

The condition

$$\int_{-\infty}^{\infty} P(x,t) dx = 1$$

is satisfied for all $t \in \mathbb{R}$.

$$\frac{d}{dt} \int_{-\infty}^{\infty} P(x,t) dx = 0.$$

linear eq
 $y = ax + b$
An equation b/w two variables that gives a straight line when plotted on a graph

homogeneous if $g(x) = 0$
if $g(x) \neq 0$ then called non-homogeneous

if $g(x) = a$ — ~~non-homogeneous~~
if $g(x) \neq 0$ then called non-homogeneous or inhomogeneous

Atomic Transitions:

Rutherford's Atomic Model:

According to Rutherford's atomic model, the orbital motion of an electron round the nucleus represents an accelerated motion, so that the electron should continuously emit electromagnetic radiation and as a result should lose energy. At the end, the electron would spiral into the nucleus. Since the orbital frequency would change continuously, the

emission spectra would be continuous. But the experiments reveal that the emission spectra are discrete, whose frequencies satisfy the generalized Balmer formula

$$\nu = R_y \left[\frac{1}{m^2} - \frac{1}{n^2} \right]$$

where R_y is the Rydberg constant, m, n are natural numbers.

Bohr Model of Hydrogen Atom

In order to explain the discrete spectra, Bohr postulated following rules:

- 1) The electron moves only in those orbits for which the magnitude of its angular momentum is an integral multiple of h :

$$|L| = L = mvr = \frac{n\hbar}{2\pi} = n\hbar$$

where $n = 1, 2, 3, \dots$

2) The electron makes discrete transitions from one ~~state~~ stable state to another and as a result radiation is emitted or absorbed. If the transition of an electron occurs from an orbit of energy E_n to an orbit of energy E_m , then the energy difference is radiated as a single photon of energy

$$h\nu_{nm} = h\omega_{nm} = E_n - E_m$$

Let us consider the example of an atom and apply Bohr's rule to get some insight. The electron of mass m is moving around the nucleus of charge Ze in a circular orbit of radius r , with linear velocity V , then according to Newton second Law, $F = m_e a_r = \frac{mV^2}{r} = F_c$.

19-a and electrostatic force, $F_e = \frac{ze^2}{r^2}$

Hence for equilibrium condition

$$F_c = F_e$$

$$\frac{mv^2}{r} = \frac{ze^2}{r^2}$$

or.

$$\frac{1}{2} mv^2 = \frac{ze^2}{2r} \quad \text{--- (1)}$$

From Bohr's quantization condition

$$mvr = n\hbar$$

$$\Rightarrow v = \frac{n\hbar}{mr}$$

Inserting in expression (1) get.

$$r = r_n = \frac{n^2 \hbar^2}{me^2 z}$$

This gives the radius of the orbit of the electron in n th state.

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The radius of the orbit of an electron of hydrogen atom in ground state is

$$\boxed{\frac{z=1}{n=1}} \quad r_1 = \frac{h^2}{m e^2} = 0.528 \times 10^{-8} \text{ cm}$$
$$= 0.528 \text{ \AA}$$

This is known as Bohr radius.
The total energy of the electron is

$$E = \underbrace{\frac{1}{2} m v^2}_{\text{K.E.}} + \underbrace{\left(- \frac{z e^2}{r} \right)}_{\text{P.E.}}$$

$$E = \frac{z e^2}{2r} - \frac{z e^2}{r} = - \frac{z e^2}{2r}$$

So the energy of the electron in its n th state is

$$E_n = - \frac{z e^2}{2 r_n} = - \frac{m z^2 e^4}{2 n^2 h^2}$$

The Bohr's second rule gives

$$h \omega_{nm} = \frac{m z^2 e^4}{2 h^2} \left[\frac{1}{m^2} - \frac{1}{n^2} \right] = E_n - E_m$$

or

$$\omega_{nm} = \frac{m z^2 e^4}{2 h^2} \left[\frac{1}{m^2} - \frac{1}{n^2} \right]$$

This explains the discrete spectra of atoms.

$$V_{nm} = \frac{m e^2 e^4}{4\pi \hbar^3} \left[\frac{1}{m^2} - \frac{1}{n^2} \right]$$

$$\boxed{h^2 v_{nm} = R_y \left[\frac{1}{m^2} - \frac{1}{n^2} \right]}$$

Wilson-Sommerfeld Quantization Rule

The Bohr's quantization rule is general for multiply periodic systems through Wilson-Sommerfeld quantization. The multiply periodic systems are with several degrees of freedom whose motion can be represented by

generalized coordinates q_i and

its conjugate momenta p_i

study of rigid body dynamics of multibody system

classical integral $\oint p_i dq_i$, the quantization condition extends over a complete period for each q_i

$$\oint p_i dq_i = n_i h, \quad i = 1, 2, 3, \dots$$

refers to the linear momenta

Parameters that describe the configuration of the system relative to some arbitrary

where n_i 's are integers and the integral ^(close) extends over a complete period for each q_i .

