24/08/2020

C11T: Quantum Mechanics and Applications

Schrodinger equation:

Time dependent Schrodinger equation. Time independent Schrodinger equation

General discussion of bound states in an arbitrary potential

General considerations. 1D square well potential. 1D SHO.

Quantum theory of hydrogen-like atoms

Angular momentum operator & quantum numbers; Radial wave functions from Frobenius method; Shapes of the PD for ground & first excited states; Orbital AM QN *l, m*; s, p, d,.. shells.

Atoms in Electric & Magnetic Fields

Atoms in External Magnetic Fields

Many electron atoms

C11T: Quantum Mechanics and Applications

Suggested Readings:

1. A Textbook of Quantum Mechanics, P.M. Mathews and K. Venkatesan, 2nd Ed., 2010, Mc Graw Hill
2. Quantum Mechanics, Robert Eisberg and Robert Resnick, 2ndEdn., 2002,Wiley.
3. Quantum Mechanics, Leonard I. Schiff, 3rdEdn. 2010, Tata McGrawHill.
4. Quantum Mechanics, G. Aruldhas, 2nd Edn. 2002, PHI Learning of India.
5. Quantum Mechanics, Bruce Cameron Reed, 2008, Jones and Bartlett Learning.
6. Quantum Mechanics: Foundations & Applications, Arno Bohm, 3rd Edn., 1993,Springer
7. Quantum Mechanics for Scientists & Engineers, D.A.B. Miller, 2008, Cambridge University Press.

Additional Books for Reference

1. Quantum Mechanics, Eugen Merzbacher, 2004, John Wiley and Sons, Inc.
2. Introduction to Quantum Mechanics, D.J. Griffith, 2nd Ed.2005, Pearson Education
3. Quantum Mechanics, Walter Greiner, 4th Edn., 2001, Springer

C11T: Quantum Mechanics and Applications

Schrodinger equation

Time dependent Schrodinger equation

Dynamical evolution of a quantum state

Properties of Wave Function.

Interpretation of Wave Function.

Probability and probability current densities in 3D.

Conditions for Physical Acceptability of Wave Functions.

Normalization. Linearity and Superposition Principles.

Eigenvalues and Eigen functions.

Position, momentum and Energy operators.

Commutator of position and momentum operators.

Expectation values of position and momentum.

Wave Function of a Free Particle.

BOOK

Mainly

Quantum Mechanics: Theory and Applications

By **Ajay Ghatak**

Chapters 4 & 5.

Other books: Aruldhas (Ch-2), Ghoshal (Ch-V)

Time dependent Schrodinger equation

1. De-Broglie hypothesis:

Photoelectric effect (1905, Einstein, Germany) and Compton Effect (1923, Compton, America) showed that light/electromagnetic wave has particle nature.

Luis De-Broglie (France) proposed that like light wave, subatomic material particles may also have dual character i.e. wave like nature along with corpuscular nature.

De Broglie proposed (1925) that the wavelength and frequency of the wave associated with a subatomic material particle of momentum p and energy E are given by:

$$\boldsymbol{\lambda = \frac{h}{p}} \quad \text{…………} \ (1.1) \qquad\qquad \boldsymbol{\nu = \frac{E}{h}} \quad \text{…………}(1.2)$$

Time dependent Schrodinger equation

1. De-Broglie hypothesis:

The wave associated with a particle is called de Broglie wave or matter wave.

From (1.1) & (1.2):

$$\boldsymbol{p} = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar \boldsymbol{k} \quad \ldots(1.3) \text{ and } \quad \boldsymbol{E} = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\boldsymbol{\omega} \quad \ldots(1.4)$$

$\boldsymbol{k}$ is called wave number or wave vector or propagation constant. Dimension: $\boldsymbol{L}^{-1}$

De Broglie wave is not a mechanical wave like sound. Also it is not an electromagnetic wave like light.

Time dependent Schrodinger equation

2. Simplest wave:

It is assumed that the trajectory of a particle can be described by a wave function. This wave function will have large amplitude in the regions where the particle is more likely to be present and the amplitude will be small, where the existence of the particle is less likely.

Let us proceed with the **simplest wave**, which **is a plane monochromatic wave**:

$$\psi(\vec{\boldsymbol{r}}, t) = Ae^{i(\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}-\omega t)} \quad \ldots\ldots\ldots (2.1)$$

This is the equation of a wave, having amplitude A and propagation vector $\vec{\boldsymbol{k}} = (2\pi/\lambda)\hat{\boldsymbol{k}}$ and travelling along $\vec{\boldsymbol{k}}$ with velocity $v = \omega/|\vec{\boldsymbol{k}}|$.

