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Unit

# Methods of Quantum Mechanics

Erwin Schrodinger
(1887 – 1961)

## Learning Objectives:

**After studying this chapter, students should be able to:**

- Understand the need of Quantum Mechanics.
- Describe the wave function and its physical meaning.
- Know about normalized wave function and expectation value of dynamical variable.
- Derive the time dependent and independent Schrodinger wave equations and its application.
- Understand the Hydrogen atom problem.
- Describe the radial and angular part of Schrodinger wave equation of Hydrogen atom.
- Explain the significance of various Quantum numbers.
- Know about degeneracy and energy level of degeneracy of Hydrogen atom.
- Explain the space quantization experiments.
- Understand about the spin.
- Explain the state of electron specified by four Quantum numbers.
- Describe the atomic wave function.
- Solve various numerical problems related with Quantum Mechanics.

## Worked Out Examples

1. **Consider the particle in the ground state is represented by a wave function $\Psi(x)$ = B Sin $\left(\frac{\pi x}{a}\right)$ within $0 < x < a$. where $B = \sqrt{\frac{2}{a}}$. What is (a) the average position (b) the average momentum (c) the average energy of such particle?** *[TU Microsyllabus 2074, W; 20.2]*

Solution:

We have the given wave function $\Psi(x) = B \text{ Sin}\left(\frac{\pi x}{a}\right) = \sqrt{\frac{2}{a}} \text{ Sin}\left(\frac{\pi x}{a}\right)$

a. The average position means the expectation value of positions $\bar{x}$ or $<x> = \int_0^a \Psi^*(x)\, x\, \Psi(x)\, dx$

$$\text{or,} \quad <x> = \frac{2}{a}\int_0^a \sin^2\left(\frac{\pi x}{a}\right) x\, dx$$

$$\text{or,} \quad <x> = \frac{2\,a^2}{a\,\pi^2}\int_0^a \underbrace{\sin^2\left(\frac{\pi x}{a}\right)}_{u}\underbrace{\left(\frac{\pi x}{a}\right)}_{v}\left(\frac{\pi}{a}\right) dx$$

$\int u.v = v\int u\,dx - \int\left[\frac{dv}{dx}\int u\,dx\right]dx$

$$= \frac{2a}{\pi^2}\left[\frac{1}{4}\left(\frac{\pi x}{a}\right)^2 - \frac{\pi x \text{ Sin}\left(\frac{2\pi x}{a}\right)}{4a} - \frac{\cos\left(\frac{2\pi x}{a}\right)}{8}\right]_0^a$$

$$= \frac{2a}{\pi^2}\left\{\left(\frac{\pi^2}{4} - 0 - \frac{1}{8}\right) - \left(0 - 0 - \frac{1}{8}\right)\right\}$$

$$\therefore \quad <x> = \frac{a}{2}$$

b. The average value of momentum can be found by

$$<p> = \bar{P} = \int_0^a \Psi^*(x)\, P\, \Psi(x) dx$$

$$\text{or,} \quad <P> = \frac{2}{a}\int_0^a \text{Sin}\left(\frac{\pi x}{a}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\sin\left(\frac{\pi x}{a}\right) dx, \qquad \text{Since, } P = -i\hbar\frac{\partial}{\partial x}.$$

$$\text{or,} \quad <P> = \frac{2}{a}\int_0^a \text{Sin}\left(\frac{\pi x}{a}\right)\left(-i\hbar\frac{\pi}{a}\cos\frac{\pi x}{a}\right) dx$$

$$= \frac{2}{a}(-i\hbar)\int_0^a\left(\text{Sin}\frac{\pi x}{a}\right)\left(\cos\frac{\pi x}{a}\right)\left(\frac{\pi}{a}\right) dx.$$

$$= \frac{2}{a}(-i\hbar)\left[\frac{\sin^2\left(\frac{\pi x}{a}\right)}{2}\right]_0^a$$

$$\therefore \quad <P> = 0.$$

This result makes physical sense. The particle is moving back and forth between the walls of the well. The probability of finding the particle moving toward right is the same as probability of finding it moving forward the left. Thus, the average value of the momentum has to be zero.

