Approximate Methods in Quantum Chemistry
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Lecture 06
Exactly Solvable Models - II (continued)

Hello students, welcome to this lecture. In the previous lecture, we were discussing about some exactly solvable models in quantum mechanics and in part of that discussion, we were looking at the problem of hydrogen atom.

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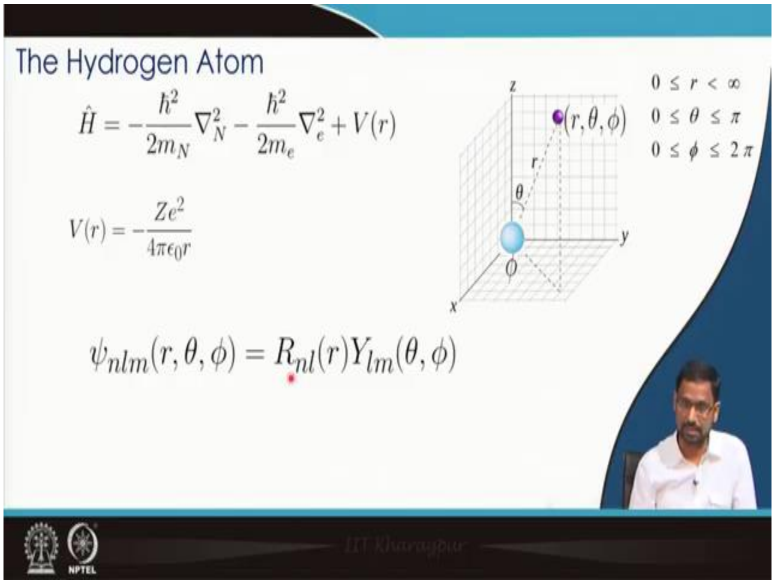

The Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r)$$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$0 \le r < \infty$

$0 \le \theta \le \pi$

$0 \le \phi \le 2\pi$

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

In hydrogen atom we see that we have an electron which moves around the environment of the nucleus. The Hamiltonian has kinetic energy operator corresponding to the nucleus, the kinetic energy operator corresponding to the electron plus the potential energy operator. The electron moves around the nucleus and we express the movement of electron in the spherical polar coordinate system, where the three coordinates are r, θ and ϕ. r is the radial part, θ and ϕ are the angular part of the wave function. We also discussed that the operator, kinetic energy operator of the electron also has this term is called the Laplacian. The Laplacian already contains the operator L^2 (the angular momentum operator). That is why in the previous class we said that the total eigenfunction of hydrogen atom that is $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$.

The angular part of the solution is essentially the eigenfunction of the angular momentum operator, because in our hydrogen atoms Hamiltonian, the only operator that had angular dependence was the L^2 operator. We know its eigenfunctions. That leaves us with the radial part of the solution. We are not going to derive the solution rather we are going to use the results of this exactly solvable model.

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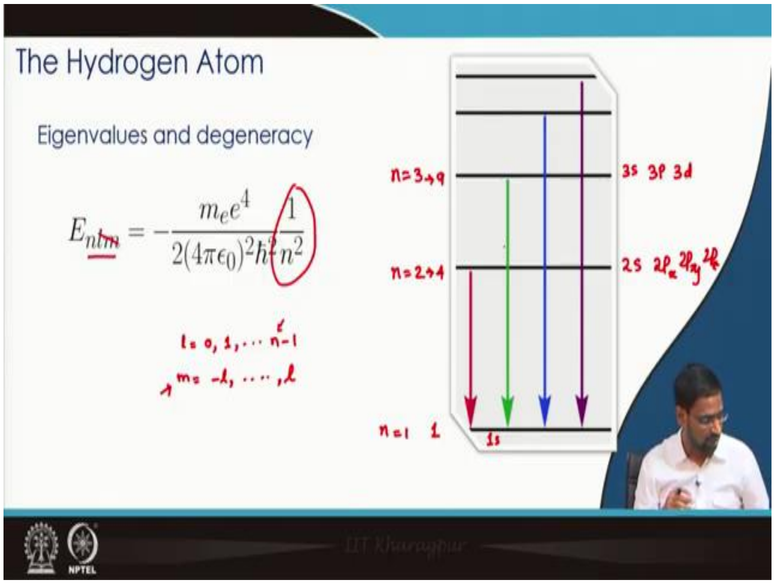