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation:

If the wave travels along x-axis then, $\vec{\boldsymbol{k}} = k\hat{\boldsymbol{x}}$ and $\vec{\boldsymbol{k}} \cdot \vec{\boldsymbol{r}} = kx$ and the equation becomes:

$$\psi(x,t) = Ae^{i(kx-\omega t)} \;\ldots\ldots\ldots(2.2)$$

Let us differentiate (2.2) as follows:

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

$$\Rightarrow \boldsymbol{i}\hbar\frac{\boldsymbol{\partial}}{\boldsymbol{\partial t}}\psi(\boldsymbol{x},\boldsymbol{t}) \;=\hbar\boldsymbol{\omega}\psi(\boldsymbol{x},\boldsymbol{t}) \qquad (2.3)$$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation:

$$-i\hbar\frac{\partial}{\partial x}\psi(x,t) = -i\hbar\frac{\partial}{\partial x}Ae^{i(kx-\omega\ )} = \hbar kAe^{i(kx-\omega t)} = \hbar k\psi(x,t) = p\psi(x,t) \quad ..(2.4)$$

From De Broglie hypothesis: $\hbar k = p$ [from (1.4)]

$$-i\hbar\frac{\partial}{\partial x}\left(-i\hbar\frac{\partial}{\partial x}\psi(x,t)\right) = \hbar^2k^2\psi(x,t)$$

$$\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2\psi(x,t) = \frac{\hbar^2k^2}{2m}\psi(x,t)$$

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{\hbar^2k^2}{2m}\psi(x,t) \quad \ldots\ldots\ldots\ldots (2.5)$$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation:

According to de Broglie hypothesis and $\hbar\omega = E$ and $\hbar k = p$ [from (1.3) & (1.4)]

Therefore (2.3) and (2.5) reduce to:

$i\hbar\frac{\partial}{\partial t}\psi(x,t) = E\psi(x,t)$ …….(2.6) $\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{p^2}{2m}\psi(x,t)$ ………(2.7)

Also for a free particle: $\frac{p^2}{2m}$ = total mechanical enetgy E …… (2.8)

From (2.6), (2.7) and (2.8) we can write:

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \qquad \text{…... (2.9)}$$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation:

Eqn. (2.9) is the time dependent Schrodinger eqn. for the 1D motion of a free particle.

Consider eqns.

$$-i\hbar\frac{\partial}{\partial x}\psi(x,t) = p\psi(x,t) \quad \ldots\ (2.4) \qquad i\hbar\frac{\partial}{\partial t}\psi(x,t) = E\psi(x,t) \quad \ldots(2.6)$$

These eqns. indicate that the dynamical variables or observables linear momentum $\boldsymbol{p}$ and total energy $\boldsymbol{E}$ can respectively be represented by the operators $-i\hbar\frac{\partial}{\partial x}$ and $i\hbar\frac{\partial}{\partial t}$.

Operator		Observable
$-i\hbar\frac{\partial}{\partial x}$	$\longrightarrow$	$\boldsymbol{p}$
$i\hbar\frac{\partial}{\partial t}$	$\longrightarrow$	$\boldsymbol{E}$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation:

$-i\hbar\frac{\partial}{\partial x}$ and $i\hbar\frac{\partial}{\partial t}$ are respectively called linear momentum operator and total energy operator and are represented by the symbols $\hat{p}$, $\hat{E}$.

$$\begin{tikzcd}
\text{Observable} & \text{Operator} & \text{Operator Symbol} \\
p \arrow[r] & -i\hbar\frac{\partial}{\partial x} \arrow[r] & \hat{p} \\
E \arrow[r] & i\hbar\frac{\partial}{\partial t} \arrow[r] & \hat{E}
\end{tikzcd}$$

More on operators will be discussed later on.

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

Equation of a monochromatic plane wave: $\psi(\vec{\boldsymbol{r}},t) = Ae^{i(\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}-\omega t)}$ ……… (2.1)

Which can be written as: $\psi(\vec{\boldsymbol{r}},t) = Ae^{i(\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}-\omega t)} = Ae^{i[(k_x x+k_y y+k_z z)-\omega t]}$

$$\boldsymbol{i}\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t) = \boldsymbol{i}\hbar\frac{\partial}{\partial t}Ae^{i[(k_x x+k_y y+k_z z)-\omega t]} = \hbar\omega\psi(\vec{\boldsymbol{r}},t)$$

$$-\boldsymbol{i}\hbar\frac{\partial}{\partial x}\psi(\vec{\boldsymbol{r}},t) = -\boldsymbol{i}\hbar\frac{\partial}{\partial x}Ae^{i[(k_x x+k_y y+k_z z)-\omega t]} = \hbar k_x\psi(\vec{\boldsymbol{r}},t)$$

$$-\boldsymbol{i}\hbar\frac{\partial}{\partial y}\psi(\vec{\boldsymbol{r}},t) = \hbar k_y\psi(\vec{\boldsymbol{r}},t); \qquad -\boldsymbol{i}\hbar\frac{\partial}{\partial z}\psi(\vec{\boldsymbol{r}},t) = \hbar k_z\psi(\vec{\boldsymbol{r}},t)$$

Note that $\boldsymbol{k_x\hat{x} + k_y\hat{y} + k_z\hat{z} = \vec{k}}$; Also: $\boldsymbol{\hbar k_x = p_x}$ etc.

