = \int \psi^* \hat{p}\psi\, dx$$

(iii) the K.E. operator $\hat{T} = \hat{p}^2/2m$ is hermitian:

$$\int \left(\hat{T}\psi\right)^* \psi\, dx = \frac{1}{2m} \int \left(\hat{p}^2\psi\right)^* \psi\, dx$$
$$= \frac{1}{2m} \int (\hat{p}\psi)^* \hat{p}\psi\, dx$$
$$= \frac{1}{2m} \int \psi^* \hat{p}^2\psi\, dx$$
$$= \int \psi^* \hat{T}\psi\, dx$$

<u>Theorem:</u> The eigenvalues of hermitian operators are real.
<u>Proof:</u> Let ψ be an eigenfunction of $\hat{A}$ with eigenvalue a:

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

then we have

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

and by hermiticity of $\hat{A}$ we also have

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

hence

$$(a^* - a) \int \psi^*\psi \, dx = 0$$

and since $\int \psi^*\psi \, dx \neq 0$, we get

$$a^* - a = 0$$

The converse theorem also holds: an operator is hermitian if its eigenvalues are real.

Example: $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p} = -i\hbar d/dx$, then we have

$$\hat{A}\hat{B}f(x) = \hat{x}\hat{p}f(x)$$

We can of course also construct another new operator:

$$\hat{p}\hat{x}$$

Then, by definition of the operator product,

$$\hat{p}\hat{x}f(x)$$

means that $\hat{x}$ is first operating on $f(x)$ and then $\hat{p}$ is operating on the function $\hat{x}f(x)$.
Compare the results of operating with the products $\hat{p}\hat{x}$ and $\hat{x}\hat{p}$ on $f(x)$:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = -i\hbar \left(x\frac{df(x)}{dx} - \frac{d}{dx}(xf(x)) \right)$$

and hence by the product rule of differentiation:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = i\hbar f(x)$$

and since this must hold for any differentiable function $f(x)$, we can write this as an operator equation:

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

Thus we have shown that the operator product of $\hat{x}$ and $\hat{p}$ is non-commuting.

Because combinations of operators of the form

$$\hat{A}\hat{B} - \hat{B}\hat{A}$$

do frequently arise in QM calculations, it is customary to use a short-hand notation:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

and this is called the commutator of $\hat{A}$ and $\hat{B}$ (in that order!).
If $[\hat{A}, \hat{B}] \neq 0$, then one says that $\hat{A}$ and $\hat{B}$ do not commute,
if $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ are said to commute with each other.
An operator equation of the form of

$$[\hat{A}, \hat{B}] = \text{something}$$

is called a commutation relation.

$$[\hat{x}, \hat{p}] = i\hbar$$

is the fundamental commutation relation.

In classical mechanics one defines the angular momentum by

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

We get the angular momentum operator by replacing the vector $\vec{r}$ by the vector operator $\hat{r} = (\hat{x}, \hat{y}, \hat{z})$ and the momentum vector by the momentum vector operator

$$\hat{p} = -i\hbar\nabla = -i\hbar(\partial_x, \partial_y, \partial_z)$$

where $\partial_x = \partial/\partial x$ etc.

The complete fundamental commutation relations of the coordinate and momentum operators are

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$$

and

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = \ldots = [\hat{z}, \hat{p}_y] = 0$$

It will be convenient to use the following notation:

$$\hat{x}_1 = \hat{x}, \quad \hat{x}_2 = \hat{y}, \quad \hat{x}_3 = \hat{z}$$

and

$$\hat{p}_1 = \hat{p}_x, \quad \hat{p}_2 = \hat{p}_y, \quad \hat{p}_3 = \hat{p}_z$$

we can then summarize the fundamental commutation relations by

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

where δ_{ij} is the Kronecker symbol:

$$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases}$$

Next consider $[\hat{x}, \hat{L}_y]$: we have

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

hence

$$[\hat{x}, \hat{L}_y] = [\hat{x}, \hat{z}\hat{p}_x] - [\hat{x}, \hat{x}\hat{p}_z] = i\hbar\hat{z}$$

and similarly

$$[\hat{x}, \hat{L}_z] = -i\hbar\hat{y}$$

etc. We can summarize the nine commutation relations:

$$[\hat{x}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$$

where

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if} \quad (ijk) = (1,2,3) \text{ or } (2,3,1) \text{ or } (3,1,2) \\ -1 & \text{if} \quad (ijk) = (1,3,2) \text{ or } (3,2,1) \text{ or } (2,1,3) \\ 0 & \text{if} \quad i = j \text{ or } i = k \text{ or } j = k \end{cases}$$

and summation over the repeated index k is implied.

