

Schroedinger Equation

In the earlier lectures, we reviewed some of the experimental results which led physicists to consider the quantum ideas. The need to explain the various details of blackbody radiation led Planck to propose the radiation is emitted in the form quanta of energy $E = nh\nu$, where n is a positive integer. The results of a photoelectric effect led Einstein to postulate that light of frequency ν consists of quanta (later named *photons*) of energy $h\nu$. Higher intensity of light means that the number of quanta is large. Compton scattering experiments further showed that the interaction of X-rays with electrons has to be explained in the form of elastic collisions of X-ray quanta (with well-defined energy and momentum) with electrons. These experiments compelled physicists to think of light as behaving both as a particle (quantum) as well as a wave.

A little later, de-Broglie proposed that this property should be shared by massive objects, such as electrons, also. Naively, one thinks of electrons as point particles. But de-Broglie said that such objects should have wave-like properties. He also proposed to identify a wavelength $\lambda = h/p$ to such particles, where p is the momentum of the particle. This hypothesis, as far as we know, was just pulled out of air. It had no experimental support. But once the proposal was made, an effort was made to look for the wave like properties of electrons and were observed by two groups: by G. P. Thomson in England and Davisson and Germer in the U.S. Both these groups observed diffraction of electrons by the lattice planes of a solid. Based on these principles, soon an *Electron Microscope* was built which enabled people to obtain "pictures" of atoms.

The net effect of all this effort is the conclusion that both radiation and matter (with mass) have simultaneous wave and particle like properties. We need a mathematical formalism which incorporates both these properties so that a complete description of all the properties of both radiation and matter can be made. Schroedinger was convinced that this means there should be a wave equation which describes the quantum dynamics. He set about to construct such an equation. In doing so, he borrowed an idea from *Hamiltonian Dynamics* of classical mechanics.

William Hamilton developed a new method of viewing classical dynamics. Usually we say, Newton's second law guides the dynamics. To get the position at any time 't', we need to know the equation of motion and the position and

velocity at $t = 0$. Hamilton pictured this in the following way: Given $x(0)$ and $v(0)$, the Newton's second law guides us from the *initial state* $x(0), v(0)$ to final state $x(t), v(t)$. To define this guidance he defined a function, which we now call Hamiltonian. If the potential in the problem depends only on the co-ordinates, then Hamiltonian is equal to the sum of kinetic energy and the potential energy, $H = T + V$. The usual phrase used in Hamiltonian Dynamics is 'The Hamiltonian guides the time evolution of a system'.

Schroedinger assumed that there is a function $\psi(x, t)$ which describes the **state** of a system in quantum mechanics. He wrote a quantum dynamical equation

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = H\psi(x, t).$$

That is, he assumed that the action of the **Operator** H on the function $\psi(x, t)$ is equivalent to the action of the operator $i\hbar \partial / \partial t$ on $\psi(x, t)$. In other words, the rate at which $\psi(x, t)$ changes with time is proportional to the action of H on $\psi(x, t)$. He also proposed that the Hamiltonian should be written as

$$H = \frac{P^2}{2m} + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x),$$

that is, he identified $p = -i\hbar \partial / \partial x$. He applied this equation to the problem of Hydrogen atom and obtained the energy levels of hydrogen as $E_n = -Ry/n^2$.

Soon after the proposal of Bohr atom, Arnold Sommerfeld constructed a relativistic version of it. In this version, the energy levels of the hydrogen are different from Bohr model by a few percent. Already, spectroscopists were able to measure these small differences which are called *fine structure effects*. Sommerfeld's model agreed well with experimental measurements. Schroedinger, in his first attempt to construct a wave equation for quantum dynamics, also attempted a relativistic equation. The concept of electron spin was not known at that time so he did not include it in his equation and got an answer which did not match the experiment. Sommerfeld's model also did not include electron spin but it also ignored a mathematical subtlety. The two omissions cancelled each other out to produce the correct answer. When Heisenberg derived the hydrogen atom spectrum using matrix mechanics, Schroedinger took a relook at his results and found that the non-relativistic limit of equation gave the correct solution and published it.

According to Schroedinger the dynamical equation for quantum mechan-

ics is

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t). \quad (1)$$

The above equation is called **Time dependent Schroedinger's equation** because it explicitly includes the time dependence of ψ . But the question is: What is this $\psi(x, t)$? We call it the wave function but what does it represent? Max Born gave the physical interpretation. He said that $|\psi(x, t)|^2 dx$ is the probability of finding the electron between x and $x + dx$ at time t . Since the electron has to be somewhere in the space, we must have

$$\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1,$$

that is, we should be able to **normalize** the wave function. A necessary condition for this to happen is that the wave function should be **square integrable**, *i.e.* the integral of its mod-square should be finite.

Now we attempt to solve Schroedinger's equation in two variables x and t . A standard technique in mathematics is *separation of variables* by which we convert the partial differential equation in two variables into two ordinary differential equations. We assume

$$\psi(x, t) = \phi(t)\psi(x),$$

and substitute it in the Schroedinger's equation. We get

$$i\hbar \frac{d\phi(t)}{dt} \psi(x) = \phi(t) \left[-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) \right].$$

We also assume that $\psi(x, t) \neq 0$ everywhere and divide the above equation by $\psi(x, t)$. We get

$$i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = \frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) \right].$$

The LHS of the above equation is purely a function of t and the RHS of the above equation is purely a function of x . Hence the equation can be satisfied only if both sides are equal to a constant E . Thus we get a pair of equations

$$\begin{aligned} i\hbar \frac{d\phi(t)}{dt} &= E\phi(t) \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) &= E\psi(x) \end{aligned} \quad (2)$$

The second of the above equations can also be written in, operator language, as

$$H\psi(x) = E\psi(x), \quad (3)$$

that is, the operator H acting on $\psi(x)$ gives us back $\psi(x)$ multiplied by E . Based on this, we identify the constant E as the energy of the electron. As mentioned earlier, the Hamiltonian is the sum of the kinetic and the potential energies. So it is equivalent to the total energy. When the Hamiltonian acts on a *state*, we can expect the net result to be the energy of the state.

