Basic postulates of Quantum mechanics and Schroedinger equation
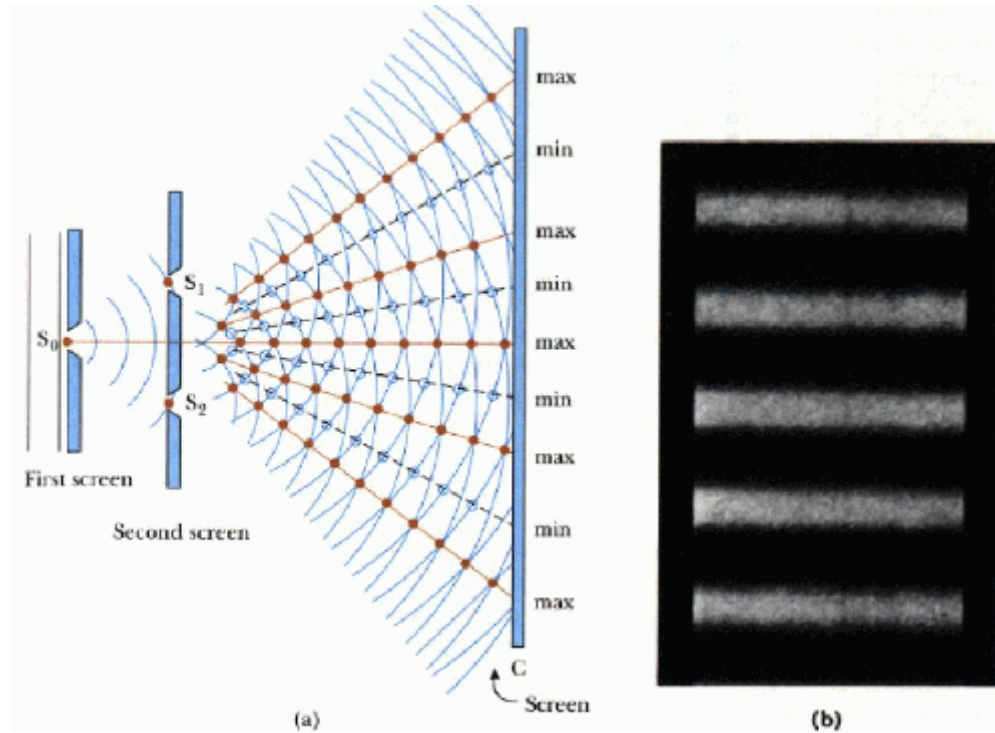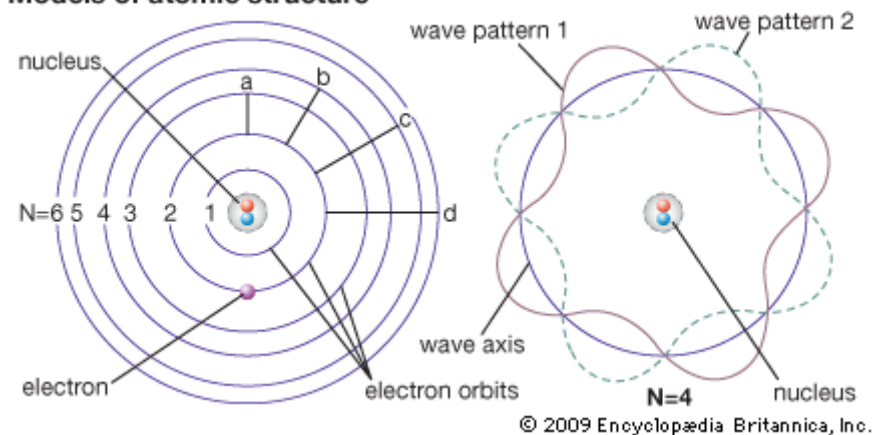
Basic ingredients of wave mechanics

The wave mechanics formulated such a way that the postulates and the experimental observations should come as outcome of the theory

Explanation of photo-electric effect says that energy of wave representing fundamental particles should be quantized

$$E = h\nu$$

Einstein's relation

De Broglie's further generalization of the wave-particle dual nature extended to electrons leads to

$$\lambda = \frac{h}{p}$$

Since wave nature of the particle are confirmed we may choose simple form of wave to represent the matter wave

Since wave nature of the particle are confirmed we may also choose simple form of wave to represent the matter wave

$$\Psi(x,t) = \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right)$$

We are familiar with such waves in a string under Cartesian coordinates

If we consider Bohr model of atoms such wave exist in spherical coordinates, therefore we may choose generalized coordinates for the formalism of the wave-mechanics with Cartesian as special case.

Schroedinger equation may be regarded an equation that gives form of the wave under correct potential. For example in Bohr model it is spherically symmetrical potential

Schroedinger equation is and equation from first principles of experimental observations listed as $E = h\nu$ and $\lambda = \dfrac{h}{p}$

It should be consistent with relation with energy momentum of a classical system

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

Since quantum waves interfere same as in the way classical wave the solutions they should be linear as in classical waves such as water waves.

Therefore if $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are two independent solution of the differential equation then

$$\Psi(x,t) = C_1 \Psi_1(x,t) + C_2 \Psi_2(x,t)$$

also must be solution to this equation – See Davisson and Germer experiment for interference of quantum waves

In case of free particles the function should be free sine or cosine wave with a constant frequency or wave length.