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

$$\boldsymbol{i}\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t)=\hbar\omega\psi(\vec{\boldsymbol{r}},t)=\boldsymbol{E}\psi(\vec{\boldsymbol{r}},t)\ldots\ (2.10)$$

$$\left.\begin{aligned}-\boldsymbol{i}\hbar\frac{\partial}{\partial x}\psi(\vec{\boldsymbol{r}},t)=\hbar k_x\psi(\vec{\boldsymbol{r}},t)=p_x\psi(\vec{\boldsymbol{r}},t)\\-\boldsymbol{i}\hbar\frac{\partial}{\partial y}\psi(\vec{\boldsymbol{r}},t)=\hbar k_y\psi(\vec{\boldsymbol{r}},t)=p_y\psi(\vec{\boldsymbol{r}},t)\\-\boldsymbol{i}\hbar\frac{\partial}{\partial z}\psi(\vec{\boldsymbol{r}},t)=\hbar k_z\psi(\vec{\boldsymbol{r}},t)=p_z\psi(\vec{\boldsymbol{r}},t)\end{aligned}\right\}\ldots\ldots\ldots\ (2.11)$$

Observable		Operator		Operator Symbol
$\boldsymbol{p_x}$	$\longrightarrow$	$-\boldsymbol{i}\hbar\frac{\partial}{\partial x}$	$\longrightarrow$	$\hat{\boldsymbol{p}}_{\boldsymbol{x}}$
etc.		**etc.**		**etc.**
$\boldsymbol{E}$	$\longrightarrow$	$i\hbar\frac{\partial}{\partial t}$	$\longrightarrow$	$\hat{\boldsymbol{E}}$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

Note that: $\hbar \boldsymbol{k_x \hat{x}} + \hbar \boldsymbol{k_y \hat{y}} + \hbar \boldsymbol{k_z \hat{z}} = \hbar \vec{\boldsymbol{k}}$

But: $\hbar \boldsymbol{k_x \hat{x}} + \hbar \boldsymbol{k_y \hat{y}} + \hbar \boldsymbol{k_z \hat{z}} = \boldsymbol{p_x \hat{x}} + \boldsymbol{p_y \hat{y}} + \boldsymbol{p_z \hat{z}} = \vec{\boldsymbol{p}}$

So, $\hbar \vec{\boldsymbol{k}} = \vec{\boldsymbol{p}}$

Eqns. (2.11) can be written as: $-\boldsymbol{i}\hbar\vec{\nabla}\psi(\vec{\boldsymbol{r}},t) = \hbar\vec{\boldsymbol{k}}\psi(\vec{\boldsymbol{r}},t) = \vec{\boldsymbol{p}}\psi(\vec{\boldsymbol{r}},t)$…….(2.12)

Observable		Operator		Operator Symbol
$\vec{\boldsymbol{p}}$	$\longrightarrow$	$-\boldsymbol{i}\hbar\vec{\nabla}$	$\longrightarrow$	$\widehat{\vec{\boldsymbol{p}}}$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)=\hbar\omega\psi(\vec{r},t)\ \ldots\ldots\ldots\ (2.10)$$

$$-i\hbar\vec{\nabla}\cdot -i\hbar\vec{\nabla}\psi(\vec{r},t)=-i\hbar\vec{\nabla}\cdot\hbar\vec{k}\psi(\vec{r},t)=\hbar\vec{k}\cdot -i\hbar\vec{\nabla}\psi(\vec{r},t)=\hbar^2k^2\psi(\vec{r},t)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)=\frac{\hbar^2k^2}{2m}\psi(\vec{r},t)\ \ldots\ldots\ldots(2.13)$$

For a free particle: $\frac{\hbar^2k^2}{2m}=\frac{p^2}{2m}=E=\hbar\omega$

Therefore, from (2.10) & (2.11): $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)\ldots\ldots\ldots(2.14)$

(2.14) is Schrodinger Eqn. for a free particle in 3D.

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

Instead of a free particle, if we assume a particle in a force field derivable from a potential $V(\vec{\boldsymbol{r}},t)$, then its total energy will be:

$$\boldsymbol{E} = \frac{\boldsymbol{p}^2}{2\boldsymbol{m}} + V(\vec{\boldsymbol{r}},t) \;\ldots\ldots\ldots\ldots\; (2.15)$$

Eqn. (2.15) can be written as:

$$\hbar\omega = \frac{\hbar^2\boldsymbol{k}^2}{2\boldsymbol{m}} + V(\vec{\boldsymbol{r}},t) \;\ldots\ldots\ldots\ldots\; (2.16)$$

Eqn. (2.10), (2.13), (2.14) and (2.16) suggest that we can write:

$$-\frac{\hbar^2}{2\boldsymbol{m}}\boldsymbol{\nabla}^2\psi(\vec{\boldsymbol{r}},t) + V(\vec{\boldsymbol{r}},t)\psi(\vec{\boldsymbol{r}},t) = \boldsymbol{i}\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t)\ldots\ldots\ldots(2.17)$$

Remember that $\psi(\vec{\boldsymbol{r}},t)$ in this equation (2.14) is not that $\psi(\vec{\boldsymbol{r}},t)$ of eqn. (2.1).