The Hydrogen Atom

Eigenvalues and degeneracy

$$E_{n\cancel{lm}} = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

$l = 0, 1, \dots n-1$

$m = -l, \dots, l$

Now, when we look at the energy of hydrogen atom, we see that the energy E_{nlm} depends on three quantum numbers; n is the leading quantum number, the principal quantum number, l and m are the trailing quantum numbers, the azimuthal quantum number and the magnetic quantum number respectively. m value depends on the value of l and l value depends on the value on n. The energy is given by in terms of a constant which is -13.6 eV multiplied by $1/n^2$. With increasing n the energy levels are shown in the diagram above. The negative energy signifies the stable atom comprising of a negatively charged electron around the positively charged nucleus. When we ionize this electron, the electron escapes the orbits and becomes a free particle.

In that case, n goes to infinite and energy becomes 0. The energy levels will be extremely close to each other and the continuous range of energies would appear. But, for the stable states, the energy states are discrete, they are well separated, they take certain values -13.6 eV/n^2.

Next we discuss the degeneracy of the energy levels. The energy expression has only n dependence while the wave function depends on n, l, and m. The energy not showing l and m dependence is a a special case for all 1-electron systems. For every value of n, we can have n number of l values (*l* = 0, …. *n*-1). The value of *m* goes from -*l* to +*l* in the step of 1. So for each value of *l*, we have got 2*l*+1 number of *m* values.

Although the wave function is different for each of the values of n, l, m, the energy only depends on n. Hence for a given value of n, all the wave functions have the same energy. They are called degenerate states. For *n* = 1, the degree of degeneracy is 1 (1s). And for *n* = 2, it is 4 fold degenerate (2s, 2px, 2py, 2pz) and so on. When *l* is 1 (i.e., *p* functions), *m* = -1, 0, +1. In Cartesian system, we refer to them as p_x, p_y, and p_z. So, the 2s 2px, 2py, 2pz orbitals have same energy for hydrogen atom, only for hydrogen atom, it does not apply to the many-electron atoms. So, in case of helium atom 2s and 2p orbitals have different energy. Of course, 2px, 2py, and 2pz have same energy even in case of helium atom (and for all other heavier atoms), because unless we have external magnetic field this degeneracy of Px Py Pz are not lifted that is why we call them as magnetic quantum numbers. In case of *n* =3, you would see the 3s, the 3 number of 3p and the 5 number of 3d orbitals (together the 9 orbitals) will have same energy. To generalize, for hydrogen atom for a given principal quantum number *n*, we have n^2 degeneracy of eigenfunction. Since each orbital now have two electrons, we can fill $2n^2$ electrons for a given value of *n*.

With the help of eigenvalues, we can easily predict the emission spectrum by calculating the difference between any two energy levels: the starting energy level and the final energy level. The energy separation corresponds to the wavelength of the emission line. So, using quantum mechanical model of hydrogen atom we can now explain the results of hydrogen atom's emission spectrum. Even Bohr's atomic model could do that, but remember Bohr's atomic model could not explain the hydrogen atom's emission spectrum in the presence of external field. But the quantum mechanical model explains the emission spectra in presence of external field or even emission spectra for hydrogen like atoms.

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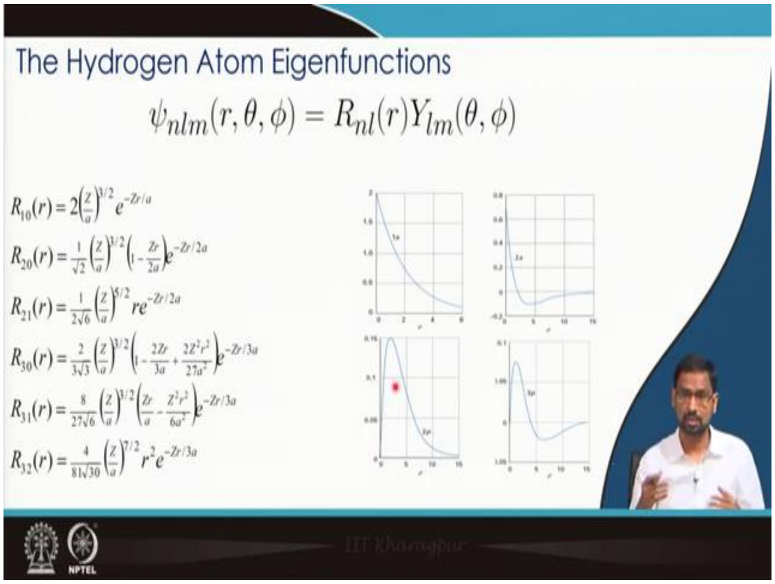

