Lecture M3L02

PH101: Physics 1

Module 3: Introduction to Quantum Mechanics

Girish Setlur & Poulose Poulose

gsetlur@iitg.ac.in

Department of Physics, IIT Guwahati poulose@iitg.ac.in

(Matter) Wave Mechanics

Schrodinger’s Equation

In January 1926, Schrödinger published in Annalen der Physik the paper "Quantisierung als Eigenwertproblem" [tr. Quantization as an Eigenvalue Problem] on wave mechanics and presented what is now known as the Schrödinger equation. In this paper, he gave a "derivation" of the wave equation for time-independent systems and showed that it gave the correct energy eigenvalues for a hydrogen-like atom. This paper has been universally celebrated as one of the most important achievements of the twentieth century and created a revolution in most areas of quantum mechanics and indeed of all physics and chemistry.

Following up on de Broglie's ideas, physicist Peter Debye made an offhand comment that if particles behaved as waves, they should satisfy some sort of wave equation. Inspired by Debye's remark, **Schrödinger** decided to find a proper 3-dimensional wave equation for the electron. He was guided by William R. Hamilton's analogy between mechanics and optics, encoded in the observation that the zero-wavelength limit of optics resembles a mechanical system — the trajectories of light rays become sharp tracks that obey Fermat's principle, an analog of the principle of least action.

By that time, Arnold Sommerfeld had refined the Bohr model with relativistic corrections. Schrödinger used the relativistic energy momentum relation to find what is now known as the Klein–Gordon equation in a Coulomb potential.

He found the standing waves of this relativistic equation, but the relativistic corrections disagreed with Sommerfeld's formula. Discouraged, he put away his calculations and secluded himself in an isolated mountain cabin in December 1925.

While at the cabin, Schrödinger decided that his earlier non-relativistic calculations were novel enough to publish, and decided to leave off the problem of relativistic corrections for the future. Despite the difficulties in solving the differential equation for hydrogen (he had sought help from his friend the mathematician Hermann Weyl) Schrödinger showed that his non-relativistic version of the wave equation produced the correct spectral energies of hydrogen in a paper published in 1926. In the equation, Schrödinger computed the hydrogen spectral series by treating a hydrogen atom's electron as a wave $\Psi(x, t)$, moving in a potential well V, created by the proton. This computation accurately reproduced the energy levels of the Bohr model.

This 1926 paper was enthusiastically endorsed by Einstein, who saw the matter-waves as an intuitive depiction of nature.

What is a wave equation ?

Typically, waves are periodic disturbances that propagate in a medium. More generally, they can be periodic disturbances in something more abstract. For example, electromagnetic waves are periodic disturbances in an abstract “Electromagnetic Field” and matter waves as we shall see in this part of the course, are periodic variations of probability amplitudes in space and time.

We may exploit this idea to write down a “wave equation” obeyed by the amplitudes. The main reason for doing this is that the simple periodic functions namely sine and cosine are not the only possibilities when it comes to describing periodic functions.

We use the simple sine and cosine periodic functions to derive a differential equation for the amplitude. Then we assert that the same equation is going to hold for more complicated types of periodic functions whose form may be hard to guess. The form of these waves have to be found by solving the differential equation for the wave called the “wave equation”.

A typical wave: $\psi(x,t) = A\sin\left(2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right)$

Amplitude Maximum amplitude Wavelength Period

Spatial periodicity: $\psi(x+\lambda, t) = \psi(x,t)$ and **Temporal periodicity:** $\psi(x, t+T) = \psi(x,t)$

This simple wave is not only periodic in space and time separately, it also moves in a fixed direction.

Suppose I shift my position of observation of the wave from x to $x + \Delta x$ at time t:

Amplitude changes from $\boldsymbol{\psi(x,t)}$ to $\boldsymbol{\psi(x+\Delta x, t)}$

I ask what is the shortest time I have to wait at this new location before this amplitude becomes the same as the original amplitude $\boldsymbol{\psi(x,t)}$?

If I wait for a time $\boldsymbol{\Delta t}$ at this new location, the amplitude becomes $\boldsymbol{\psi(x+\Delta x, t+\Delta t)}$. But I want this to be the same as $\boldsymbol{\psi(x,t)}$.