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

Note: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) = \frac{\hbar^2 k^2}{2m}\psi(\vec{r},t) = \frac{p^2}{2m}\psi(\vec{r},t)$

$-\frac{\hbar^2}{2m}\nabla^2$ is called the kinetic energy operator and is written as $\hat{T}$.

$V(\vec{r},t)$ is a multiplicative operator, called potential energy operator and is written as $\hat{V}$.

$-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) \equiv \hat{T} + \hat{V}$ represents the total mechanical energy and is an is called the Hamiltonian operator $\widehat{H}$

Then the Schrodinger eqn. becomes:

$$\widehat{\boldsymbol{H}}\psi(\vec{\boldsymbol{r}},t) = \boldsymbol{i}\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t) \quad \text{………(2.18)}$$

Time dependent Schrodinger equation

2. Time Dependent Schrodinger Wave equation in Three Dimensions:

Did we derived Schrodinger Equation?

Did Schrodinger derived his equation?

Derivation of Schrodinger equation is not possible.

Schrodinger only proposed it.

Feynman:

> *Where did we get that (equation) from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrodinger.*

Time dependent Schrodinger equation

3. Dynamical evolution of a quantum state

Will be discussed later on

Time dependent Schrodinger equation

4. Properties of Wave Function

In classical mechanics we describe the state of a system with the help of the real real physical variables position ($\vec{r}$) and momentum ($\vec{p}$).

In quantum mechanics we describe the state of a system with the help of a complex function $\psi(\vec{r},t) = \psi(x,y,z,t)$ of position and time. This is called the wave function of the system.

Every thing, that can be known about a system, can be known from the wave function of the system.

A physically acceptable wave function must have the following properties:

Time dependent Schrodinger equation

4. Properties of Wave Function

ψ must be **finite**, **continuous** and **single valued** everywhere in the domain of the variables of ψ.

Also first derivatives of ψ, i.e. $\frac{\partial \psi}{\partial x}$ in 1D case and $\frac{\partial \psi}{\partial x}$, $\frac{\partial \psi}{\partial y}$ and $\frac{\partial \psi}{\partial z}$ in 3D must be **finite**, **continuous** and **single valued** everywhere in the domain of the variables of ψ.

$\psi(\vec{r},t)$ must be **square-integrable,** i.e. the integration $\int \psi^* \psi \, d\tau = \int |\psi|^2 d\tau$ over all space must be finite.

i.e. $\int_{\tau=\infty} \psi^* \psi \, d\tau = \int_{\tau=\infty} |\psi|^2 d\tau$ =finite.

For this to happen $\psi(x, y, z, t)$ must remain finite or become zero as x, y, z tend to infinity.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Position Probability Density: Born proposed the statistical interpretation of ψ in 1926: The product of $\psi(\vec{r},t)$ and its complex conjugate $\psi^*(\vec{r},t)$ is the probability density $P(\vec{r},t)$ of finding the particle at the position $\vec{r}$ at time t.

i.e. Position probability density $\boldsymbol{P(\vec{r},t)} = \psi^*(\boldsymbol{\vec{r},t})\psi(\boldsymbol{\vec{r},t}) = |\psi(\boldsymbol{\vec{r},t})|^{\mathbf{2}}$**…(5.1)**

Therefore the quantity $|\psi(\vec{r},t)|^2 d\tau$ is the probability of finding the particle in a small volume $d\tau$ around the position $\vec{r}$ at time t.

Obviously $\int_{-\infty}^{+\infty}|\psi(\vec{r},t)|^2 d\tau$ is the probability of finding the particle any where in the space and therefore it should be equal to unity:

$$\int_{-\infty}^{+\infty}|\psi(\boldsymbol{\vec{r},t})|^{\mathbf{2}}\boldsymbol{d\tau} = \mathbf{1} \quad \ldots(5.2)$$

5. Interpretation of Wave Function

Normalization:

A wave function satisfying the eqn. (5.2) is called normalized.

Schrodinger equation is a linear differential eqn. Therefore, if a wave function $\psi(\vec{r},t)$ satisfies this eqn., then any constant multiple of $\psi(\vec{r},t)$, let $N\psi(\vec{r},t)$, will also satisfy it and will be a wave function of the system. N may be real or complex.

If by solving Schrodinger eqn. we do not get a normalized $\psi(\vec{r},t)$, then we can suitably chose N, so that $N\psi(\vec{r},t)$ is normalized, i.e.

$$\boldsymbol{|N|^2 \int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau = 1 \quad \Rightarrow |N|^2 = 1/\int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau} \ldots (5.3)$$

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Normalization:

$$|N|^2 \int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau = 1 \quad \Rightarrow |N|^2 = 1/\int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau \ldots (5.3)$$

N is called normalization constant, and the process of obtaining the normalized wave function $N\psi(\vec{r},t)$ from an un-normalized one is called normalization.