c. The average energy $\bar{E}$ or $<E>$ can be calculated as

$$<E> = \int_0^a \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi\, dx. \qquad \text{Since, } E = i\hbar\frac{\partial}{\partial t}.$$

$$\text{or,} \quad <E> = \int_0^a \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi_o\, e^{\frac{-E_o t}{\hbar}}\, dx$$

Where, to describe the particle in the infinite potential well is described by $\Psi = Ae^{\frac{-iEt}{\hbar}}$

i.e., $\Psi = A \sin \omega t = Ae^{-i\omega t} = Ae^{\frac{-iEt}{\hbar}}$ for $E = \hbar\omega$.

$$\therefore \quad \langle E \rangle = \int_0^a \Psi^* (i\hbar) \left(\frac{-iE_o}{\hbar}\right) \Psi_o e^{\frac{-iE_o t}{\hbar}} dx$$

$$\text{or,} \quad \langle E \rangle = \int_0^a E_o \Psi^* \Psi \, dx$$

$$\therefore \quad \langle E \rangle = \langle E_o \rangle$$

Thus, when the particle is in the ground state, the Eigen function associated with the particle was given b

$\Psi = A e^{\frac{-iE_o t}{\hbar}}$. In this case the particle has a well defined energy $E = E_o$. We expect that the average value wi be the actual value.

**2. Calculate the normal Zeeman splitting of the calcium 4226 Å line when the atoms ar placed in a magnetic field of 1.2 Tesla.** ***[TU Microsyllabus 2074, W; 21.1***

**Solution:**

The wave length ($\lambda$) = 4226 Å = $4226 \times 10^{-10}$m.

Magnetic field (B) = 1.2T

Normal Zeeman splitting ($d\lambda$) = ?

We know that, $|dE| = \Delta E = \frac{|e|}{2m} B\hbar$

$$|dE| = \frac{1.6 \times 10^{-19} \times 1.2 \times 1.05 \times 10^{-34}}{2 \times 9.1 \times 10^{-31}} \qquad \text{Where, } \hbar = \frac{h}{2\pi}$$

$$dE = 1.11 \times 10^{-23}\,\text{J} = 6.92 \times 10^{-5}\,\text{eV}.$$

We know that, $E_{photon} = h\upsilon = \frac{hc}{\lambda}$

$$dE = -\frac{hc}{\lambda^2} d\lambda$$

$$|dE| = \frac{hc}{\lambda^2} |d\lambda|$$

$$dλ = \frac{eh}{4\pi m} B$$

So, $|d\lambda| = \frac{\lambda^2}{hc} |dE|$

$$|d\lambda| = \frac{4.226 \times 10^{-7} \times 1.11 \times 10^{-23}}{6.63 \times 10^{-34} \times 3 \times 10^{8}} = 9.96 \times 10^{-12}\,\text{m} = 0.0996\text{Å}$$ Answrong

Thus, The normal Zeeman splitting $|d\lambda| = 0.0996$Å.

**3. A beam of Hydrogen atom is used in Stern-Gerlach type experiment. The atom emerges from the oven with a velocity $10^4$ m/sec. They enter a region 20 cm long where there is a magnetic field gradient $3 \times 10^4$T/m. The field gradient is perpendicular to the incident velocity of the atoms. The mass of the Hydrogen atom is $1.67 \times 10^{-27}$ kg. What is the separation of the two components of the beam as they emerge from the magnet?**

***[TU Microsyllabus 2074, W; 21.2]***

**Solution:**

Velocity of atom (v) = $10^4$m/sec

Magnetic field gradient $\left(\frac{dB}{dz}\right) = 3 \times 10^4$ J/m.

Mass of Hydrogen atom (m) = $1.67 \times 10^{-27}$ kg.

Separation of the two components of beam = ?