Hence $\boldsymbol{\sin\left(2\pi\left(\frac{x+\Delta x}{\lambda} - \frac{t+\Delta t}{T}\right)\right) = \sin\left(2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right)}$ or v = $\frac{\Delta x}{\Delta t} = \frac{\lambda}{T} > 0$ is the speed of the wave and it moves in the positive x direction.

Derivation of a classical wave equation

It may seem odd that we want to derive an equation for $\psi(x,t)$ when we already have an answer for it as shown in the previous slide. It is somewhat like wanting to find the quadratic equation for which the roots are 3 and 4. If you already know the roots why do need the equation? Because there are situations where the equation is more general than the special roots from which the equation was generated. Just as a quadratic equation as a concept allows for complex roots as well, our use of the simple roots 3 and 4 to arrive at a general form of the quadratic equation is really useful.

To do this let us differentiate $\psi(x,t)$ twice with respect to x keeping the time t. The notation for differentiating with respect to x while keeping t fixed is $\frac{\partial}{\partial x}$. It is basically the same as $\frac{d}{dx}$ but since t is also a variable, extra effort is made to remind everyone that t is being held fixed.

$$\frac{\partial^2}{\partial x^2}\psi(x,t) = -\left(\frac{2\pi}{\lambda}\right)^2 A\sin(2\,\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right))$$

Similarly,

$$\frac{\partial^2}{\partial t^2}\psi(x,t) = -\left(\frac{2\pi}{T}\right)^2 A\sin(2\,\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right))$$

Since $\lambda = \mathrm{v}\,T$ this leads to the classical wave equation,

$$\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{1}{\mathrm{v}^2}\frac{\partial^2}{\partial t^2}\psi(x,t)$$

Just as the quadratic equation has many unusual solutions, this wave equation has many more solutions than the simple special form of a periodic travelling wave from which it was generated.

In fact, it could describe standing waves which are two waves travelling in opposite directions

$$\psi(x,t) = A\sin\left(2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right) + A\sin\left(2\pi\left(\frac{x}{\lambda} + \frac{t}{T}\right)\right)$$

It could even describe waves that are travelling in the positive x direction but are not periodic

$$\psi(x,t) = A\,\mathrm{e}^{-\left(\frac{x}{\lambda} - \frac{t}{T}\right)^2}$$

Indeed, the most general solution to this classical wave equation may be written as,

$$\psi(x,t) = u(x - \mathrm{v}\,t) + w(x + \mathrm{v}\,t)$$

where u and w can be any functions of their respective arguments.

Derivation of the matter wave equation

In a similar vein, Schrodinger wanted to derive such a wave equation for matter waves obeying the de Broglie relation.

He also said that the amplitude $\psi(x, t)$ could be complex since only the square of its modulus has physical meaning – as the probability per unit length of finding the particle at position x at time t.

Another reason for this choice of a complex amplitude is that free particles not acted upon by forces – simplest situation in Newtonian particle mechanics – should have a matter wave description corresponding to the simplest situation in wave theory - namely sinusoidal waves with fixed wavelength and period. But a choice we had studied earlier $\psi(x, t) = A\, sin\left(2\, \pi \left(\frac{x}{\lambda} - \frac{t}{T}\right)\right)$ is not suitable since even though it meets all the required criteria, the probability of finding the particle at some point varies periodically from point to point and from one time to the next. This implies a certain sequence of points in space at which the probability density is maximum are more special than others which is not acceptable. So he suggested,

$$\psi(x, t) = A\, e^{2\pi i\left(\frac{x}{\lambda} - \frac{t}{T}\right)}$$

This is simple and periodic in both space and time and corresponds to a wave moving in the positive x-direction and most importantly the absolute square of the amplitude which is the probability per unit length of finding the particle at x and t is independent of position and time which ensures that no point in space is more special than others.

$$|\psi(x, t)|^2 = |A|^2$$

Wave-particle duality

$$Wave\ property\ =\ \frac{h}{Particle\ property}\quad \begin{cases} \lambda = \dfrac{h}{p} \\[2ex] \mathrm{T} = \dfrac{h}{E} \end{cases}$$

$$\mathrm{E} = \mathrm{h}\,\nu$$

$$\mathrm{T} = \frac{1}{\nu}$$

Substituting this into Schrodinger's matter wave we get,

$$\psi(x,t) = A\,\mathrm{e}^{\frac{2\pi i}{h}(p\,x\,-E\,t)}$$

Differentiating twice with respect to *x*,

$$\frac{\partial^2}{\partial x^2}\psi(x,t) = p^2\left(\frac{2\pi i}{h}\right)^2 A\,\mathrm{e}^{\frac{2\pi i}{h}(p\,x\,-E\,t)}$$