Note that if you use multiply $Ne^{\pm i\alpha}$ in place of N, where α is a constant, the eqn. (5.3) remains unaffected. Thus all of $Ne^{\pm i\alpha}$ and N can be taken as the normalization constant. i.e. the normalization constant remains undefined up to the extent of a phase factor.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Total probability of finding the particle any where in the space is equal to unity:

$$\int_{-\infty}^{+\infty} \boldsymbol{P}(\vec{\boldsymbol{r}},\boldsymbol{t})\boldsymbol{d\tau} = \mathbf{1}$$

Therefore if the probability of finding a particle in a volume element $\boldsymbol{d\tau}$ decreases with time, then the probability of finding the particle some where outside this element must increase so that the total probability remains unity – as if the probability is flowing out across the boundary of the volume element.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

This situation is similar to that of flow of charge out of a volume element. In that case we know that time rate of decrease of charge inside a volume element is equal to the rate of flowing out of charge per second across the boundary of that volume element.

In electrostatics, this is expressed by the equation of continuity:

$$\boldsymbol{\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0} \quad \ldots\ldots\ldots \text{(5.4)}$$

where $\boldsymbol{\rho}$ is the volume density of charge and $\vec{\boldsymbol{J}}$ is the current density.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Let us examine the time rate of change of the probability of finding the particle in a finite volume $\boldsymbol{\tau}$:

$$\frac{\partial}{\partial t}\int_\tau P(\vec{r},t)d\tau = \frac{\partial}{\partial t}\int_\tau \psi^*\psi d\tau = \int_\tau \left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)d\tau\ldots\ldots\ (5.5)$$

Now (2.17): $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t) = -i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t),$ [Schrodinger Eqn.]

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

Then: $\frac{\partial\psi}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi$ and $\frac{\partial\psi^*}{\partial t} = -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi^*$

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Then $\frac{\partial\psi^*}{\partial t}\psi+\psi^*\frac{\partial\psi}{\partial t}=\left[-\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\psi^*\right]\psi+\psi^*\left[\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\psi\right]$

$$=\left[-\frac{i\hbar}{2m}\nabla^2\psi^*\right]\psi+\psi^*\left[\frac{i\hbar}{2m}\nabla^2\psi\right]-\frac{1}{i\hbar}V\psi^*\psi+\psi^*\frac{1}{i\hbar}V\psi$$

$$=-\frac{i\hbar}{2m}(\nabla^2\psi^*)\psi+\frac{i\hbar}{2m}\psi^*\nabla^2\psi-\frac{1}{i\hbar}V\psi^*\psi+\frac{1}{i\hbar}V\psi^*\psi$$

$$=-\frac{i\hbar}{2m}(\psi\nabla^2\psi^*-\psi^*\nabla^2\psi)$$

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Now from vector analysis $\vec{\nabla}\cdot\left(u\vec{\nabla}v\right) = u\nabla^2 v + \vec{\nabla}u\cdot\vec{\nabla}v$

And $\vec{\nabla}\cdot\left(v\vec{\nabla}u\right) = v\nabla^2 u + \vec{\nabla}v\cdot\vec{\nabla}u$

Therefore:

$$\vec{\nabla}\cdot\left(u\vec{\nabla}v - v\vec{\nabla}u\right) = u\nabla^2 v + \vec{\nabla}u\cdot\vec{\nabla}v - v\nabla^2 u - \vec{\nabla}v\cdot\vec{\nabla}u = u\nabla^2 v - v\nabla^2 u$$

Then $\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} = -\frac{i\hbar}{2m}\left(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi\right) = -\vec{\nabla}\cdot\frac{i\hbar}{2m}\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right)$

$= -\vec{\nabla}\cdot\vec{J}$ (say)

Where $\vec{J} = \frac{i\hbar}{2m}\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right)$ ……(5.6)

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Then $\frac{\partial}{\partial t}\int_\tau P(\vec{r},t)d\tau = \int_\tau \frac{\partial P(\vec{r},t)}{\partial t}d\tau = -\int_\tau \vec{\nabla}\cdot\vec{J}\,d\tau$ ……(5.7)

$$\Rightarrow \int_\tau \left(\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{J}\right)d\tau = 0$$

And since $d\tau$ is arbitrary, the integrand must vanish.

$\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0$ ……. (5.8)

Before discussing the significance of eqn. (5.8), let us try to understand $\vec{J}$ of eqn. (5.6).

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

From eqn. (5.7), using Gauss's divergence theorem:

$$-\frac{\partial}{\partial t}\int_{\tau} P(\vec{r},t)d\tau = \oiint_{s} \vec{J}\cdot\hat{n}\,ds \quad \ldots\ldots(5.9)$$

Where s is the boundary surface of the volume τ and $\hat{n}$ is the unit normal on the surface at ds.