In the ground state, Hydrogen atom has no net orbital magnetic dipole moment. The only dipole moment is the one associated with the spin of the electron in the 1s state, that is $(\mu_s) = -\frac{|e|}{m}\vec{s}$

So, from Stern-Gerlach experiment

$$F_z = \mu_s \frac{dB}{dz} = -\frac{|e|}{m} S_z \frac{dB}{dz} = \pm\frac{1}{2}\frac{|e|}{m}\hbar\frac{dB}{dz}$$ Since, m = mass of element

Using Newton's Second law, $F_z = a_z m_{atom}$

$$\text{or,}\quad a_z = \frac{F_z}{m_{atom}} = \frac{|e|\,\hbar\frac{dB}{dz}}{2m\, m_{atom}}$$

$$\therefore\quad a_z = \frac{1.60\times10^{-19}\times1.05\times10^{-34}\times3\times10^{4}}{2\times9.1\times10^{-31}\times1.67\times10^{-27}} = 1.65\times10^{8}\ \text{m/sec}^2$$

The deflection of each component in the direction of the force (z -axis) will be

$$\Delta z = \frac{1}{2}a_z t^2$$ Where, t is the time that the atom spend in the magnet.

This time can be found by dividing the length of the magnet by the incident velocity of the atoms.

$$\text{So,}\quad t = \frac{0.20\ \text{m}}{10^4\text{m/sec}} = 2\times10^{-5}\ \text{sec.}$$

$$\text{Therefore, } \Delta z = \frac{1}{2}\times1.65\times10^{10}\times4\times10^{-10}$$

$$\Delta z = 3.3\times10^{-2}\ \text{m} = 3.3\ \text{cm.}$$

The two possible values for $m_s$. Some atoms will be deflected upward and some downward. Therefore, the separation between the two components of the beam will be $2\Delta z$. So, $2\times3.3$ cm = 6.6 cm.

**4. Show by direct substitution into the time dependent Schrodinger equation for the free particle, that $\psi(x, t) = A\cos(kx - \omega t)$ is not a solution.** ***[TU Microsyllabus 2074, P;20.1]***

Solution:

Here is given, Wave function $\psi(x, t) = A\cos(kx - \omega t)$ ... (1)

We know that, time dependent Schrödinger wave equation

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

From equation (1) and (2), we get

$$\frac{-\hbar^2}{2m}\frac{\partial^2[A\cos(kx-\omega t)]}{\partial x^2} = i\hbar\frac{\partial[A\cos(kx-\omega t)]}{\partial t}$$

$$\frac{\hbar^2k^2}{2m}A\cos(kx-\omega t) = i\hbar(\omega)A\sin(kx-\omega t)$$

$$\frac{\hbar^2k^2}{2m}\psi(x,t) = i\omega\hbar A\sin(kx-\omega t) \qquad \textbf{(not satisfied)}$$

Hence, $\psi(x, t) = A\cos(kx - \omega t)$ is not a solution of time dependent Schrodinger equation for the free particle.

**5. For a free Quantum particle show that the wave function $\Psi(x, t) = A\cos kx\, e^{-i\omega t}$ satisfies the time dependent Schrodinger equation.** ***[TU Microsyllabus 2074, P; 20.2 and TU Model 2074]***

Solution

Here,wave function $\Psi(x, t) = A\cos kx\, e^{-i\omega t}$ ...(1)

We know that, time dependent Schrodinger wave equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \quad \text{...(2)}$$

From equation (1) and (2), we get

$$-\frac{\hbar^2}{2m}\frac{\partial^2(A\cos kx\, e^{-i\omega t})}{\partial x^2} = i\hbar\frac{\partial(A\cos kx\, e^{-i\omega t})}{\partial t}$$

$$\text{or,}\quad \frac{\hbar^2k^2}{2m}\Psi(x,t) = \hbar\omega\Psi(x,t)$$

$$\text{or,}\quad \frac{p^2}{2m}\Psi(x,t) = E\Psi(x,t) \quad \text{...(3)}$$ Since, $p = \hbar k$ and $E = \hbar\omega$

Again, time dependent Schrodinger wave equation can be written as,

$$E\Psi(x, t) = H\Psi(x, t) \quad \ldots(4)$$

Hence, equation (3) and (4) are same so the given wave function satisfies the time dependent Schrodinger equation.