Eq. (3) is an example of a general equation in operator theory. For a given operator, we can ask the question, "Are there any special functions related to this operator, which have the property that when the operator acts on the function we get back the function with a multiplicative constant?" As an equation, this takes the form

$$\mathcal{O}f_\lambda(x) = \lambda f_\lambda(x),$$

where λ is a constant (usually real for well behaved operators). If the above equation is satisfied, we say that $f_\lambda(x)$ is an **eigenfunction** of \mathcal{O} with **eigenvalue** λ . In every case, an eigenfunction on operator is identified by its eigenvalue. Using the same language, we rewrite eq. (3) as

$$H\psi_E(x) = E\psi_E(x).$$

In words, we say, $\psi_E(x)$ is an energy eigenfunction of the Hamiltonian H with energy eigenvalue E . The full version of the above equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_E(x)}{dx^2} + V(x)\psi_E(x) = E\psi_E(x),$$

which is called **Time Independent Schroedinger Equation**. As discussed above, by solving it, we obtain the energy eigenvalues and the corresponding energy eigenfunctions. Quite often, the above equation is written in the form of a second order ordinary differential equation for $\psi_E(x)$

$$\frac{d^2\psi_E(x)}{dx^2} = \frac{2m[V(x) - E]}{\hbar^2} \psi_E(x). \quad (4)$$

Energy eigenstates have a very special status in quantum mechanics. We gain an insight to this by solving the time part of the differential equation in eq. (2). This equation can be rewritten as

$$\frac{d\phi(t)}{dt} = \frac{-iE}{\hbar} \phi(t).$$

By simple inspection, we can verify that the solution is

$$\phi(t) = \exp(-iEt/\hbar)\phi(0),$$

where $\phi(0)$ is a constant. Hence the solution for the full wave function is

$$\psi_E(x, t) = \exp(-iEt/\hbar)\psi_E(x, 0),$$

where $\psi_E(x, 0) = \psi_E(x)\phi(0)$. From this equation, we find

$$|\psi_E(x, t)|^2 = |\psi_E(x, 0)|^2.$$

If the electron is in an energy eigenstate, it will remain in that state for all time!. Hence, the energy eigenstates are also called **stationary states**.

Properties of Wavefunctions

From eq. (4), we see that the second derivative $d^2\psi_E/dx^2$ has to be finite (because we will consider only finite potentials). From the definition of derivatives, we can argue that if second derivative is finite, then the first derivative should be continuous. This in turn implies that the first derivative should be continuous and should not have any kinks. Thus all wave functions should necessarily satisfy the following properties:

- They should be single valued. If not, the probability interpretation will not make sense. It is non-sense to say that the probability of finding a particle between x and $x + dx$ can have two different values.
- They should be square-integrable.
- The above point implies that they should be finite at all x .
- $\psi_E(x)$ should be continuous at all x .
- $\psi_E(x)/dx$ should be continuous at all x .
- They should satisfy the boundary conditions imposed on them by the potential $V(x)$.

Going to Three Dimensions

So far we have limited ourselves to problems in one spatial dimension. In three dimensions we have three momenta p_x, p_y and p_z . They are identified with operators $-i\hbar\partial/\partial x, -i\hbar\partial/\partial y$ and $-i\hbar\partial/\partial z$. We also define a vector operator

$$\nabla = \hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z.$$

Here \hat{x}, \hat{y} and \hat{z} are the usual Cartesian unit vectors. In terms of this operator, we define $\vec{p} = -i\hbar\nabla$. The time dependent Schroedinger equation is

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

The operator ∇^2 is

$$\nabla\cdot\nabla = (\hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z)\cdot(\hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z) = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2.$$

The time independent Schroedinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi_E(\vec{r}) + V(\vec{r})\psi_E(\vec{r}) = E\psi_E(\vec{r}).$$

The above form of ∇^2 is useful when the potential $V(\vec{r})$ is specified in terms of cartesian coordinates. In a large number of cases, the potential is simple to write in terms of other form of coordinates. For example, in hydrogen atom the potential is written in terms of spherical coordinate r (the distance between the proton and the electron). In such cases, one should rewrite ∇^2 in terms of the spherical polar coordinates r (radial distance $= \sqrt{x^2 + y^2 + z^2}$), θ (polar angle, defined by $\cos\theta = z/\sqrt{x^2 + y^2 + z^2}$ equivalent to latitude) and ϕ (azimuthal angle, defined by $\tan\phi = y/x$ equivalent to longitude).

In three dimensions, the probability interpretation is: $|\psi_E(\vec{r})|^2 d^3r$ is the probability of finding the electron in the infinitesimal volume $d^3r = dx * dy * dz$ surrounding the point given by the position vector \vec{r} . Conservation of probability means

$$\int |\psi_E(\vec{r})|^2 d^3r = 1,$$

where the integral is over the whole space. This again means that the wave-function should be square-integrable or equivalently it should be **normalizable**. In addition, the properties such as finiteness, single valuedness, continuity and continuity of derivatives should hold.