Combining the equation we have we can rewrite the classical equations as

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

$$E = h\nu$$

$$\frac{h^2}{2m\lambda^2} + V(x,t) = h\nu$$

$$\lambda = \frac{h}{p}$$

Using the change of variable

$$k = \frac{2\pi}{\lambda}$$ wavenumber

$$\omega = 2\pi\nu$$

$$\frac{\hbar^2 k^2}{2m} + V(x,t) = \hbar\omega$$

In order to maintain linearity assumption term on the differential equation depend only on the first power of $\Psi(x,t)$, i.e., all term should contain this function

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$$\Psi(x,t)=\sin 2\pi\left(\frac{x}{\lambda}-vt\right)$$

Using the change of variable $\quad k=\dfrac{2\pi}{\lambda} \qquad \omega=2\pi v$

$$\Psi(x,t)=\sin(kx-\omega t)$$

$$\frac{\hbar^2 k^2}{2m}+V(x,t)=\hbar\omega$$

In this equation if expressed in the form of the differential equation in order to get k^2 in the LHS we need second order differential operator with space

Also in order to get ω on RHS we need a differential equation that is first order in time.

We may propose an empirical form of the equation of a matter wave

$$\alpha\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t)=\beta\frac{\partial\Psi(x,t)}{\partial t}$$

Where α and β are undetermined constants

$$\alpha \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta \frac{\partial \Psi(x,t)}{\partial t}$$

$$\Psi(x,t) = \sin(kx - \omega t)$$

With the trial solution under constant potential V_0 the differential equation becomes

$$-\alpha \sin(kx - \omega t)k^2 + \sin(kx - \omega t)V_0 = -\beta \cos(kx - \omega t)\omega$$

This is possible in the special case of x, t where

$$\cos(kx - \omega t) = \sin(kx - \omega t)$$

This difficulty can be overcome by using a trial solution that is a combination of sine and cosine waves

$$\Psi(x,t) = \cos(kx - \omega t) + \gamma \sin(kx - \omega t)$$

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Finding the derivatives with space

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -k^2 \cos(kx - \omega t) - k^2 \gamma \sin(kx - \omega t)$$

Finding the derivatives with time

$$\frac{\partial \Psi(x,t)}{\partial t} = -\omega \sin(kx - \omega t) - \omega \gamma \cos(kx - \omega t)$$

Substituting in the equation with constant potential V_0

$$\alpha \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta \frac{\partial \Psi(x,t)}{\partial t}$$

Substituting in the equation with constant potential

$$\alpha \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta \frac{\partial \Psi(x,t)}{\partial t}$$

$$-\alpha k^2 \cos(kx - \omega t) - \alpha k^2 \gamma \sin(kx - \omega t) +$$

$$V_0 \cos(kx - \omega t) + V_0 \gamma \sin(kx - \omega t) =$$

$$-\beta \omega \sin(kx - \omega t) + \beta \omega \gamma \cos(kx - \omega t)$$

Placing together the coefficients of sine and cosine functions

$$\left(-\alpha k^2 + V_0 + \beta \omega \gamma\right) \cos(kx - \omega t)$$

$$\left(-\alpha k^2 \gamma + V_0 \gamma - \beta \omega\right) \sin(kx - \omega t) = 0$$

Meaningful solutions are possible when the coefficients vanish
leading to two algebraic equations

$$\left(-\alpha k^2 + V_0 + \beta \omega y\right)\cos\left(k x - \omega t\right)$$

$$\left(-\alpha k^2 y + V_0 y - \beta \omega\right)\sin\left(k x - \omega t\right) = 0$$

The two equations are

$$-\alpha k^2 + V_0 = -\beta \omega y$$

$$-\alpha k^2 + V_0 = \beta \omega / y$$

By subtracting one from other

$$0 = -\beta \omega y - \beta \omega / y$$

$$-y = 1/y$$

$$y^2 = -1$$

$$y = \pm i$$

Using this result we may obtain value of other constants

$$-\alpha k^2 + V_0 = -\beta \omega \gamma \qquad \gamma = \pm i$$

$$-\alpha k^2 + V_0 = \mp i \beta \omega$$

By comparing with the equation equating different parts of the energy

$$\frac{\hbar^2 k^2}{2m} + V_0 = \hbar \omega$$

$$\alpha = -\frac{\hbar^2}{2m}$$

$$\hbar = \mp i \beta \omega$$

$$\beta = \pm i \hbar$$

No specific difference is there for selection of either positive or negative sign for beta, therefore choosing positive sign as choice

$$\beta = +i \hbar$$

With the selection of constants we arrive at the form the equation

$$\alpha \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta \frac{\partial \Psi(x,t)}{\partial t}$$

With new value of the constants $\quad \alpha = -\frac{\hbar^2}{2m} \qquad \beta = +i\hbar$

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

This is the wave equation satisfying all assumption of the quantum mechanics

So far we have not proved that this equation is valid for any arbitrary potential other than free particle. In any arbitrary potential we need to prove the validity from the experimental results

Meaning and properties of wave functions

Wave functions give state of a system, the time evolution of a classical state is given time variation of the wave functions

$$\psi(\vec{r}, t)$$

Position vector in a three dimensional space

Wave function contains all information about the state of system

$\psi(\vec{r}, t)$ is interpreted as the probability amplitude of the particle's presence

$\vec{r}$ $\longrightarrow$ can take any value in the space

$d P(\vec{r}, t)$ $\longrightarrow$ Probability of finding a particles in the in the volume element $d r^3 = dx\, dy\, dz$