Similarly one can show

$$[\hat{p}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

after which it is straight forward to deduce:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

The important conclusion from this result is that *the components of angular momentum have no common eigenfunctions.*

Of course, we must also show that the angular momentum operators are hermitian. This is of course plausible (reasonable) since we know that the angular momentum is a dynamical variable in classical mechanics. The proof is left as an exercise.

We can construct one more operator that commutes with all components of $\hat{L}$: define the square of $\hat{L}$ by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

then

$$\begin{aligned} [\hat{L}_x, \hat{L}^2] &= [\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] \\ &= [\hat{L}_x, \hat{L}_y^2] + [\hat{L}_x, \hat{L}_z^2] \end{aligned}$$

Now there is a simple technique to evaluate a commutator like $[\hat{L}_x, \hat{L}_y^2]$: write down explicitly the known commutator $[\hat{L}_x, \hat{L}_y]$:

$$\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z$$

multiply this on the left by $\hat{L}_y$, then multiply on the right by $\hat{L}_y$:

$$\hat{L}_y\hat{L}_x\hat{L}_y - \hat{L}_y^2\hat{L}_x = i\hbar\hat{L}_y\hat{L}_z$$
$$\hat{L}_x\hat{L}_y^2 - \hat{L}_y\hat{L}_x\hat{L}_y = i\hbar\hat{L}_z\hat{L}_y$$

and if we add these commutation relations we get

$$\hat{L}_x\hat{L}_y^2 - \hat{L}_y^2\hat{L}_x = i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$$

and similarly

$$\hat{L}_x\hat{L}_z^2 - \hat{L}_z^2\hat{L}_x = -i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$$

hence

$$[\hat{L}_x, \hat{L}^2] = 0$$

and similarly

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

Expectation values.

The expectation value of an operator $\hat{A}$ that operates on ψ is defined by

$$\langle\hat{A}\rangle \equiv \int \psi^* \hat{A}\psi \, dx$$

The Heisenberg Uncertainty Relations

The wave function $\psi(x)$ cannot describe a particle that is both well-localized in space and has a sharp momentum. The uncertainty in the measurement is given by

$$\Delta x \, \Delta p \geq \hbar/2$$

where $\Delta x = \left[\langle x^2\rangle - \langle x\rangle^2\right]^{1/2}$ and $\Delta p = \left[\langle p^2\rangle - \langle p\rangle^2\right]^{1/2}$

to be evaluated using position and momentum operators.

This is in great contrast to classical mechanics. What the relation states is that there is a quantitative limitation on the accuracy with which we can describe a system using our familiar, classical notions of position and momentum. Position and momentum are said to be *complementary (conjugate)* variables.

Example 1:   A particle of mass m is in the state

$$\Psi(x, t) = Ae^{-a[(mx^2/\hbar)+it]},$$

where A and a are positive real constants. (a) Find A. (b) Calculate the expectation values of <x>, <x²>, <p>, and <p²>. (d) Find σ_x and σ_p. Is their product consistent with the uncertainty principle?

(a) $1 = 2|A|^2 \int_0^\infty e^{-2amx^2/\hbar} dx = 2|A|^2 \frac{1}{2}\sqrt{\frac{\pi}{(2am/\hbar)}} = |A|^2 \sqrt{\frac{\pi\hbar}{2am}};$ $\boxed{A = \left(\frac{2am}{\pi\hbar}\right)^{1/4}}.$

(b) $\langle x \rangle = \int_{-\infty}^\infty x|\Psi|^2 dx = \boxed{0.}$ [Odd integrand.]

