

## Lecture 5

### Schrodinger Equation

This led to realizations that we need to treat electrons as waves. Electron in an atom cannot be treated as a particle- maybe we have to treat its wave-like properties. That led Schrodinger to write down an equation of motion of waves...

If a particle has a wavelength in the size of its environment, maybe the wavelength has an effect.

An equation of motion for matter waves:  $H\psi = E\psi$

### Schrodinger Equation

Schrodinger assumed that maybe he needed to treat the electron was a wave .....maybe the electron in the H-atom can not be treated as a particle but as wave.....electron has a de Broglie wavelength in the order of size of its environment and maybe in these cases the electron needs to be treated as a wave...not a particle using classical mechanics

The reason we do not pay order to our wavelengths is that it is in the order of  $10^{-30}\text{m}$ , which is much larger than the size of the environment

He wrote an equation of motion for waves:  $H\psi=E\psi$ ,  $\psi$  is a wave...it is going to be called a wave function, the electron is going to be treated as a wave function.....The energy  $E$  here is the binding energy of the electron in the atom. The "H" is called the Hamiltonian operator....that operator is specific to a particular problem....we will look at the Hamiltonian operator for a H-atom.....this operator is operating on  $\psi$  and giving back the same function times the binding energy. How did he derive this equation?

What he did was to just guess at a wave function....he would say let us guess this wave function:

$$\psi(x) = 2^{-a} \cos\left(\frac{2\pi x}{\lambda}\right)$$

He needs to know how  $\psi$  changes with  $x$ , in an equation of motion if we want to know how  $\psi$  changes with  $x$ , would just take the derivative:

Rate of change of  $\psi$  with  $x$ :

$$\frac{d\psi(x)}{dx} = -2a \left(\frac{2\pi}{\lambda}\right) \sin\left(\frac{2\pi x}{\lambda}\right)$$
$$\frac{d^2\psi(x)}{dx^2} = -2a \left(\frac{4\pi^2}{\lambda^2}\right) \underbrace{\cos\left(\frac{2\pi x}{\lambda}\right)}_{\psi(x)}$$
$$\frac{d^2\psi(x)}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x) \Rightarrow \text{derive. Schrodinger equation}$$

This is a classical wave equation....have just taken derivative....there is nothing quantum mechanical about it. Here comes the big leap Schrodinger made:

He substituted for  $\lambda$ , the momentum  $p$  for the particle....since it is a matter wave....he could do it since de Broglie taught him how to do that. De Broglie said:

$$\lambda = \frac{h}{p}$$

$$\text{Then } \Rightarrow \frac{d^2 \psi(x)}{dx^2} = -\frac{p^2}{\hbar^2} \psi(x) \quad \hbar = \frac{h}{2\pi}$$

We have an equation of motion of a matter wave....we have an equation which tells how the  $\psi(x)$  changes with  $x$  and I have the momentum of the particle buried in here.....

$$E = K + U = \frac{p^2}{2m} + U(x)$$

$$p^2 = 2m[E - U(x)]$$

$$\frac{d^2 \psi(x)}{dx^2} = -\frac{2m}{\hbar^2} [E - U(x)] \psi(x)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + U(x) \psi(x) = E \psi(x)$$

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E \psi(x)$$

H

$$\hat{H} \psi(x) = E \psi(x)$$

The Hamiltonian is a combination of kinetic energy operator and a potential energy operator....the key is the substitution of a de Broglie equation into an ordinary wave equation...

Schrodinger's equation is to quantum mechanics what Newton's equation is to classical mechanics.....Newton's equation will not work on something whose wavelength is the size of its environment....Classical mechanics is a subset of quantum mechanics...it is embedded in it...

For H-atom, we have to think of wave function in 3-D....typically we would use  $x, y, z$ ....but this problem is much more solvable if we use spherical co-ordinates....instead of  $x, y$ , and  $z$ ....we will

replace with  $R$ ,  $\theta$  and  $\phi$ . Set up  $H$  for H-atom using spherical coordinates.... in 3-D we would have a partial differential equation which has a double derivative with respect to  $x$ ,  $y$  and  $z$ ....makes the problem unsolvable. But when we move it to the spherical coordinates...this can be solved

Spherical coordinates: Like latitude and longitude.  $\theta$  ranges from 0 to  $\pi$  while  $\phi$  ranges from 0 to  $2\pi$ .

Solving the Schrodinger equation means calculate these  $E$ 's, i.e. the binding constants of the electron to the nucleus, called the Eigen Value ...the other thing we are going to solve for is  $\psi$ , that is the actual form of the wave function...that we can get out of solving the diff eq. The functional form will be complicated.....but we will look at them later. Those wave functions are what you have studied in school- they are the orbitals: s, p, d and f. They come from solving the Schrodinger equation. They are what is known as the spatial part of the wave function....there is also what is known as the spin part of the wave function....we are going to use orbitals and wave function sort of interchangeably.