**6. Explain, why the following Eigen function are not acceptable solution of the Schrodinger equation.** *[TU Microsyllabus 2074, P; 20.3]*

a. $\chi(x) = 0$ for $x \le 0$

$\chi(x) = A \cos kx$ for $x \ge 0$

b. $\chi(x) = A \dfrac{e^{iKx}}{x}$

c. $\chi = A\, \ell nkx$

**Solution:**

Here is given, wave functions are as following;

a. $\chi(x) = 0$ for $x \le 0$

$\chi(x) = A \cos kx$ for $x \ge 0$

b. $\chi(x) = A \dfrac{e^{iKx}}{x}$

c. $\chi = A\, \ell nkx$

We know that, time independent Schrodinger wave equation

$$\frac{-\hbar^2}{2m}\frac{\partial^2\chi}{\partial x^2} = E\chi + E_p\chi \qquad \text{For potential energy } E_p = 0$$

$$\text{or,} \quad \frac{\partial^2\chi}{\partial x^2} + \frac{2m}{\hbar^2}(E - E_p)\chi = 0 \qquad \ldots (1) \text{ For certain potential } E_p$$

Then, those solutions are acceptable which satisfied equation (1).

**For (a):**

$\chi(x) = 0$ for $x \le 0$. It is not a solution of S.W.E because S.W.E. has finite wave function as a solution not zero and there is no meaning.

For (a) $\chi(x) = A \cos kx$ for $x \ge 0$

$$\text{Equation (1), will be } \frac{d^2(A\cos kx)}{dx^2} + \frac{2m(E - E_p)\chi}{\hbar^2} = 0$$

$$-k^2 A \cos kx + \frac{2m(E - E_1)\chi}{\hbar^2} = 0$$

$$-k^2\chi + \frac{2m}{\hbar^2}(E - E_p)\chi = 0$$

$$\text{Again, for (b) } \chi = \frac{A e^{ikx}}{x}$$

$$\text{Here, } \frac{d\chi}{dx} = \frac{A ike^{ikx}}{x} + A e^{ikx}\left(\frac{-1}{x^2}\right)$$

$$\frac{d^2\chi}{dx} = \frac{A(ik)^2 e^{ikx}}{x} + A ik e^{ikx}\left(\frac{-1}{x^2}\right) - \frac{A ike^{ikx}}{x^2} + A e^{ikx}(-)(-2)\frac{1}{x^3}$$

$$= \frac{-Ak^2 e^{ikx}}{x} - \frac{2A ik}{x^2} e^{ikx} + \frac{2Ae^{ikx}}{x^3}$$

$$= -k^2\chi - \frac{2ik\chi}{x} + \frac{2\chi}{x^2}$$

The Schrodinger wave equation,

$$\frac{d^2\chi}{dx^2} + \frac{2m}{\hbar^2}(E - E_p)\,\chi = 0$$

$$\text{or,}\quad -k^2\chi - \frac{2ik\,\chi}{x} + \frac{2\,\chi}{x^2} + \frac{2m}{\hbar^2}(E - E_p)\,\chi = 0$$

i.e., $-k^2 - \frac{2ik}{x} + \frac{2}{x^2} + \frac{2m}{\hbar^2}(E - E_p) = 0$ has no solution and meaningless.

c. For $\chi = A\,\ell nkx$ .Then,

$$\frac{d\chi}{dx} = \frac{d(A\,\ell nkx)}{dx} = \frac{Ad\,\ell nkx}{d(kx)}\frac{d(kx)}{dx}$$

$$= Ak\frac{1}{kx}$$

$$= \frac{A}{x} \text{ and } \frac{d^2\chi}{dx^2} = -\frac{A}{x^2}$$

Now, Schrodinger wave equation,

$$\frac{d^2\chi}{dx^2} + \frac{2m}{\hbar^2}(E - E_p)\,\chi = 0$$

$$-\frac{A}{x^2} + \frac{2m}{\hbar^2}(E - E_p)\,\chi = 0$$

Hence, given Eigen functions are not acceptable solution of the Schrodinger equation because they does not satisfied in the equation which are discussed above.