$\left| \psi(\vec{r}, t) \right|^2$ $\longrightarrow$ Is interpreted as probability density

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$$dP(\vec{r},t) = C\left|\psi(\vec{r},t)\right|^2 d^3r$$

Is interpreted as probability density

Normalization constant

Consider the wave function representing total solution of the Schrodinger equation

$$\psi(\vec{r},t)$$

The total solution of the system may be decomposed in terms multiple states in which system exist

$$\psi(\vec{r},t) = c_1\psi_1(\vec{r},t) + c_2\psi_2(\vec{r},t) + \ldots + c_n\psi(\vec{r},t)$$

complex coefficient

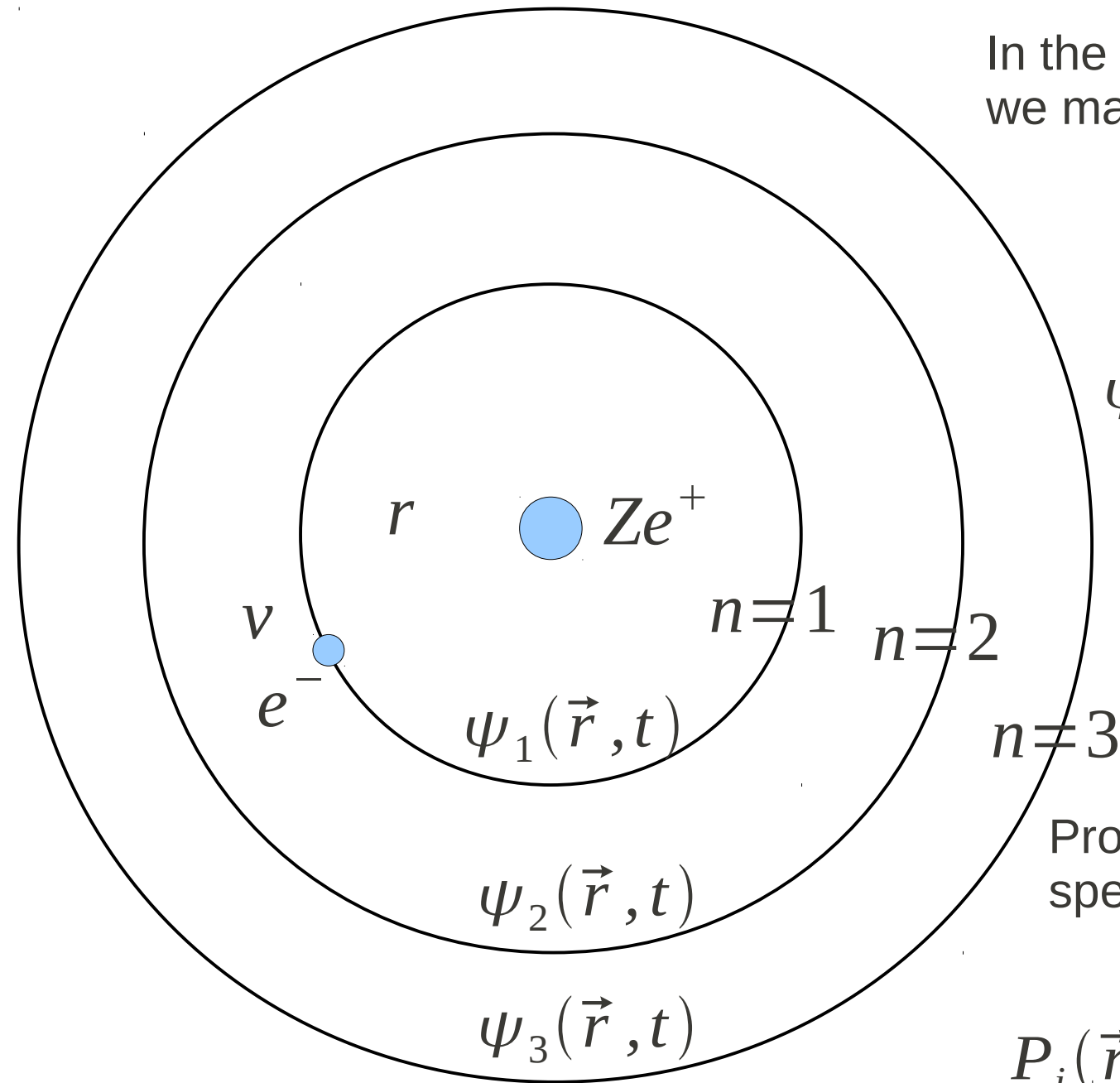$$\psi(\vec{r},t) = \sum_{i=1}^{n} c_i\psi_i(\vec{r},t)$$

In the case of atomic orbitals we may identify the following

$$\psi(\vec{r},t) = \sum_{i=1}^{n} c_i \psi_i(\vec{r},t)$$

Normalized wave function

r Ze^+

v

e^-

$\psi_1(\vec{r},t)$

$n=1$ $n=2$

$n=3$

$\psi_2(\vec{r},t)$

$\psi_3(\vec{r},t)$

Probability finding particle in a specific i th orbital is given by

$$P_i(\vec{r},t) = \frac{\left|c_i\right|^2}{\sum_{i=1}^{n}\left|c_i\right|^2}$$

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The general form the Schrodinger equation for three dimensional space

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

This is a fully phenomenological equation that can be arrived only by argument validity of which can verified only by experiments.