$\langle x^2 \rangle = 2|A|^2 \int_0^\infty x^2 e^{-2amx^2/\hbar} dx = 2|A|^2 \frac{1}{2^2(2am/\hbar)}\sqrt{\frac{\pi\hbar}{2am}} = \boxed{\frac{\hbar}{4am}}.$

$\langle p \rangle = m\frac{d\langle x \rangle}{dt} = \boxed{0.}$

Remember:

$\int_0^\infty e^{-ax^2}\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

$\int_0^\infty x^2\, e^{-ax^2}\, dx = \frac{1}{4a}\left(\frac{\pi}{a}\right)^{1/2}$

$\langle p^2 \rangle = \int \Psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 \Psi\, dx = -\hbar^2 \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx$

$= -\hbar^2 \int \Psi^* \left[-\frac{2am}{\hbar}\left(1 - \frac{2amx^2}{\hbar}\right)\Psi\right] dx = 2am\hbar\left\{\int |\Psi|^2 dx - \frac{2am}{\hbar}\int x^2 |\Psi|^2 dx\right\}$

$= 2am\hbar\left(1 - \frac{2am}{\hbar}\langle x^2 \rangle\right) = 2am\hbar\left(1 - \frac{2am}{\hbar}\frac{\hbar}{4am}\right) = 2am\hbar\left(\frac{1}{2}\right) = \boxed{am\hbar.}$

(c) $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{\hbar}{4am} \implies \boxed{\sigma_x = \sqrt{\frac{\hbar}{4am}}};$

$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = am\hbar \implies \boxed{\sigma_p = \sqrt{am\hbar}.}$

$\sigma_x \sigma_p = \sqrt{\frac{\hbar}{4am}}\sqrt{am\hbar} = \frac{\hbar}{2}.$

This is consistent with the uncertainty principle.

Example 2:

Consider a particle whose normalized wave function is

$$\psi(x) = 2\alpha\sqrt{\alpha}\, xe^{-\alpha x} \qquad x > 0$$
$$= 0 \qquad x < 0$$

(a) For what value of x does $P(x)=|\psi|^2$ peak? (b) Calculate $<x>$, $<x^2>$ and $<p>$, $<p^2>$.
(c) Verify uncertainty relation.

(a)   The peak in P(x) occurs when $dP(x)/dx = 0$ that is, when

$$\frac{d}{dx}(x^2 e^{-2\alpha x}) = 2x(1 - \alpha x)e^{-2\alpha x} = 0 \qquad\Longrightarrow\qquad x = 1/\alpha.$$

(b) $\langle x\rangle = \int\limits_{0}^{\infty} dx\, x(4\alpha^3 x^2 e^{-2\alpha x}) = \frac{1}{4\alpha}\int\limits_{0}^{\infty} dy\, y^3 e^{-y} = \frac{3!}{4\alpha} = \frac{3}{2\alpha}$

$\langle x^2\rangle = \int\limits_{0}^{\infty} dx\, x^2(4\alpha^3 x^2 e^{-2\alpha x}) = \frac{4!}{8\alpha^2} = \frac{3}{\alpha^2}$

Gamma functions: $\Gamma(n) = \int\limits_{0}^{\infty} x^{n-1}e^{-x}dx$ for $n > 0, \Gamma(n+1) = n\Gamma(n)$;

$\Gamma(n) = (n-1)!$ for n is poistive integer. $\Gamma(1) = 1$ and $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$\langle p\rangle = -i\hbar\left(4\alpha^3\right)\int\limits_{0}^{\infty} xe^{-\alpha x}\frac{\partial}{\partial x}\left(xe^{-\alpha x}\right)dx = 0$ (Has to be real)

$\langle p^2\rangle = -\hbar^2\left(4\alpha^3\right)\int\limits_{0}^{\infty} xe^{-\alpha x}\frac{\partial^2}{\partial x^2}\left(xe^{-\alpha x}\right)dx = -\hbar^2\left(4\alpha^3\right)\left[-2\alpha\int\limits_{0}^{\infty} xe^{-2\alpha x}dx + \alpha^2\int\limits_{0}^{\infty} x^2 e^{-2\alpha x}dx\right]$