Then the term in the *r.h.s* of the above equation represents total outward normal flux of $\vec{J}$ across the surface of the volume .

But the *l.h.s* is the rate of decrease of probability in the volume τ. Therefore $\vec{J}$ must be interpreted as flow of probability per second per unit area across s normally. Thus $\vec{J}$ is called the probability current density.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density- Conservation of Probability:

Now, with the interpretation of $P(\vec{r},t)$ as probability density and as $\vec{J}$ the probability current density, we can call eqn. (5.8) the equation of continuity in quantum mechanics. When written in the form of eqn. (5.9), it can be easily understood as the statement of conservation of probability.

$$\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0 \;\ldots\ldots\; (5.8)$$

$$-\frac{\partial}{\partial t}\int_{\tau} P(\vec{r},t)\,d\tau = \oiint_{s} \vec{J} \cdot \hat{n}\, ds \;\ldots\ldots(5.9)$$

End of Class 24/08/2020

Questions from today's class
(24/08/2020)

1. **Chose correct answer:** De Broglie wave is an electromagnetic wave / a mechanical wave / not any electromagnetic or mechanical wave.
2. Give the symbols and expressions of total energy operator, momentum operator, kinetic energy operator and Hamiltonian operator.
3. Give the symbols and expressions of of probability density $P(\vec{r},t)$ and probability current density $\vec{J}$.
4. What are the dimensions of probability density $P(\vec{r},t)$ and probability current density $\vec{J}$ (3D).
5. Interpret the eqn. of continuity in quantum mechanics.

Answers of Questions of 24/08/2020

1. De Broglie wave is not any electromagnetic or mechanical wave.

2.

Observable	Operator
Total Energy $\boldsymbol{E}$	$\hat{\boldsymbol{E}} \equiv i\hbar \frac{\partial}{\partial t}$
Linear Momentum $\vec{\boldsymbol{p}}$	$\hat{\vec{\boldsymbol{p}}} \equiv -\, \boldsymbol{i}\hbar\vec{\nabla}$
Kinetic Energy $\boldsymbol{T}$	$\hat{\boldsymbol{T}} \equiv -\frac{\hbar^2}{\boldsymbol{2m}}\boldsymbol{\nabla}^2$
Hamiltonian $\boldsymbol{H}$	$\hat{\boldsymbol{T}} \equiv -\frac{\hbar^2}{\boldsymbol{2m}}\boldsymbol{\nabla}^2 + \boldsymbol{V}(\vec{\boldsymbol{r}}, \boldsymbol{t})$

3. Probability density $P(\vec{r},t) = \psi^*(\vec{r},t)\psi(\vec{r},t) = |\psi(\vec{r},t)|^2$
   Probability current density $\vec{J} = -\frac{i\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right)$.

4. Probability has no dimension. Probability density = probability per unit volume. Therefore it has dimension is L^{-3}.
   From equation of continuity, $\frac{\partial P(\vec{r},t)}{\partial t} = -\vec{\nabla}\cdot\vec{J} \Rightarrow \frac{L^{-3}}{T} = \frac{1}{L}[\vec{J}] \Rightarrow [\vec{J}] = L^{-2}T^{-1}$

Answers of Questions of 24/08/2020

5. Interpretation of the eqn. of continuity:

Integrating the eqn. of continuity $\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$ and rearranging, we get:

$\int_\tau \frac{\partial P(\vec{r},t)}{\partial t} d\tau = -\int_\tau \vec{\nabla} \cdot \vec{J}\, d\tau = -\oint\!\!\oint_s \vec{J} \cdot \hat{n}\, ds$, where s is the boundary surface of the volume τ. Gauss's divergence theorem has been used.

Or, $-\frac{\partial}{\partial t} \int_\tau P(\vec{r},t) d\tau = \oint\!\!\oint_s \vec{J} \cdot \hat{n}\, ds$

The right hand side of the above equation is the total outward flow of probability per second across the boundary surface s of the volume τ. The left hand side is the rate of decrease of total probability in the volume τ. Thus the above equation states that the rate of decrease of probability in a volume is equal to the rate of flowing out of probability across the boundary surface of that volume. This is a statement of conservation of probability.

Therefore the equation of continuity is a statement of conservation of probability, in differential form.