For a system consists of one particle the total probability of finding a particle anywhere in space is given by

$$\int dP(\vec{r},t)=1$$

In this case the wave function must be square integrable, that is

$$\int\left|\psi(\vec{r},t)\right|^2d^3r \quad \text{is finite}$$

$$\int\left|\psi(\vec{r},t)\right|^2d^3r=\frac{1}{C} \qquad \longrightarrow \text{is normalizatio n constant}$$

$$\int\left|\psi(\vec{r},t)\right|^2d^3r=1 \qquad \text{for normalized wave function}$$

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The state of classical particle at time t is determined by position $\vec{r}$ and the momentum $\vec{p}$

In Quantum mechanics infinite number of parmeters is associated with the state of a particle at any time $\psi(\vec{r},t)$ (infinite number of points are in this function)

Quantum mechanical description of the free particle

Schroedinger equation for a free particles

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

This differential equation is satisfied by the equation of the form

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$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

This differential equation can have trial solution

$$\psi(\vec{r},t)=Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

According to de Broglie hypothesis a plane wave should satisfy the condition

$$\hbar\omega=\frac{\hbar^2\vec{k}^2}{2m}\quad\longrightarrow\quad\text{wavevector}$$

Which is equivalent to classical condition $\quad E=\frac{p^2}{2m}$

$$\left|\psi(\vec{r},t)\psi^*(\vec{r},t)\right|=\left|Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}A^*e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right|^2$$

$$\left|\psi(\vec{r},t)\right|^2=\left|A\right|^2$$

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Plane wave predict uniform probability in the space

principle of super position says that plane wave with any wave length is a solution to Schroedinger equation

$$\psi(\vec{r},t) = A_1\psi_1(\vec{r},t) + A_2\psi_2(\vec{r},t) + ... + A_n\psi_n(\vec{r},t) ....$$

Normalization factor of the wave-function at a particular momentum

$$A_n = A_n(k)$$

For free particle there must be a continuous distribution of wavelengths, then the summation can be replaced with an integral

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}} \int g(\vec{k}) e^{i(\vec{k}\cdot\vec{r} - \omega(\vec{k})t)} d^3k$$

A constant arising from the normalizing factor of Fourier transform 3d

Now for the sake of simplicity let us assume plane waves parallel to x axis

$$\psi(x,t) = \frac{1}{(2\pi)^{1/2}} \int g(k) e^{i(\vec{k}x - \omega(k)t)} dk$$

If we choose at a particular origin of time this wave can be further simplifies as

$$\psi(x,0)=\frac{1}{(2\pi)^{1/2}}\int g(k)e^{ikx}dk$$

This is the mathematical representation a Fourier transform of function, $g(k)$ therefore the validity of the formula is not limited to free particle.

Form of wave packet at given time

$|g(k)|$

Δk

k_0

k
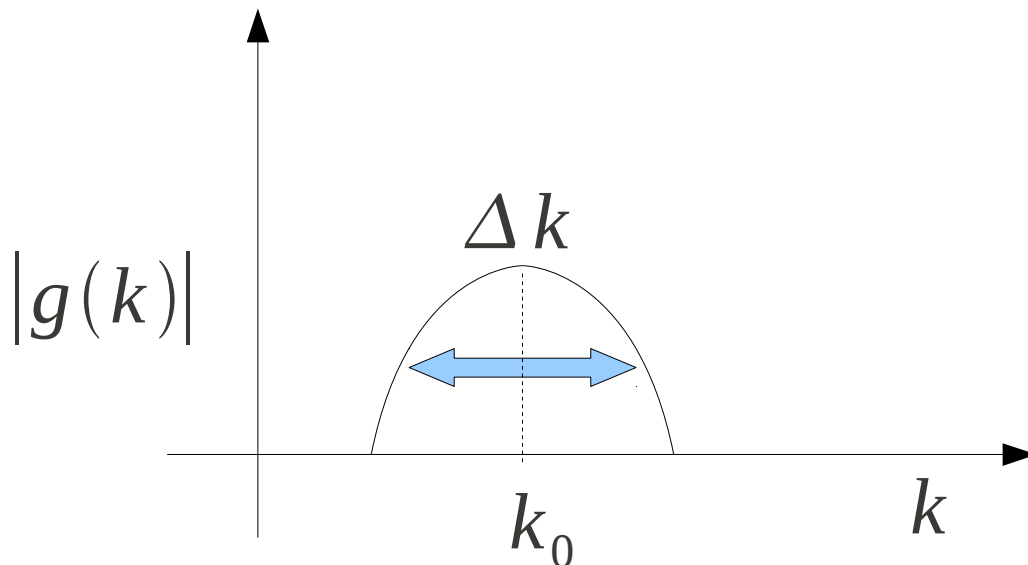
Behavior of such wave packets may be studies using simple case of interference of waves

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The qualitative behavior of the interference of the wave can be identified with interference of three waves