The Hydrogen Atom Eigenfunctions

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{Zr}{2a}\right)e^{-Zr/2a}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}$$

$$R_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{2Zr}{3a}+\frac{2Z^2r^2}{27a^2}\right)e^{-Zr/3a}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}-\frac{Z^2r^2}{6a^2}\right)e^{-Zr/3a}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}$$

Now, after discussing the eigenvalues, let us look at the eigenfunctions of the hydrogen atom. The hydrogen atoms eigenfunctions are shown here. The full wave function contains a radial and an angular part. We have already discussed the angular part as the eigenfunctions of angular momentum operator. The form of the shape of s orbital, shape of p orbital, shape of d orbitals that we are already familiar with are the results of this spherical harmonics. In this discussion for hydrogen atom solution, we will not bother about the Y_{lm} because they are simply the angular part of the solution.

We will be more interested in the new feature that we have encountered, i.e., the radial dependence. The radial dependence comes because the electron in this hydrogen atom can now explore the entire region, entire length scale starting from the nucleus to large separation from nucleus. The radial parts of these equations are quite scary, but do not worry about them. Just like we did for other systems, we will also look at the qualitative features arising from these equations.

In R_{10}, the first index is for n (=1 here) and, the second index is for l (=0 here), thus indicating 1s function. The radial dependence of 1s orbital is shown in the image above.

In R_{10}, $2(Z/a)^{3/2}$ (Z = nuclear charge = 1 for H and a = Bohr radius) is the normalization constant. In atomic unit, $(Z/a)^{3/2} = 1$. This leaves us with the $e^{-Zr/a}$ term (or e^{-a} in atomic unit for H) as an exponentially decaying function. The function starts from a finite value at r = 0 and as you go away from the nucleus, the wavefunction approaches 0, suggesting a vanishing probability of finding an 1s electron at very large r. You may get confused by this finite value of the radial part of the wave function at $r = 0$, which means that as if the electron is sitting right on top of the nucleus. We will resolve this issue when we discuss the probability density.

Now, come to 2s orbital. Apart from the constants, we have $e^{-Zr/2a}$ as the exponentially decaying function ($e^{-r/2}$ in atomic unit for H) and a polynomial of r. We are not introducing here but we can actually use the Laguerre polynomials to describe the hydrogen atom solution. The polynomial you see is the first order polynomial. There will be one value of r at which this polynomial will become 0. At that value of r, the wave function would become 0, producing a radial node. If you see the figure for the 2s radial function, you see that this function develops a radial node. Similarly, when I look at the 2p orbital, ($n = 2$ and $l = 1$), it has again a polynomial of r. At $r=0$, the wave function is 0. At lower values of r, the r term dominates and for larger r, the exponential decaying term pulls down the wave function, giving rise to a maximum.

For 3p, the radial function has an exponentially decaying function multiplied by the polynomial ($r-r^2/6$, with $Z=1$ and $a=1$) which becomes zero at $r = 0$ and at $r = 6$. There is, thus, one node in 3p orbital (as we do not consider $r = 0$ as a node, the trivial solution of the polynomial).