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density

$$\vec{J} = -\frac{i\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right) = -\frac{\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right)$$

$$= \left(-\frac{i\hbar}{2m}\psi^*\vec{\nabla}\psi\right) + \left(\frac{i\hbar}{2m}\psi\vec{\nabla}\psi^*\right) = \left(-\frac{i\hbar}{2m}\psi^*\vec{\nabla}\psi\right) + \left(-\frac{i\hbar}{2m}\psi^*\vec{\nabla}\psi\right)^*$$

$$= 2Re\left(-\frac{i\hbar}{2m}\psi^*\vec{\nabla}\psi\right) = Re\left(\psi^*\frac{-i\hbar\vec{\nabla}}{m}\psi\right)$$

$$= Re\left(\psi^*\frac{\hat{\vec{p}}}{m}\psi\right)$$

$$= Re\left(\psi^*\,\hat{\vec{v}}\,\psi\right)$$

Time dependent Schrodinger equation

5. Interpretation of Wave Function

Probability Current Density

$\vec{J} = Re\left(\psi^* \,\hat{\vec{v}}\, \psi\right)$……………..(5.10)

with $\psi^*\psi = P$ (probability density)

Comparing with the expression of electric current density $\vec{J} = \rho\vec{v}$, we can see the justification of interpreting as probability current density.

Time dependent Schrodinger equation

6. Condition of Physical Acceptability of Wave function:

$\psi(\vec{r}, t)$ must be **square-integrable,** i.e. the integration $\int \psi^* \psi \, d\tau = \int |\psi|^2 d\tau$ over all space must be finite.

i.e. $\int_{\tau=\infty} \psi^* \psi \, d\tau = \int_{\tau=\infty} |\psi|^2 d\tau$ =finite.

For this to happen $\psi(x, y, z, t)$ must remain finite or become zero as x, y, z tend to infinity.

Time dependent Schrodinger equation

7. Normalisation:

$\int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau$ is the probability of finding the particle any where in the space and therefore it should be equal to unity:

$$\int_{-\infty}^{+\infty} |\psi(\vec{r},t)|^2 d\tau = 1 \quad \ldots(7.1)$$

A wave function satisfying the eqn. (7.1) is called normalized.

Schrodinger equation is a linear differential eqn. Therefore, if a wave function $\psi(\vec{r},t)$ satisfies this eqn., then any constant multiple of $\psi(\vec{r},t)$, let $N\psi(\vec{r},t)$, will also satisfy it and will be a wave function of the system. N may be real or complex.

Time dependent Schrodinger equation

7. Normalisation:

If, by solving Schrodinger eqn. we do not get a normalized $\psi(\vec{r},t)$, then we can suitably chose N, so that $N\psi(\vec{r},t)$ is normalized, i.e.

$$|N|^2\int_{-\infty}^{+\infty}|\psi(\vec{r},t)|^2 d\tau = 1 \quad \Rightarrow |N|^2 = 1/\int_{-\infty}^{+\infty}|\psi(\vec{r},t)|^2 d\tau \ldots(7.2)$$

N is called normalization constant, and the process of obtaining the normalized wave function $N\psi(\vec{r},t)$ from an un-normalized one is called normalization.

Note that if you use multiply $Ne^{\pm i\alpha}$ in place of N, where α is a constant, the eqn. (5.3) remains unaffected. Thus all of $Ne^{\pm i\alpha}$ and N can be taken as the normalization constant. i.e. the normalization constant remains undefined up to the extent of a phase factor.

Time dependent Schrodinger equation

8. Linearity and Superposition Principle:

Schrodinger eqn. is a 2nd order ***linear*** partial differential equation.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)\ldots\ldots\ldots(2.17)$$

If ψ_1 and ψ_2 are two separate solutions of a ***linear*** differential equation, then any linear combination of ψ_1 and ψ_2, say, $C_1\psi_1+C_2\psi_2$, where C_1 and C_2 are constants (generally complex), will also be a solution of that equation. This is valid for any number of separate solutions.

Thus if ψ_n are separate solutions of a ***linear*** differential equation, then any linear combination of the solutions ψ_n i.e.

$$\psi(\vec{r},t)=\sum_n C_n\psi_n(\vec{r},t)\ldots\ldots\ldots\ldots(8.1)$$

where C_n are constants (in general complex), will also be a solution of that eqn.

This statement is called the superposition principle of the solutions of a linear differential equation.

Time dependent Schrodinger equation

8. Linearity and Superposition Principle in Quantum Mechanics:

Each solution ψ_n of Schrodinger equation represents a quantum state. Thus any linear combination of them will also represent a quantum state.

Linear combination of solutions of a linear differential equation can be physically interpreted as the superposition of states represented by the solutions.

In classical mechanics, we are familiar with that concept in case of vibration of strings. In that problem, the superposition of all possible harmonics of a vibrating string stretched between two fixed points, construct the vibrational state of the string.

In quantum mechanics, any superposition of a number of possible quantum states, is also a quantum state. This statement is called the principle of superposition. This principle is realized by the linear nature of Schrodinger eqn.

Time dependent Schrodinger equation

9. Eigen value and eigen function:

- Before entering in to the discussion of **Eigen value and eigen function**, it will be helpful if we go through the solution of the Schrodinger eqn.
- Schrodinger eqn. for a time independent potential (we will confine to time independent potentials in all of our future discussions):

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V(\vec{r})\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)\ldots\ldots\ldots(2.17)$$

- Left side of the above PDE contains only space dependent operators and the right side contains only time dependent operators. So we can apply the method of separation of variables to solve it.