$= -\hbar^2\left[-\frac{2\alpha\left(4\alpha^3\right)}{\left(2\alpha\right)^2}\int\limits_{0}^{\infty} ye^{-y}dy + \alpha^2\left(4\alpha^3\int\limits_{0}^{\infty} x^2 e^{-2\alpha x}dx\right)\right] = -\hbar^2\left[-2\alpha^2 + \alpha^2\right] = \alpha^2\hbar^2$

(c) $\Delta x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{3}{\alpha^2} - \left(\frac{3}{2\alpha}\right)^2 = \frac{3}{4\alpha^2}; \ \Delta x = \frac{\sqrt{3}}{2\alpha},$

$\Delta p^2 = \langle p^2\rangle - \langle p\rangle^2 = \alpha^2\hbar^2; \ \Delta p = \alpha\hbar;$

$\Delta x\Delta p = \frac{\sqrt{3}}{2\alpha}\alpha\hbar = \frac{\sqrt{3}}{2}\hbar > \frac{\hbar}{2}$

Eigen Function and Eigen Value

If an operator operates on a wave function and after the operation the wave function remains unchanged, then that wave function is known as the eigen function corresponding to that operator and the constant is known as the eigen value.

Here

$$\hat{A}f(x) = af(x)$$

where a is some constant of proportionality. In this case $f(x)$ is called an eigenfunction of $\hat{A}$ and a the corresponding eigenvalue.

Example: Consider the function $f(x,t) = e^{i(kx-\omega t)}$.
This represents a wave travelling in x direction.
Operate on $f(x)$ with the momentum operator:

$$
\begin{aligned}
\hat{p}f(x) &= -i\hbar \frac{d}{dx}f(x) = (-i\hbar)(ik)e^{i(kx-\omega t)} \\
&= \hbar k f(x)
\end{aligned}
$$

Theorem:

if two operators $\hat{A}$ and $\hat{B}$ commute, then they have common eigenfunctions.

Proof: Let ψ be an eigenfunction of $\hat{A}$ with eigenvalue a:

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

operating on both sides with $\hat{B}$ we get

$$\hat{B}(\hat{A}\psi) = a\hat{B}\psi$$

on the l.h.s. we can write $\hat{B}\hat{A}\psi$, and then since by assumption $\hat{A}$ and $\hat{B}$ commute, we get

$$\hat{A}\hat{B}\psi = a\hat{B}\psi$$

thus $\hat{B}\psi$ is an eigenfunction of $\hat{A}$ with the same eigenvalue as ψ; therefore $\hat{B}\psi$ can differ from ψ only by a constant factor, i.e. we must have

$$\hat{B}\psi = b\psi$$

i.e. ψ is also an eigenfunction of $\hat{B}$.

Schrodinger Wave Equation

The wave function of a particle of fixed energy E could most naturally be written as a linear combination of wave functions of the form

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

representing a wave travelling in the positive x direction, and a corresponding wave travelling in the opposite direction, so giving rise to a standing wave, this being necessary in order to satisfy the boundary conditions.

The above equation can be converted in terms of energy and momentum, expressed as

$$\Psi(x,t) = Ae^{-i(px-Et)/\hbar}$$

We adopt the wave function above as being the appropriate wave function for a *free* particle of momentum $p = \hbar k$ and energy $E = \hbar\omega$.

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi$$

which can be written, using $E = p^2/2m = \hbar^2 k^2/2m$:

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

Similarly

$$\frac{\partial \Psi}{\partial t} = -i\omega\Psi$$

which can be written, using $E = \hbar\omega$:

$$i\hbar\frac{\partial \Psi}{\partial t} = \hbar\omega\psi = E\Psi.$$

We now generalize this to the situation in which there is both a kinetic energy and a potential energy present, then $E = p^2/2m + V(x)$, so that

$$E\Psi = \frac{p^2}{2m}\Psi + V(x)\Psi$$

where, Ψ is now the wave function of a particle moving in the presence of a potential $V(x)$.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial \psi}{\partial t}$$

which is the famous time dependent Schr̈odinger wave equation.