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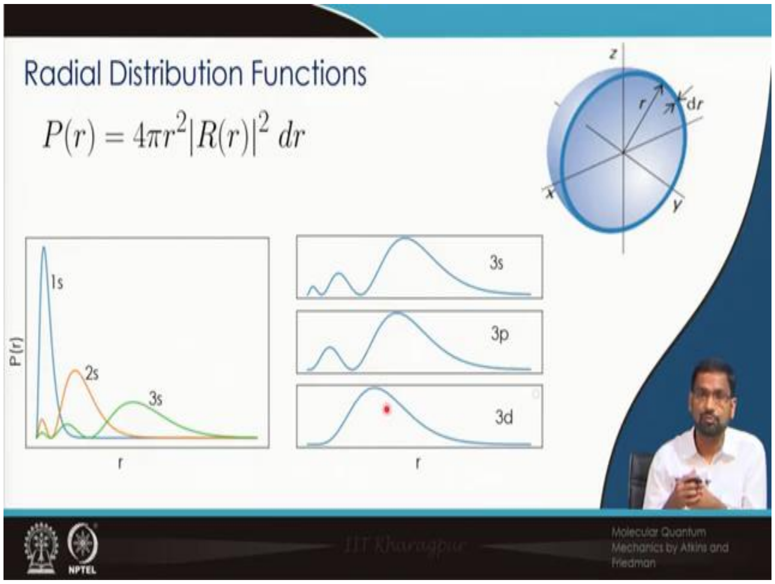

Radial Distribution Functions

$$P(r) = 4\pi r^2 |R(r)|^2 \, dr$$

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Molecular Quantum Mechanics by Atkins and Friedman

While you were discussing about this radial part of this wave function, we always had this thing in mind that the electron is not actually going only along the radial direction, electron is also making an angular movement along theta and phi direction. Imagine, what we actually want to know is to find out the probability of finding this electron at a certain value of *r* away from the nucleus, does not matter what is the value of theta and phi. It is as if we are trying to calculate the probability distribution in this ring, which is separated, which is given by this radius r and radius r + dr.

We can obtain that value, if we integrate out the two angular coordinates (theta and phi) and only write the radial part of the solution. When you integrate out the angular part, we get this 4π and then we have the radial part of the solution that is r^2 d*r* as the volume element in the spherical polar coordinate system corresponding to *r* and the square of R_{nl}(r) term.

We are trying to get the probability distribution for a value of *r* between *r* and *r*+d*r*, no matter what is the value of theta and phi. The resulting function is called the radial distribution function. Now, this radial distribution function is a very interesting quantity that gives many useful features about the hydrogen atom problem.

We see the radial distribution function for 1s orbital shows a single sharp peak at a small value of *r*, which means that the electron in 1s orbital are more likely to be found closer to the nucleus and they are found in a very localized region of space. The 2s radial distribution function shows a small probability at a small value of *r* (the distance between the nucleus and the electron) and a larger probability at a large value of *r*. In between the two peaks, there is a node. This indicates that, if the electron is in 2s orbital, we have some small probability of finding it close to the nucleus and then there will be a nodal region where we will never find an electron and most of the times we are going to find the electron at this large value of *r*. So, average distance of the electron when it is in 2s orbital is certainly greater than that, when it is in 1s orbital as the radial distribution function shows. Since the 2s orbitals are spherically symmetric, the shape of 2s orbital shows a sphere inside a sphere. For 3s orbital radial distribution function, there are 3 places at which the function shows maximum, and there are two places at which it shows node. The radial distribution function of 1s orbital falls sharply, 2s orbital shows a slow decay and 3s orbital shows very slow decay. This indicates as we go for higher *n* value, the electrons are diffused or they can be found farther from the nucleus.

In case of 3p function, you have got 1 radial node, while 2p does not have a radial node. We see 2p orbital as a dumbbell shape, due to the angular nodal plane. For 3p, you can imagine a dumbbell within a dumbbell and in between the two dumbbells, there is no electron density, showing the radial plane. In case of 3d, there is no radial node.

Comparing the radial distribution functions of 3s, 3p, and 3d, you should notice that the 3s electron is found at larger distances compared to 3p and 3d. That is because, the overall probability is 1 and since you have got two nodal structures for 3s orbital, to compensate that the function decays at even greater value of *r*. And in case of 3d, you would see the average value of the radial distribution function is smaller than that of 3p and 3s orbital.

Hydrogen atom is the only problem which can be exactly solved. All other heavier atomic systems and all other molecular systems mimic the solution that we obtained for the hydrogen atom. We can not solve those problems exactly, and this is where we require approximate methods. And some of those methods will be the topic of our discussion in our future classes. Thank you for your attention.