Let the wavenumber corresponding these three waves are given by
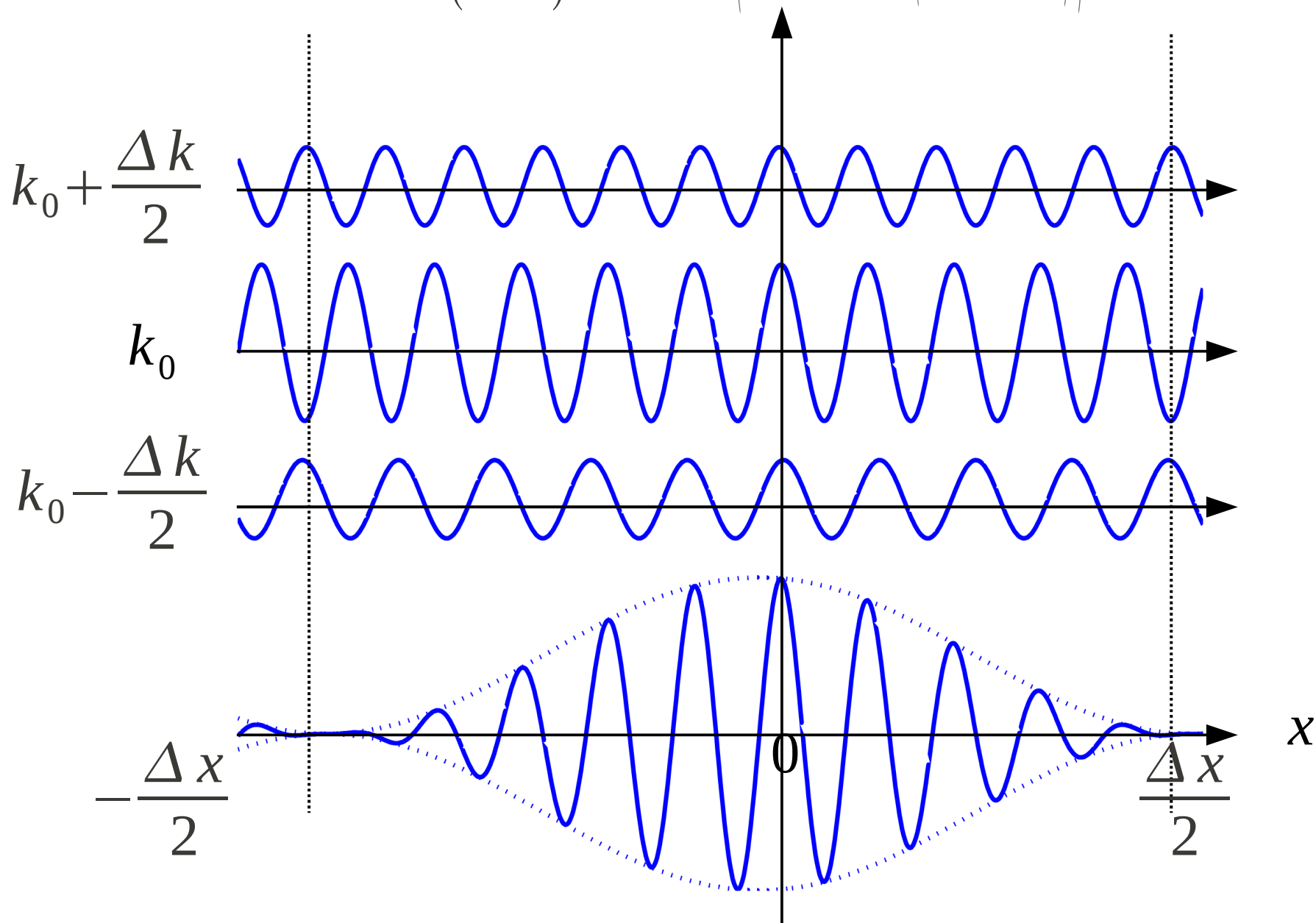
$$k_0 - \frac{\Delta k}{2}, \qquad k_0, \qquad k_0 + \frac{\Delta k}{2}$$

And let their amplitudes are proportional respectively $\frac{1}{2}, 1, \frac{1}{2}$

We then have

$$\psi(x,t) = \frac{g(k_0)}{(2\pi)^{1/2}} \left(e^{i k_0 x} + \frac{1}{2} e^{i\left(k_0 - \frac{\Delta k}{2}\right)x} + \frac{1}{2} e^{i\left(k_0 + \frac{\Delta k}{2}\right)x} \right)$$

$$= \frac{g(k_0)}{(2\pi)^{1/2}} e^{i k_0 x} \left(1 + \cos\left(\frac{\Delta k}{2} x\right) \right)$$

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$$\psi(x,t)=\frac{g(k_0)}{(2\pi)^{1/2}}e^{ik_0x}\left(1+\cos\left(\frac{\Delta k}{2}x\right)\right)$$

The interference between completely destructive when the phase difference between $e^{i k_0 x}$ and $e^{i \left(k_0 \pm \frac{\Delta k}{2} \right) x}$

out of phase $e^{i \left(\frac{\pm \Delta k}{2} \right) x} = e^{i \pi}$

$$\left| \frac{\Delta k}{2} \right| x = \pm \pi$$

That mean between two destructive interference we can have relation for the products

$$\Delta k \, \Delta x = 4 \pi$$

A single particle moving in space given as interference of collection waves of different wavelengths and frequencies which constructively interfere in a region around mean position of the particle – from this relation we may derive a relation between mean change in position and momentum of the particle

$$\Delta k \, \Delta x = 4 \pi$$

$$(k-k_0)(x-x_0)=4\pi$$

mean wavenumber

mean position

$$(\frac{2\pi}{\lambda}-\frac{2\pi}{\lambda_0})(x-x_0)=4\pi$$

Multiplying both sides with Planck's constant

$$(\frac{2\pi h}{\lambda}-\frac{2\pi h}{\lambda_0})(x-x_0)=4\pi h$$

$$(p-p_0)(x-x_0)=2h$$

$$\Delta p\,\Delta x=2h$$

This means that when we measure the momentum or position of a particle simultaneously we cannot measure the with accuracy specified by this relation