Bohr-Quantization Conditions

The condition for quantization of angular momentum in an atom is

$$mvr = \frac{nh}{2\pi}$$

$$2\pi r = \frac{nh}{mv}$$

$$2\pi r = n\lambda$$

It is the distance around the circle = $\pi \times \text{diameter}$
 $d = 2r$
 $= 2\pi r$
 $\lambda = \frac{h}{mv} = \frac{h}{p}$

$2\pi r$ is the circumference of a circular orbit of radius r . The rule states that the length of the circumference of the orbit is an integral multiple of wavelength.



circumference

$$2\pi r = \lambda$$



$$2\pi r = 2\lambda$$



$$2\pi r = 3\lambda$$

The Schrödinger Equation \Rightarrow

The Schrödinger equation is the basic equation of quantum mechanics which describes propagation of matter waves. Let us consider a single free particle of mass "m" moving in a +x-direction with momentum p.

The energy of the particle is

$$E = \frac{p^2}{2m} \quad \text{--- (1)}$$

In quantum mechanics, a particle is described by a wavefunction $\psi(x,t)$. A typical wave of wave number k and angular frequency $\omega = E/\hbar$ is given by

$$\begin{aligned} \psi(x,t) &= A e^{i(kx - \omega t)} \\ &= A e^{i(px - Et)/\hbar} \quad \text{--- (2)} \end{aligned}$$

where A is a constant.

The angular frequency of matter waves is connected with the wave number is given by

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

or.
$$\omega = \frac{\hbar k^2}{2m}$$

Effect of dispersion in a medium on the properties of a wave traveling within that medium.

This is known as dispersion relation.

Now differentiating equation (2) with respect to t , one gets

$$\frac{\partial \psi}{\partial t} = -i \frac{E}{\hbar} \psi$$

or
$$i \hbar \frac{\partial \psi}{\partial t} = E \psi \quad \text{--- (3)}$$

Again differentiating equation (2) two times with respect to x , one gets:

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

or.

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

or

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E \psi, \quad E = \frac{p^2}{2m}$$

or.

$$\boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i \hbar \frac{\partial \psi}{\partial t}} \quad \text{--- (4)}$$

because

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

This is time-dependent Schrödinger equation for a particle of mass "m". It is a linear and homogeneous 1-D particle differential equation for wave variable $\psi(x, t)$. In particular, it is satisfied by wave-packets of the form

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p) e^{i/\hbar (px - Et)} dp$$

which is associated with a localized free particle moving in 1-D. If we make the replacement

$$p \rightarrow i\hbar \frac{\partial}{\partial x}$$

$$E \rightarrow i\hbar \frac{\partial}{\partial t}$$

in classical equation (1)

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

and act all the differential operators on the wave function $\psi(x,t)$, we get eqn (4) which represents the quantum mechanical analogue of classical equation (1).

In 3-Dimensions, the time-dependent Schrodinger equation is

$$i\hbar \frac{\partial}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right)$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \psi$$

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where

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

In three dimensions, the wavepacket associated with a localized free particle is

$$\psi(x, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} A(\underline{p}) e^{i(\underline{p} \cdot \underline{x} - Et/\hbar)} d\underline{p}$$

In classical mechanics the quantity $p^2/2m$ is called the Hamiltonian of free particle. In quantum mechanics the Hamiltonian of a particle is represented by the differential operator

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

known as the Hamiltonian operator of a free particle of mass m .

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The time-dependent Schrödinger equation can be written as

$$H\psi = E\psi$$

The free particle Schrödinger equation can be generalized to the case of a particle moving in an external field of force

$$F(x,t) = -\nabla V(x,t)$$

In this case the total energy of the particle is

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

The replacement

$$E \rightarrow i\hbar \frac{\partial}{\partial t}$$

$$p \rightarrow -i\hbar \nabla$$

gives

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x,t) \right] \psi$$

This is time-dependent Schrödinger wave equation for a particle moving

24-a in a potential $V(\underline{x}, t)$ anal

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{x}, t)$$

is the corresponding Hamiltonian operator.

Examples: 1.2, 1.3, 1.4, 1.5, 1.6, 1.7

Solved Problems: 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.9
1.11, 1.12, 1.13

Exercise: 1.1, 1.2, 1.3, 1.7, 1.8, 1.10, 1.11, 1.12
1.13, 1.14, 1.15, 1.21, 1.22, 1.33