Let $\psi(\vec{r},t)=u(\vec{r})\varphi(t)\ \ldots\ldots\ldots(9.1)$

Time dependent Schrodinger equation

9. Eigen value and eigen function:

Then $-\frac{\hbar^2}{2mu(\vec{\boldsymbol{r}})}\nabla^2 u(\vec{\boldsymbol{r}})+\frac{1}{u(\vec{\boldsymbol{r}})}V(\vec{\boldsymbol{r}})u(\vec{\boldsymbol{r}})=\frac{1}{\varphi(t)}i\hbar\frac{\partial}{\partial t}\varphi(t)$………(9.2)

On the two sides of eqn. 9.2 are functions which depends on different variables and can vary independently. Therefore this eqn. holds only if both sides are equal to a constant, say E. Then after rearranging we get:

$-\frac{\hbar^2}{2m}\nabla^2 u(\vec{r})+V(\vec{r})u(\vec{r})=Eu(\vec{r})$ …(9.3) and $i\hbar\frac{d}{dt}\varphi(t)=E\varphi(t)$ ……(9.4)

Eqn. (9.4) has solution: $\varphi(t)=e^{\frac{E}{i\hbar}t}$…….. (9.5)

Expression of $u(\vec{r})$ can not be obtained from eqn. (9.3) until $V(\vec{r})$ is known.

The final solution can be written as $\psi(\vec{\boldsymbol{r}},\boldsymbol{t})=u(\vec{r})e^{\frac{E}{i\hbar}t}$ ……(9.6)

Time dependent Schrodinger equation

9. Eigen value and eigen function:

If an operator $\hat{A}$ operating on a function u generates another function which differs from u only by a constant multiplicative factor λ i.e. $\hat{A}u = \lambda u$, then u is called eigen function of the operator $\hat{A}$ belonging to the eigen value λ. The eqn.: $\hat{A}u = \lambda u$ is called eigen value eqn.

Now, from eqn. (9.6), $i\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t) = i\hbar\frac{\partial}{\partial t}u(\vec{r})e^{\frac{E}{i\hbar}t} = u(\vec{r})Ee^{\frac{E}{i\hbar}t}$

$\Rightarrow i\hbar\frac{\partial}{\partial t}\psi(\vec{\boldsymbol{r}},t) = \boldsymbol{E}\psi(\vec{\boldsymbol{r}},t)$……(9.7)

Then from (2.17), $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t) = E\psi(\vec{r},t)$

$\Rightarrow \hat{H}\psi(\vec{\boldsymbol{r}},\boldsymbol{t}) = \boldsymbol{E}\psi(\vec{\boldsymbol{r}},\boldsymbol{t})$…….(9.8)

Time dependent Schrodinger equation

9. Eigen value and eigen function:

Eqns. (9.7) and (9.8) can be recognized as eigen value equations. Thus the separation constant $\boldsymbol{E}$ Is the eigen value of both the operators $i\hbar\frac{\partial}{\partial t}$ and $\hat{H}$.

We know that $i\hbar\frac{\partial}{\partial t}$ is the total energy operator. And $\hat{H}$ is the Hamiltonian operator, which represent the sum of kinetic and potential energies i.e. the total energy. Thus the eigen value $\boldsymbol{E}$ is called the energy eigen value.

Remember the equations (9.3): $\hat{H}u(\vec{r}) = Eu(\vec{r})$

(9.3) is called energy eigen value equation. The Hamiltonian operator $\hat{H}$ has eigen function $u(\vec{r})$, belonging to the energy eigen value E. Note that $u(\vec{r})e^{\frac{E}{i\hbar}t}$ is also an eigen function of $\hat{H}$ belonging to the eigen value E.

Time dependent Schrodinger equation

9. Eigen value and eigen function:

Conditions to be satisfied by a function to be an quantum mechanical eigen function:

(i) Eigen function must be single valued everywhere.

(ii) Eigen function must be continuous everywhere.

(iii) Eigen function must be square-integrable i.e. $\int_{-\infty}^{\infty} u_n{}^{*} u_n dx = finite.$

(iv) For eigen value equation involving differential operators it may be required that both the eigen function and its derivative remain continuous at all points.

Time dependent Schrodinger equation

9. Eigen value and eigen function:

Properties of quantum mechanical eigen functions:

(i) Eigen values of a quantum mechanical operator $\hat{\alpha}$ are real and eigen functions of a quantum mechanical operator are orthogonal. [For proof see 2.c &d)].

(ii) Eigen functions $u_n(x)$ of a quantum mechanical operator forms a complete set i.e. they have completeness property. This means that any arbitrary continuous function $\psi(x)$ satisfying the same boundary conditions as $u_n(x)$ can be expanded in terms of the eigen functions $u_n(x)$as:

$\psi(x) = \sum_n C_n u_n(x)$, where C_n are constants.

End of Class 29/08/2020