Differentiating once with respect to *t*,

$$\frac{\partial}{\partial t}\psi(x,t) = -E\,\frac{2\pi i}{h}A\,\mathrm{e}^{\frac{2\pi i}{h}(p\,x\,-E\,t)}$$

Keeping in mind that for a nonrelativistic particle, $E = \frac{p^2}{2m}$ and comparing the earlier two equations allows us to write (where ħ $= \frac{h}{2\pi}$ is sometimes called the Planck Dirac constant),

$$\underbrace{i\hbar\frac{\partial}{\partial t}}_{\mathrm{E}}\psi(x,t) = \underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}}_{\frac{p^2}{2m}}\psi(x,t)$$

The above was for a free particle. Schrodinger saw immediately that the right hand side has kinetic energy and the left hand side has total energy - they are equal for a free particle. For a particle acted upon by a force he added the potential energy to the right hand side to obtain his celebrated **Schrodinger equation**,

$$\underbrace{i\hbar\frac{\partial}{\partial t}}_{\mathrm{E}}\psi(x,t) = \underbrace{\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right)}_{\frac{p^2}{2m}+V(x,t)}\psi(x,t)$$

Wave packets and Heisenberg's uncertainty relation

According to Schrodinger, $\psi(x,t) = A\ \mathrm{e}^{\frac{2\pi i}{h}(p\,x\,-E\,t)}$ represents the probability amplitude for finding a particle not acted upon by any forces with momentum p and energy $E = \frac{p^2}{2m}$. This means that the probability for finding the particle between x and $x + dx$ is,

$$|\psi(x,t)|^2\,dx = |A|^2\,dx$$

It says that a quantum particle [a hybrid of a wave and particle since there are no pure particles or pure waves in QM] with a given momentum is equally likely to be found at some time t between x_0 and $x_0 + dx$ as it is between between x_1 and $x_1 + dx$. This is unlike what happens in classical physics where a particle with some momentum p not acted upon by a force is always going to be found at one location only at time t namely at $x = x(0) + \frac{p}{m}\,t$

We have to see how this ultra-quantum hybrid particle and wave which has a well defined momentum and energy but no well defined position can be utilized to generate something resembling a classical particle that has both a well defined momentum and a well defined position. Of course since classical physics is only an approximation to reality we shall be content at obtaining something similar to a classical particle. These are called wave packets (for want of a better name). The idea is to superpose many of these ultra-quantum wave-particle hybrids with momenta between $p_0 - \frac{\Delta p}{2}$ and $p_0 + \frac{\Delta p}{2}$ so that we can be sure that the resultant superposition has a momentum p_0 , on an average.

$$\psi(x,t) = \int_{p_0 - \frac{\Delta p}{2}}^{p_0 + \frac{\Delta p}{2}} dp \;\; A(p) \;\; \mathrm{e}^{\frac{2\pi i}{h}\left(p\, x - \frac{p^2}{2m}\, t\right)}$$

We want this to approximately represent a classical particle that is present at location x_0 at time t_0 and moving with speed $\frac{p}{m}$.

For this, a choice $\mathrm{A(p)} = \mathrm{A}(0)\, \mathrm{e}^{-\frac{2\pi i}{h}\left(p\, x_0 - \frac{p^2}{2m}\, t_0\right)}$ will be shown to be suitable.

$$\psi(x,t) = A(0) \int_{p_0 - \frac{\Delta p}{2}}^{p_0 + \frac{\Delta p}{2}} dp\ \mathrm{e}^{\frac{2\pi i}{h}\left(p\,(x-x_0)\ - \frac{p^2}{2m}(t-t_0)\right)}$$

We make the substitutions $p = p_0 + p'$ and $\frac{p^2}{2m} = \frac{(p_0+p')^2}{2m} \approx \frac{p_0^2}{2m} + \frac{p_0}{m} p'$

With p' small compared to p_0

$$\psi(x,t) = A(0)\, \mathrm{e}^{\frac{2\pi i}{h}\left(p_0\,(x-x_0)\ - \frac{p_0^2}{2m}(t-t_0)\right)} \int_{-\frac{\Delta p}{2}}^{\frac{\Delta p}{2}} dp'\ \mathrm{e}^{\frac{2\pi i}{h}\left(p'\,(x-x_0)\ - \frac{p_0}{m} p'(t-t_0)\right)}$$