The Schrodinger equation solution is going to show that the H-atom is stable....this is in contrast to classical ideas.

$$E = -\frac{1}{n^2} \left[ \frac{me^4}{8\epsilon_0^2 h^2} \right] \Rightarrow R_H \text{ Rydberg constant}$$

$$R_H = 2.17987 \times 10^{-18} \text{ J}$$

$$E = -\frac{R_H}{n^2}$$

$n = \text{principal quantum no.}$   
 allowed values  $\Rightarrow n = 1, 2, 3, \dots \infty$

Allowed energies in H atom are quantized written in terms of quantum numbers

These values tell us the energies the electron is supposed to have when it is bound to the hydrogen nucleus. When  $n=1$ , binding energy is  $-R_H$ . When  $n=2$ , binding energy is  $1/4^{\text{th}}$  of  $-R_H$ ....binding energy decreases as  $n$  increases. When  $n=\text{infinity}$ , the electron and nucleus are not bound to each other. The energies are discrete....they are quantized. This means only certain specific values are allowed...for example, values between  $-E$  and  $-E/4$  are not allowed. How did this quantization come from- by solving the Schrodinger equation. When you solve diff eq to solve a physical problem, in order to make it specific for the physical problem you include boundary conditions, here the allowed values of  $\theta$  and  $\phi$ .

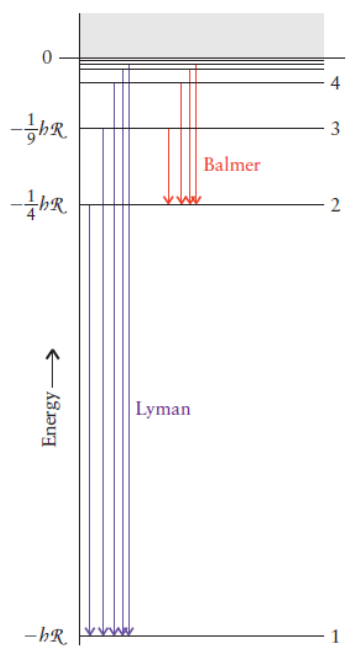
Significance of binding energies: When electron is bound to the nucleus with energy  $-R_H$ , we say that the Hydrogen atom is in the  $n=1$  state, the ground state. It is the lowest energy state- the electron is most strongly bound. The physical significance is that the binding energy is (-) ionization energy. The  $n=1$  is the first excited state, consequently the ionization energy from the less excited state is less.

The Schrodinger equation solution also predicts energy levels of all 1 electron atoms such as  $\text{He}^+$ .

The energy is predicted by:

$$E = -\frac{Z^2 R_H}{n^2} \Rightarrow Z e = \text{charge of nucleus}$$

$Z e \times e \Rightarrow \text{Coulomb interaction}$



$$\Delta E = -R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

## Lecture 6

N principal quantum number: 1,2,3 up to  $\infty$

$\Psi$  in general is a function of  $r, \theta, \phi$  and  $t$  denoted as  $\Psi(r, \theta, \phi, t)$ . We will look at wave functions which are called stationary waves, i.e.  $\Psi$  which are not dependent on  $t$ . This means we will not look at a wave function when a chemical reaction is happening, it will be before and after. In those cases we are looking at  $\Psi$  when the atom is stable and sitting idle. The  $\Psi$  we will look at will be  $\Psi(r, \theta, \phi)$  also known as time-independent QM. When we go and solve Schrodinger equation for  $\Psi(r, \theta, \phi)$ , two more quantum numbers drop out in the differential equation.

We get a new quantum number  $l$ , called the angular momentum quantum number because it dictates how much angular momentum the electron has. It also has allowed values. They are 0, 1, 2, ...,  $(n-1)$ . Why should it be smaller than  $n$ . Classically thinking  $l$  would denote the angular momentum.

The third quantum number which drops out is  $m$ , called the magnetic quantum number, since it dictates how an atom moves in a magnetic field. But more precisely what  $m$  is the  $z$ -component of the angular momentum  $l$ . The allowed values of  $m$  are  $m=0, +1, +2, \dots, +l$ . The largest value is  $l$ . Since it is a  $z$  component it also has direction, so  $m$  can be  $-1, -2, \dots, -l$ .

For  $n=1, l=0, m=0$ .....called 100 state and if we have an electron in the 100 state we are going to describe the electron by a wave function  $\psi_{100}$ .

For  $n=2, l=0, m=0$ : the wave function is  $\psi_{200}$ . The other wave functions possible for  $n=2$  are  $\psi_{210}, \psi_{211}$  and  $\psi_{21-1}$ . All these four states have the same energy i.e.  $-R_H/4$ . They are what we call degenerate.

The other way of representing the wave function is an orbital...the orbital is actually the wave-function. If  $l=0$ , we call it  $s$ . For  $l=1$ , we call it  $p$ . If  $l=2$ , we call it  $d$ . So all  $\psi_{210}, \psi_{211}$  and  $\psi_{21-1}$  would be called  $2p$ .

When  $l=1, m=0$ , we call it  $p_z$ . When  $m=1$ , it is  $p_x$  and when  $m=-1$  it is  $p_y$ . This is not fully correct because the Schrodinger equation solution of  $\psi_{211}$  and  $\psi_{21-1}$  are complex wave functions. For us to think about  $p_x$  and  $p_y$  wave functions, we take a linear combination.  $p_x$  is  $\psi_{211} + \psi_{21-1}$  while  $p_y$  is  $\psi_{211} - \psi_{21-1}$  - this gives you real functions.

For  $n=1$ , only one state. In  $n=2$ , four degenerate states. For  $n=3$ , 9 states.

For  $l=2, m=-2$  is  $3d_{xy}$ ,  $m=-1$  is  $d_{yz}$ ,  $m=0$  is  $d_{z^2}$ ,  $m=1$  is  $d_{xz}$ ,  $m=2$  is  $d_{x^2-y^2}$ .

For  $m=-2, -1, +1$  and  $+2$ , those wave functions when we solve Schrodinger's equation are complex wave functions. Again we take linear combination to make them real. For  $m=0$  the  $d_{z^2}$  is a real function.