**7. What is the probability of finding a particle in a well of width 'a' at a position $\frac{a}{4}$ from the wall if n = 1, if n = 2, if n = 3. Use the normalized wave function, $\psi(x, t) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\, e^{\frac{-iEt}{\hbar}}$.** *[TU Microsyllabus 2074, P; 20.12]*

Solution:

Here is given, width of well = a

Position (x) = $\frac{a}{4}$

Normalized wave function $\psi(x, t) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\, e^{\frac{-iEt}{\hbar}}$

We know that, probability of finding a particle, P = $\psi^*\psi$

Then, at $x = \frac{a}{4}$

$$P = \left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}\cdot\frac{a}{4}e^{\frac{+iEt}{\hbar}}\right)\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}\cdot\frac{a}{4}e^{\frac{-iEt}{\hbar}}\right)$$

$$P = \frac{2}{a}\sin^2\frac{n\pi}{4} \qquad \dots (1)$$

If n = 1, $P_1 = \frac{2}{a}\sin^2\frac{\pi}{4} = \frac{2}{a}\left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{a}$

For n = 2, $P_2 = \frac{2}{a}\sin^2\frac{2\pi}{4} = \frac{2}{a}$

And for n = 3, $P_3 = \frac{2}{a}\sin^2\frac{32\pi}{4} = \frac{2}{a}\sin^2 135^\circ = \frac{2}{a}\left(\frac{1}{\sqrt{2}}\right)^2$

$\therefore\quad P_3 = \frac{1}{a}$

Hence, the probability of finding a particle in a well of width of a position $x = \frac{a}{4}$ form the wall for n = 1, n = 2 and n = 3 are $\frac{1}{a}, \frac{2}{a}$ and $\frac{1}{a}$ respectively.

**8. In the Bohr Model of hydrogen atom, the electron is assumed to move in circular orbits around the proton, that is motion takes place in a plane that we call the any plane. Use the uncertainty principle in z-direction, i.e. $\Delta P_z \geq \hbar$ and the fact that $\overline{P_z^2} \geq (\Delta P_z)^2$ to show that the motion of the electron cannot be planar motion.** *(TU Microsyllabus 2074, P. 21.3)*

Solution:

According to uncertainity principle position of a particle is more accurately (i.e., smaller $\Delta x$), the momentum is less accurately (i.e., larger $\Delta p$) and vice-varsa. If the particle is fully move in xy-plane the uncertainty in z is zero. i.e., $\Delta z = 0$ but the uncertainity principle suggest that,

$$\Delta z\, \Delta P_z \geq \hbar$$

It will be violated if $\Delta z$ is zero and $\Delta P_z$ is finite. Therefore $\Delta z$ should be greater than zero it means the motion of the particle cannot be planar.

**9. (a) How many atomic states are there in Hydrogen with n = 3?**

**(b) How are they distributed among the sub shells? Label each state with appropriate set of Quantum numbers n, $\ell$, $m_\ell$, $m_s$.**

**(c) Show that the number of states in a shell, that is, states having the same n, is given by $2n^2$.** *[TU Microsyllabus 2074, P; 21.6 and TU Exam 2074]*

Solution:

Here is given,

a. Principle Quantum number (n) = 3

Number of atomic states $= \dfrac{n(n+1)}{2} = \dfrac{3(3+1)}{2} = 6$

They are

1s

2s 2p

3s 3p 3d

b.

| SN | State | n | $\ell$ | $m_\ell$ | $m_s$ | No. of states in shell |
|---|---|---|---|---|---|---|
| 1 | For 1s state | 1 | 0 | 0 | $\frac{1}{2}$ | 1 |
| 2 | For 2s state | 2 | 0 | 0 | $\frac{1}{2}$ | 1 |
| 3 | For 2p state | 2 | 1 | 0, $\pm 1$ | $\frac{1}{2}$ | 3 |
| 4 | For 3s state | 3 | 0 | 0 | $\frac{1}{2}$ | 1 |
| 5 | For 3p state | 3 | 1 | 0, $\pm 1$ | $\frac{1}{2}$ | 3 |
| 6 | For 3d state | 3 | 2 | 0, $\pm 1$, $\pm 2$ | $\frac{1}{2}$ | 5 |

c. Now, number of states in shell having Quantum number $1s^2$, $2s^2$, $2p^6$, $3s^2\, 3p^6$ i.e., 18.