Let the trial solution of the Scrodinger's wave equation can be given by

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

i.e. where the space and the time dependence of the complete wave function are contained in separate factors

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}e^{-iEt/\hbar} + V(x)\psi(x)e^{-iEt/\hbar} = i\hbar. - iE/\hbar e^{-iEt/\hbar}\psi(x) = E\psi(x)e^{-iEt/\hbar}$$

We now see that the factor $\exp[-iEt/\hbar]$ cancels from both sides of the equation, giving us

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

If we rearrange the terms, we end up with

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \left(E - V(x)\right)\psi(x) = 0$$

which is the time independent Schr̈odinger equation.

Time independent Schrodinger's Wave equations can be established by the methods of separation of variable. Let us take the solution for ψ(t; x) as

$$\psi(t,x) = \psi(x)f(t)$$

and insert it into the time dependent Schrödinger equation

$$i\hbar\,\psi(x)\,\frac{\partial f(t)}{\partial t} \;=\; -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\,f(t) + V(x)\,\psi(x)f(t) \qquad \Big|\;\cdot\;\frac{1}{\psi(x)\,f(t)}$$

$$i\hbar\,\frac{1}{f(t)}\frac{df(t)}{dt} \;=\; -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x)\,.$$

Since now the left hand side in above Eq. is only dependent on t and the right hand side only on x, both sides must be equal to a constant, which we will call E, and we can thus solve each side independently. The left side yields

$$i\hbar\,\frac{1}{f(t)}\frac{df(t)}{dt} = E \quad\Rightarrow\quad \frac{df}{f} = -\frac{i}{\hbar}E\,dt$$

$$\Rightarrow\quad \ln(f) = -\frac{i}{\hbar}E\,t + \text{const.} \quad\Rightarrow\quad f = \text{const.}\,e^{-i\,E\,t/\hbar}\,.$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = E \quad\Rightarrow\quad \underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x)}_{H\,\psi(x)} = E\,\psi(x)\,.$$

Stationary states

*A state is called **stationary**, if it is represented by the wave function*

$$\psi(t,x) = \psi(x)\,e^{-i\,E\,t/\hbar}\,.$$

For such states the probability density is time independent

$$|\psi(t,x)|^2 = \psi^*(x)\,\psi(x)\,\underbrace{e^{i\,E\,t/\hbar}\,e^{-i\,E\,t/\hbar}}_{1} = |\psi(x)|^2\,.$$

If a particle of mass *m* has a definite energy E, its wave function Ψ(x, y, z, t) is a product of a time-independent wave function ψ(x, y, z) and a factor that depends on time but not position. Then the probability distribution function | Ψ(x, y, z, t)|² = | ψ(x, y, z)|² does not depend on time (*stationary states*).

$$\Psi(x,y,z,t) = \psi(x,y,z)\,e^{-iEt/\hbar}$$

Particle in One-dimensional Box

Suppose we have a single particle of mass *m* confined to within a region 0 < *x* < *L* with potential energy *V* = 0 bounded by infinitely high potential barriers, i.e. *V* = ∞ for *x* < 0 and *x* > *L*. The potential experienced by the particle is then:

In the regions for which the potential is infinite, the wave function will be zero, for exactly the same reasons that it was set to zero in Section 5.3, that is, there is zero probability of the particle being found in these regions. Thus, we must impose the boundary conditions

$$\psi(0) = \psi(L) = 0$$

Meanwhile, in the region 0 < *x* < *L*, the potential vanishes, so the time independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x).$$

To solve this, we define a quantity k by

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

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

whose general solution is

$$\psi(x) = A\sin(kx) + B\cos(kx).$$

It is now that we impose the boundary conditions, that at $x = 0$:

$$\psi(0) = B = 0$$

Next, applying the boundary condition at $x = L$ gives

$$\psi(L) = A\sin(kL) = 0$$

which tells us that either $A = 0$, in which case $\psi(x) = 0$, which is not a useful solution (it says that there is no partilce in the well at all!) or else $\sin(kL) = 0$, which gives an equation for k:

$$kL = n\pi, \quad n = 0, \pm 1, \pm 2, \ldots.$$

$$k_n = n\pi/L, \quad n = 1, 2, \ldots$$

We exclude the $n = 0$ possibility as that would give us, once again $\psi(x) = 0$, and we exclude the negative values of n as the will merely reproduce the same set of solutions (except with opposite sign4) as the positive values. Thus we have