This result is spacial case of the Heisenberg Uncertainty principle which is in the form of an inequality

$$\Delta p \, \Delta x \geq \frac{\hbar}{2}$$

Take the case of a single plane wave

$$\psi(x,0) = A \, e^{ikx}$$

Since this wave have a well defined wavenumber the the uncertainty in the position is infinite

In the similar fashion for a point particle the uncertainty in the momentum is infinite

In stead of considering a stationary wave, if we take the case of time variation only in a wave we can get an uncertainty relation connecting energy and time associated with wave

$$\Delta E \, \Delta t \geq \frac{\hbar}{2}$$

Uncertainty relation and atomic parameters

Consider an electric field in the Coulomb field of an electron

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

$$V(r) = \frac{-k^2}{r}$$ → All constants of the problem

Assume that the wavefunction of ground state is described by a spherically symmetrical wave function let the average position of the electron is given by r_0

Therfore the potential energy becomes $\bar{V} \simeq \frac{-k^2}{r_0}$

Note that as electrons have wave nature position is not exact

If electron is confined in a space having dimension r_0 the momentum is given by

$$\Delta p \, \Delta x \geq \frac{\hbar}{2}$$

If electron is confined in a space having dimension r_0 the momentum is given by

$$\Delta p \, \Delta x \geq \frac{\hbar}{2}$$

$$\Delta p \geq \frac{\hbar}{r_0}$$

The average momentum in this case is zero however average kinetic energy is not zero

$$\bar{T} \geq T_{min} = \frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2mr_0^2}$$

$$\bar{V} \simeq \frac{-k^2}{r_0}$$

Total energy compatible with the uncertainty relation is given by

$$\bar{E} = \bar{T} + \bar{V} = \frac{\hbar^2}{2mr_0^2} - \frac{k^2}{r_0}$$

The value of r_0 is given by minimum of this function

Let

$$f(r) = \frac{a}{r_0^2} - \frac{b}{r_0}$$

$$f(r) = \frac{a}{r_0^2} - \frac{b}{r_0}$$

$$\frac{df(r_0)}{dr_0} = \frac{-2a}{r_0^3} + \frac{b}{r_0^2}$$

Minimum is at value $0 = \frac{-2a}{r_0^3} + \frac{b}{r_0^2}$

$$b r_0 = 2a \qquad k^2 r_0 = 2 \frac{\hbar^2}{2m}$$

$$r_0 = \frac{\hbar^2}{mk^2}$$

Substituting this in energy relation

$$\bar{E} = \frac{\hbar^2}{2mr_0^2} - \frac{k^2}{r_0} = \frac{\hbar^2}{2m\left(\frac{\hbar^2}{mk^2}\right)^2} - \frac{k^2}{\left(\frac{\hbar^2}{mk^2}\right)}$$

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$$\bar{E} = \cfrac{\hbar^2}{2m\left(\cfrac{\hbar^2}{mk^2}\right)^2} - \cfrac{k^2}{\left(\cfrac{\hbar^2}{mk^2}\right)}$$

$$= \frac{mk^4}{2\hbar^2} - \frac{mk^4}{\hbar^2} \qquad = -\frac{mk^4}{2\hbar^2} \qquad \textcolor{darkred}{k^2 = \frac{e^2}{4\pi\epsilon_0}}$$

$$\bar{E} = -\cfrac{m\left(\cfrac{e^2}{4\pi\epsilon_0}\right)^2}{2\hbar^2}$$

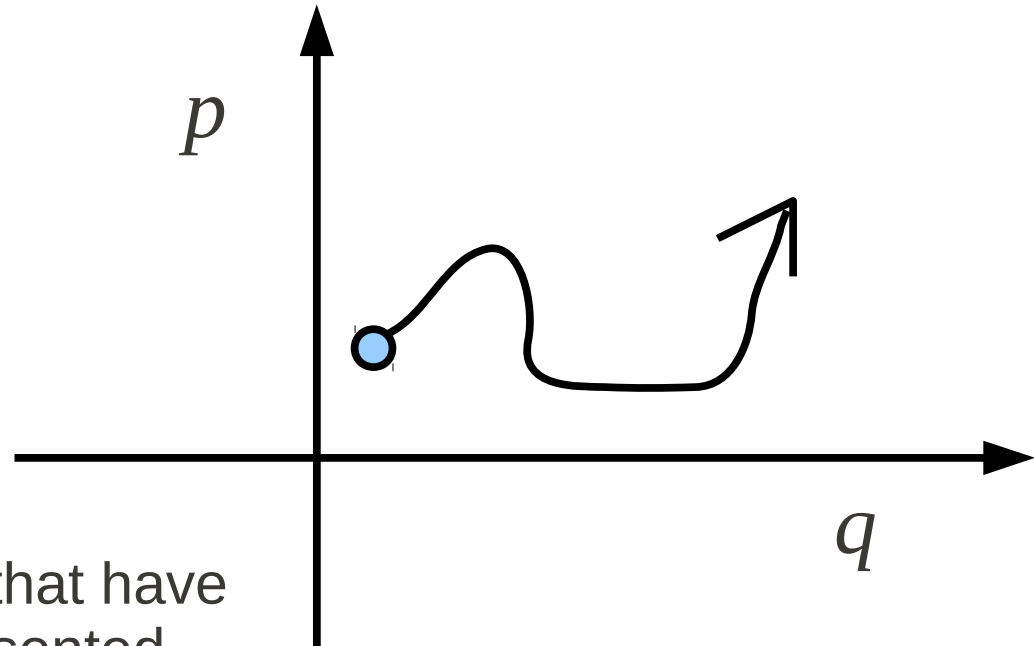$$E = -\left(\frac{1}{\left(4\pi\epsilon_0\right)^2}\frac{me^4}{2\hbar^2}\right)$$