In other words, $|\psi(x,t)|^2 = \mathrm{A}^2(0)\left(\frac{h\sin[\frac{\pi X \Delta\mathrm{p}}{\mathrm{h}}]}{\pi X}\right)^2$ where $X = (x - x_0) - \frac{p_0}{m}\ (\mathrm{t} - \mathrm{t}_0)$

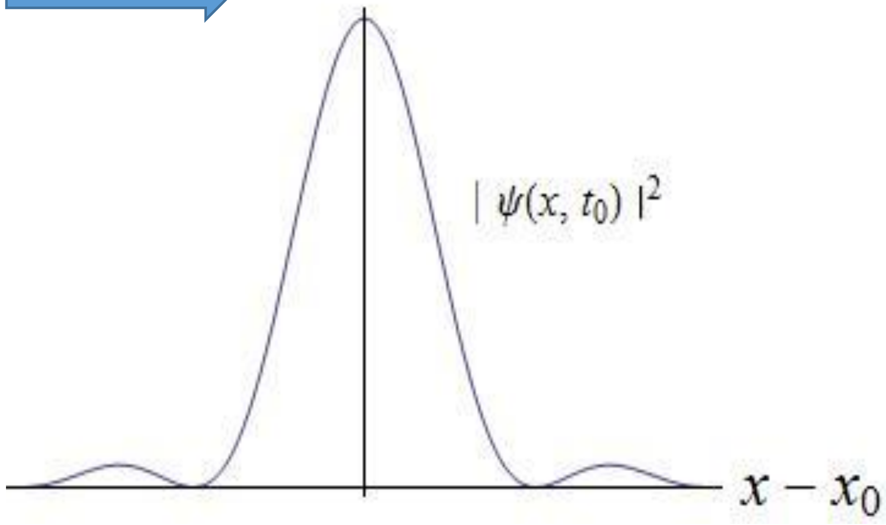
The total probability of finding the particle somewhere between $-\infty$ to $+\infty$ should be one. Imposing the condition,

$$\int_{-\infty}^{+\infty} dX\ \ \mathrm{A}^2(0)\left(\frac{h\sin[\frac{\pi X \Delta\mathrm{p}}{\mathrm{h}}]}{\pi X}\right)^2 = 1 \ \text{ or, } \quad \mathrm{A}^2(0) = \frac{1}{h\,\Delta p}$$

So the wave packet corresponding to a (semi)classical free particle moving with speed $\mathrm{v}_0 = \frac{p_0}{m}$ which is classically at $\mathrm{x} = \mathrm{x}_0$ at time $\mathrm{t} = t_0$ has a probability density equal to,

$$|\psi(x,t)|^2 = \frac{1}{h\,\Delta p}\left(\frac{h\sin[\frac{\pi X \Delta\mathrm{p}}{\mathrm{h}}]}{\pi X}\right)^2$$

A plot looks like this



The most probable situation is when $|\psi(x,t)|^2$ is maximum. This happens at $X = 0$ or when $(x - x_0) = \frac{p_0}{m}\ (\mathrm{t} - \mathrm{t}_0)$ which is nothing but the trajectory of a classical particle.

We can see that the average position of the particle is x_0 at $t = t_0$

$$< x > = \int_{-\infty}^{+\infty} dx \;\; x \;|\psi(x, t_0)|^2 \; = x_0$$

The rms deviation $(\Delta x)/2$ from this average position may be estimated by the smallest value of $\Delta x/2 = |x - x_0|$ at which the square of the wavefunction becomes zero.

This means $\frac{\pi \, \Delta x \, \Delta \mathrm{p}}{2\mathrm{h}} = \pi$ or $\Delta x \, \Delta \mathrm{p} = 2\mathrm{h}$

This is a special case of **Heisenberg's uncertainty relation** that says that the precision to which you can simultaneously determine the position and momentum of a quantum particle is limited by the inequality

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

Forthcoming topics….

- Postulates of quantum mechanics
- The ‘Copenhagen interpretation’ of the wave function in QM
- Measurement in QM. The nature of the observer and the observed
- Counter intuitive phenomena:

  – quantum tunneling and zero point motion