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1, 2, \ldots$$

we have seen that the boundary conditions, have the effect of restricting the values of the energy of the particle to those Eq. The associated wave functions will be as, that is we apply the normalization condition to determine A (up to an inessential phase factor) which finally gives

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin(n\pi x/L) \quad 0 < x < L$$
$$= 0 \qquad\qquad\qquad x < 0, \quad x > L.$$

Particle in a three-dimensional box

In analogy with our infinite square-well potential ($U(x) = 0$ inside, $U(x) = \infty$ outside), let us consider a three-dimensional region in space (box) of equal sides of length L, with the same potential ($U(x) = 0$ inside, $U(x) = \infty$ outside).

We will consider the wave function as separable, that is, can be written as a product of the three independent dimensions x, y and z:
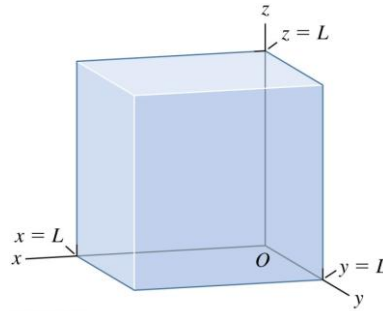
$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

The Schrödinger equation inside the box becomes

$$-\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{\partial^2 X(x)}{\partial x^2} + X(x)Z(z)\frac{\partial^2 Y(y)}{\partial y^2} + X(x)Y(y)\frac{\partial^2 Z(z)}{\partial z^2}\right) = EX(x)Y(y)Z(z)$$

Or, dividing by $X(x)Y(y)Z(z)$ we have:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2}\right) = E$$

This says that the total energy is contributed to by three terms on the left, each depending separately on x, y and z. Let us write $E = E_x + E_y + E_z$. Then this equation can be separated into three equations:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 X(x)}{\partial x^2} = EX(x)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Y(y)}{\partial y^2} = EY(y)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Z(z)}{\partial z^2} = EZ(z)$$

These obviously have the same solutions separately as our original particle in an infinite square well, and corresponding energies:

$$X_{n_X}(x) = C_X \sin\frac{n_X \pi x}{L} \quad (n_X = 1,2,3...) \qquad E_X = \frac{n_X^2 \pi^2 \hbar^2}{2mL^2} \quad (n_X = 1,2,3...)$$

$$Y_{n_Y}(y) = C_Y \sin\frac{n_Y \pi y}{L} \quad (n_Y = 1,2,3...) \qquad E_Y = \frac{n_Y^2 \pi^2 \hbar^2}{2mL^2} \quad (n_Y = 1,2,3...)$$

$$Z_{n_Z}(z) = C_Z \sin\frac{n_Z \pi z}{L} \quad (n_Z = 1,2,3...) \qquad E_Z = \frac{n_Z^2 \pi^2 \hbar^2}{2mL^2} \quad (n_Z = 1,2,3...)$$

A particle's wave-function is the product of these three solutions,

$$\psi(x,y,z) = X(x)Y(y)Z(z) = C\sin\frac{n_X \pi x}{L}\sin\frac{n_Y \pi y}{L}\sin\frac{n_Z \pi z}{L}$$