This is the same expression we get the Bohr model for first orbit of Hydrogen

$$\textcolor{green}{E_n = -\left(\frac{1}{\left(4\pi\epsilon_0\right)^2}\frac{mZ^2e^4}{2\hbar^2}\right)\frac{1}{n^2}\Bigg|_{Z=1,n=1}}$$

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Phase space and Hilbert Space (q,p)

Hamiltonian dynamics is best represented in phase space which is similar to configuration space but include the momentum coordinates also

Representation of one dimensional motion in the phase space

In phase space for system that have n degrees freedom is represented by a point that have 2n coordinates

$$(q_{1}, q_{2,} .... q_{n}, p_{1,} p_{2,} .... p_{n})$$

In quantum mechanics state of system is represented in Hilbert space it is a form of the abstract linear vector space

$$\psi(\vec{r},t)=\sum_{i=1}^{n} c_i \psi_i(\vec{r},t)$$

In quantum mechanics state of system is represented in Hilbert space, each vector

$$\psi_i(\vec{r},t) \longrightarrow$$

Each vector is orthogonal to each other

A particular state of the system is given by $\quad \psi_i(\vec{r},t)$

In Hilbert space the inner product is defined as

$$\int \psi_i^*(\vec{r},t)\psi_j(\vec{r},t)d^3 r$$

When the state vectors are orthogonal

$$\int \psi_i^*(\vec{r},t)\psi_j(\vec{r},t)d^3 r=C\,\delta_{ij}$$

Summary - Postulates of Quantum Mechanics

Quantum mechanics is formulated based on these postulates, we have already discussed some these, therefore, we may summarize

1) State of system is represented by a vector in the Hilbert space

$$\psi_i(\vec{r},t)$$

2) Every measurable physical quantity is A is described by an operator $\hat{A}$ acting on the Hilbert space representing the system

Consider the example of a plane wave here wavefunction is given by

$$\psi(x,t)=A\,e^{i(kx-\omega t)}$$

As every information is contained in this function the momentum also may be obtained from this

Momentum of this plane wave is obtained from the wavefunction by application of the operator

$$\hat{p} = -i\hbar \vec{\nabla}$$

In one dimension $\hat{p} = -i\hbar \dfrac{\partial}{\partial x}$

Momentum of the plane wave is given by

$$\hat{p}\,\psi(r,t) = -i\hbar \frac{\partial}{\partial x} A\,e^{i(k_x x - \omega t)}$$

$$= \hbar k_x A\,e^{i(\vec{k}_x x - \omega t)}$$

$$= \hbar k_x \psi(x,t)$$

We can identify from the de Broglie relation that

$$\hbar k_x = \frac{h}{2\pi}\frac{2\pi}{\lambda_x} = p_x$$

$$\hat{p}\,\psi(r,t) = \hbar k_x \psi(x,t) = p_x \psi(x,t)$$

$$\hat{p}\,\psi(x,t)=p_x\,\psi(x,t)$$

This is the form of an eigenvalue equation – just like in the theory of matrices and linear algebra

The general form of this equation is

$$\hat{A}\,\psi(\vec{r},t)=a\,\psi(\vec{r},t)$$

operator vector Number vector

This form is called eigenvalue equation familiar in matrix form

Operator transform a vector (wavefunction) to a new one. If the transformation involves only the scaling of a vector (wavefunction) then it is the eigenvalue of the problem

Eigenvalue problem is also a part of matrix algebra

In the same manner in which we obtain the value of momentum we can obtain other observables like position and energy from the wave function- take case of 1d plane wave wavefunction $\psi(x,t)=A e^{i(kx-\omega t)}$

$$\hat{x}\,\psi(x,t)=x\,\psi(x,t)$$

form of the operator $\hat{x}=x$

$$\hat{x}\,A\,e^{i(k_x x-\omega t)}=x\,A\,e^{i(k_x x-\omega t)}=x\,\psi(x,t)$$

The energy operator is given as

$$\hat{E}\,\psi(x,t)=e\,\psi(x,t)$$

form of the operator $\quad \hat{E}=i\hbar\dfrac{\partial}{\partial t}$

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=i\hbar\frac{\partial}{\partial t}A\,e^{i(kx-\omega t)}=\hbar\omega\,A\,e^{i(kx-\omega t)}$$

Eigenvalue of energy

Now take the case of full wavefunction representing the state of a system

According the **principle of super position** the system exist in a super position of all possible states of the system

$$\psi(\vec{r},t) = \sum_{i=1}^{n} c_i \psi_i(\vec{r},t)$$

$n \longrightarrow$ can have finite or infinite number of states

When the states are orthogonal we have the relation

$$\int \psi_i^*(\vec{r},t)\psi_j(\vec{r},t)d^3r = C\delta_{ij}$$

When they are orthogonal and normalized

$$\int \psi_i^*(\vec{r},t)\psi_j(\vec{r},t)d^3r = \delta_{ij}$$

When an observation is made on the system the system falls into one of the possible states of the system

$$\psi(\vec{r},t) = \psi_i(\vec{r},t)$$

with probability $|c_i|^2$

Now the postulate regarding the measurement can be stated as

In the case of discrete solution of the wave function we can write

$$\psi(\vec{r},t)=\sum_{i=1}^{n} c_i \psi_i(\vec{r},t) \qquad \int \psi^*(\vec{r},t)\psi(\vec{r},t)d^3r=1$$