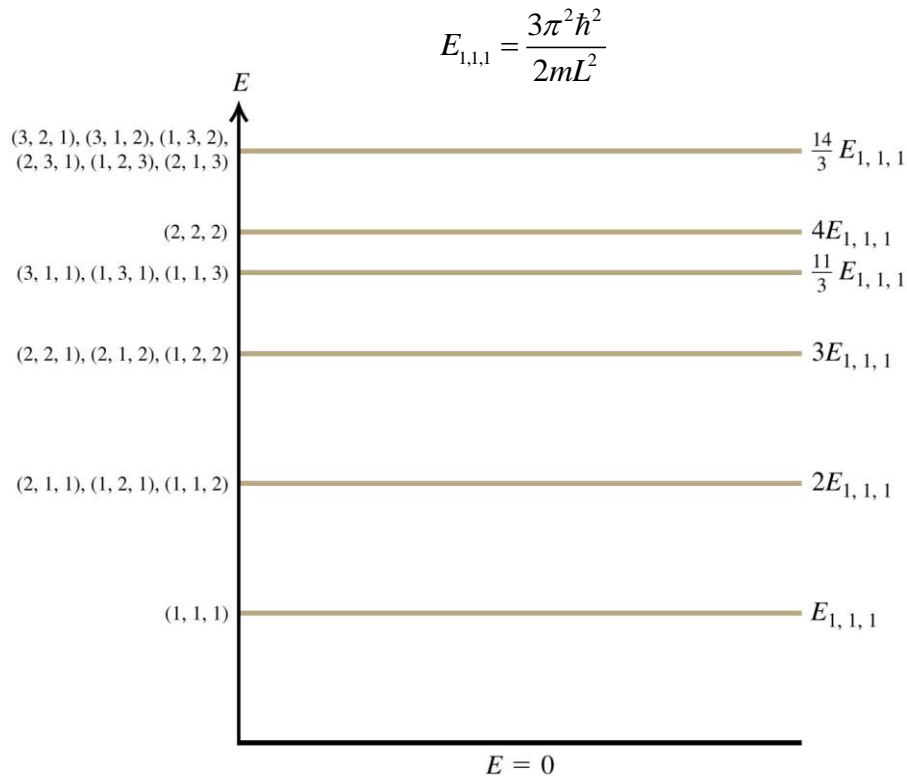We can use the three quantum numbers n_X, n_Y, and n_Z to label the stationary states (states of definite energy). Here is an example of a particle in three possible states (n_X, n_Y, n_Z) = (2, 1, 1), (1, 2, 1) or (1, 1, 2).

The three states shown here are *degenerate:* Although they have different values of n_X, n_Y, and n_Z, they have the same total energy E.

$$E = E_X + E_Y + E_Z = \frac{4\pi^2\hbar^2}{2mL^2} + \frac{\pi^2\hbar^2}{2mL^2} + \frac{\pi^2\hbar^2}{2mL^2} = \frac{3\pi^2\hbar^2}{mL^2}$$

Energy Degeneracy
- For a particle in a three-dimensional box, the allowed energy levels are surprisingly complex. To find them, just count up the different possible states.
- Here are the first 6 for an equal-sided box:

$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2mL^2}$$

States	Energy
(3, 2, 1), (3, 1, 2), (1, 3, 2), (2, 3, 1), (1, 2, 3), (2, 1, 3)	$\frac{14}{3}E_{1,1,1}$
(2, 2, 2)	$4E_{1,1,1}$
(3, 1, 1), (1, 3, 1), (1, 1, 3)	$\frac{11}{3}E_{1,1,1}$
(2, 2, 1), (2, 1, 2), (1, 2, 2)	$3E_{1,1,1}$
(2, 1, 1), (1, 2, 1), (1, 1, 2)	$2E_{1,1,1}$
(1, 1, 1)	$E_{1,1,1}$

$E = 0$

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If length of sides of box are different:

$$E = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2} + \frac{n_Z^2}{L_Z^2} \right) \frac{\pi^2\hbar^2}{2m}$$

(breaks the degeneracy)

1. For a one-dimensional particle in a box system, the solution of the Schrödinger equation leads to the quantized energy $E_n = \frac{n^2 h^2}{8mL^2}$. What is the zero-point energy for the system?

The zero-point energy (ZPE) for a quantum mechanical system is defined as the lowest possible energy allowed. In the case of the harmonic oscillator, the energy depends on the quantum number n, and n=1,2,3, ...

Thus, $ZPE = E_1 = \frac{1^2 h^2}{8mL^2} = \frac{h^2}{8mL^2}$.

2. The π-electron of a conjugated polyene molecule can be modeled as a particle in a box. Assuming a length of 0.6 nm for the one-dimensional box,

A. calculate the energy gap between the first excited state and the ground state for the electron.

For the one-dimensional particle in a box, the energy is given by

$$E_n = \frac{n^2 h^2}{8mL^2}.$$

The energy gap between the first excited state (n= 2) and the ground state (n=1) is

$$\Box E = E_2 \Box E_1$$

$$= \frac{2^2 h^2}{8m_e L^2} \Box \frac{1^2 h^2}{8m_e L^2}$$

$$= \frac{3h^2}{8m_e L^2}$$

$$= \frac{3 \times (6.626 \times 10^{\Box 34} Js)^2}{8 \times 9.1093897 \times 10^{\Box 31} kg \times (6 \times 10^{\Box 10} m)^2}$$

$$= 5.02 \times 10^{\Box 19} J.$$

B. what is the corresponding frequency of the photon absorbed as the electron makes a transition from the ground state to the first excited state?

$$\because \quad \Delta E = h\nu$$

$$\therefore \quad \nu = \Delta E / h = 5.02 \times 10^{-19} J / 6.626 \times 10^{-34} Js = 7.58 \times 10^{14} \ Hz$$

3. For a one-dimensional particle in a box system, the solution of the Schrödinger equation generates a wave function $\Psi_n(x) = \sqrt{\frac{2}{L}} \sin(\frac{n\pi}{L} x)$ for the state n. Verify that $\Psi_n(x)$ satisfies the Schrödinger equation.

For the one-dimensional particle in a box system, the Hamiltonian operator can be defined as

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

When we operate the Hamiltonian on the wavefunction, we obtain

$$\hat{H} \Box_n(x) = \Box \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sqrt{\frac{2}{L}}\sin(\frac{n\Box}{L}x)$$

$$= \frac{\hbar^2}{2m}(\frac{n\Box}{L})^2\sqrt{\frac{2}{L}}\sin(\frac{n\Box}{L}x)$$

$$= \frac{n^2 h^2}{8mL^2}\sqrt{\frac{2}{L}}\sin(\frac{n\Box}{L}x)$$

$$= E_n \Box_n(x).$$

Thus, the given wavefunction $\Psi_n(x)$ satisfies the Schrödinger equation.

4. For the ground state of the particle in a box system $\Psi_1(x) = \sqrt{\dfrac{2}{L}} \sin\dfrac{\pi x}{L}$, calculate the probability of finding the particle between x=0 and x=L/2.

[Useful integral: $\int \sin^2(\alpha x)dx = \dfrac{1}{2}x - \dfrac{1}{4\alpha}\sin(2\alpha x)$]

The probability of finding the particle between x=0 and x=L/2 is

$$p = \int_0^{L/l} \Psi^*(x)\Psi(x)dx = \frac{2}{L}\int_0^{L/2} \sin(\frac{\pi}{L}x)\sin(\frac{\pi}{L}x)dx = \int_0^{L/2} \sin^2(\frac{\pi}{L}x)dx.$$

According to the given above, $\int \sin^2(\alpha x)dx = \dfrac{1}{2}x - \dfrac{1}{4\alpha}\sin(2\alpha x)$,

we have

$$P = \frac{2}{L}[\frac{1}{2}x - \frac{L}{4\pi}\sin(\frac{2\pi}{L}x)] \Big|_0^{L/2}$$

$$= \frac{2}{L}\{\frac{L}{4} - \frac{L}{4\pi}[\sin(\frac{2\pi}{L}\frac{L}{2}) - \sin(0)]\}$$

$$= \frac{2}{L}\frac{L}{4} = \frac{1}{2}.$$

5. Find out the degeneracies of the lowest four energy levels for the three- dimensional particle in a box system with the dimension $L_x=L_y=L_z$.

The energy for the three-dimensional particle in a box system is given by

$$E = E_x + E_y + E_z = \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2} + \frac{n_z^2 h^2}{8mL_z^2}.$$

If $L_x=L_y=L_z$, the above expression reduces to

$$E = \frac{h^2}{8mL_x^2}(n_x^2 + n_y^2 + n_z^2).$$

The degeneracy of an energy level equals to the number of quantum states for the given energy. The lowest four energy levels and the corresponding degeneracy is listed below:

Energy Levels (in units of $\dfrac{h^2}{8mL_x^2}$)	Possible States $n_x\ n_y\ n_z$	Degeneracy
3	1 1 1	1
6	1 2 1, 2 1 1, 1 1 2	3
9	2 1 2, 2 2 1, 1 2 2	3
12	2 2 2	1