Each of the state vectors obey eigenvalue equation

$$\hat{A}\psi_i(\vec{r},t)=a_i\psi_i(\vec{r},t)$$

When the operator operates on the total wave function of the system the probability finding a particular eigenvalue $P(a_i)$ is given by

$$P(a_i)=|c_i|^2=\left|\int \psi_i^*(\vec{r},t)\psi(\vec{r},t)d^3r\right|^2$$

$$=\left|\int \psi_i^*(\vec{r},t)\sum_{i=1}^{n} c_i \psi_i(\vec{r},t)d^3r\right|^2$$

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4) When the physical quantity A is measured on a system in the normalized state $\psi(\vec{r},t)$ the probability of finding the *non-degenerate* eigenvalue a_i of the corresponding observable is

$$P(a_i) = \left| \int \psi_i^*(\vec{r},t)\psi(\vec{r},t)\, d^3 r \right|^2$$

where $\psi_i(\vec{r},t)$ is the normalized eigenvector of $\hat{A}$ associated eigenvalue a_i

5) time evolution of the state vector $\psi(\vec{r},t)$ is governed by the Schroedinger equation

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

Hamiltonian operator of the system: corresponding observable give total energy of the system

Expectation value

The expectation value is the mathematical expectation, for the result of a single measurement. On otherwise, it is the average of results of large number of measurements on an independent system

$$\langle \vec{r} \rangle = \int \vec{r}\, P(\vec{r}, t)\, d^3 r$$

$$= \int \psi^*(\vec{r}, t)\, \vec{r}\, \psi(\vec{r}, t)\, d^3 r$$

Particle in a time–independent scalar potential

Separation of variables in Schrodinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Let us look if there exist solutions of the form

$$\psi(\vec{r},t)=\phi(\vec{r})\chi(t)$$

Let us look if there exist solutions of the form

$$-\chi(t)\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+\chi(t)V(\vec{r},t)\phi(\vec{r})=i\hbar\phi(\vec{r})\frac{\partial\chi(t)}{\partial t}$$

Dividing all terms by the relation $\phi(\vec{r})\chi(t)$

$$-\frac{1}{\phi(r)}\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+V(\vec{r},t)=i\hbar\frac{1}{\chi(t)}\frac{\partial\chi(t)}{\partial t}$$

space dependent part
time dependent part

$$-\frac{1}{\phi(r)}\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+V(\vec{r},t)=i\hbar\frac{1}{X(t)}\frac{\partial X(t)}{\partial t}$$

The space dependent part and time dependent part of the can be equated if and only if both sides of the equation can be equated to a constant we choose that constant to be $\hbar\omega$

$$-\frac{1}{\phi(r)}\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+V(\vec{r},t)=i\hbar\frac{1}{X(t)}\frac{\partial X(t)}{\partial t}$$

$$-\frac{1}{\phi(r)}\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+V(\vec{r},t)=\hbar\omega$$

$$i\hbar\frac{1}{X(t)}\frac{dX(t)}{dt}=\hbar\omega$$

The time dependent part can be solved get solution in the differential equation as

$$i\hbar \frac{1}{\chi(t)} \frac{d\chi(t)}{dt} = \hbar\omega$$

$$\Rightarrow \frac{d\chi(t)}{\chi(t)} = -i\omega\, dt$$

By integration

$$\chi(t) = A\, e^{-i\omega t}$$

We may set the constant as one and move that part to space dependent solution, that is

$$\psi(\vec{r},t) = \phi(\vec{r})\, e^{-i\omega t}$$

Similarly the space dependent part should satisfy the differential equation

$$-\frac{1}{\phi(r)} \frac{\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + V(\vec{r},t) = \hbar\omega$$

$$-\frac{\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + V(\vec{r},t)\phi(r) = \hbar\omega\,\phi(r)$$

A stationary state is state with well defined energy $\hbar\omega = E$

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})+V(\vec{r},t)\phi(r)=E\phi(r)$$

In the compact form

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r},t)\right]\phi(r)=E\phi(r)$$

The LHS of the equation may be written as

$$\hat{H}\phi(r)=E\phi(r)$$

Operator form of the Hamiltonian

$\hat{H}$ is a linear operator since

$$\hat{H}\left[\lambda_1\phi_1(r)+\lambda_1\phi_1(r)\right]=\lambda_1\hat{H}\phi_1(r)+\lambda_1\hat{H}\phi_1(r)$$

$$\hat{H}\phi(r)=E\phi(r)$$

Eigenvalue equation of a linear operator

Required properties of eigenfunctions (wavefunctions)

$$\psi(x)$$

finite

$$\frac{d\,\psi(x)}{d\,x}$$

single valued

continuous

This is a fundamental requirement as the evaluation of position and momentum involves these conditions for conservation and for making these quantities well defined

f(x)

Not finite

0   x_0 x

f(x)

Not single valued

0   x_0 x

f(x)

Not continuous

0   x_0 x