Approximate Methods in Quantum Chemistry
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Lecture 05
Exactly Solvable Models – II

Hello students! Welcome to this lecture. In the last lecture, we discussed a few exactly solvable quantum mechanical models, e.g., the particle-in-a-box and harmonic oscillator. These two problems dealt with motion of a single particle in one-dimension. Now, we are trying to understand what if the particle shows a circular motion.

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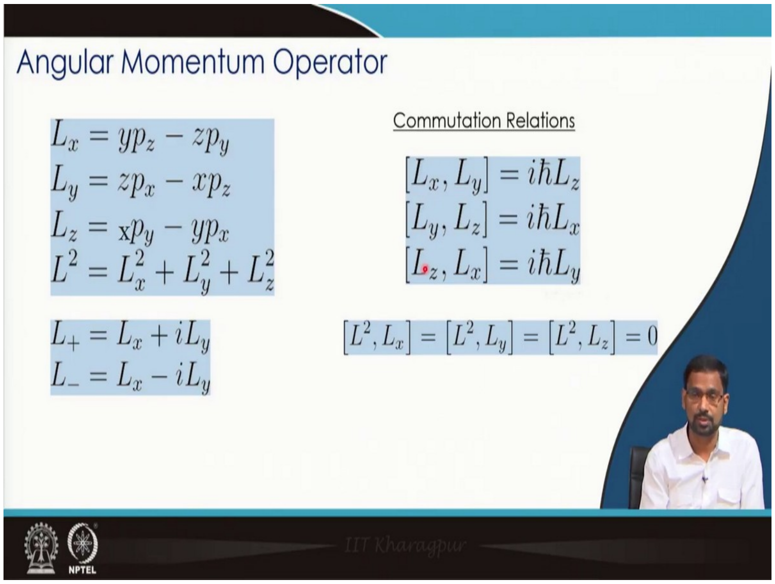

Angular Momentum Operator

$$L_x = yp_z - zp_y$$
$$L_y = zp_x - xp_z$$
$$L_z = xp_y - yp_x$$
$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$L_+ = L_x + iL_y$$
$$L_- = L_x - iL_y$$

Commutation Relations

$$[L_x, L_y] = i\hbar L_z$$
$$[L_y, L_z] = i\hbar L_x$$
$$[L_z, L_x] = i\hbar L_y$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$

In such a case, the angular momentum operator is useful. In the last lecture we defined the quantum mechanical form of the angular momentum operator, which is the cross product of *r* and *p*. We can construct the Cartesian components of this angular momentum operator Lx Ly, Lz. We also discussed about L^2 square, and the step-up/step-down operators (L_+, L_-). The three Cartesian components of the angular momentum operator do not commute with each other, while they commute with L^2. That brings an interesting situation. If we consider L^2 and Lz pair, they commute, and they can have a common complete set of eigenfunctions. Since in the spherical polar coordinates, the Lz operator has a simple form, Lz is considered to be the operator for which simultaneous eigenfunctions are obtained.

Next, lets discuss the eigenfunctions and eigenvalues of the L^2 and Lz operators. These eigenfunctions are called spherical harmonics ($Y_{l,m}$).

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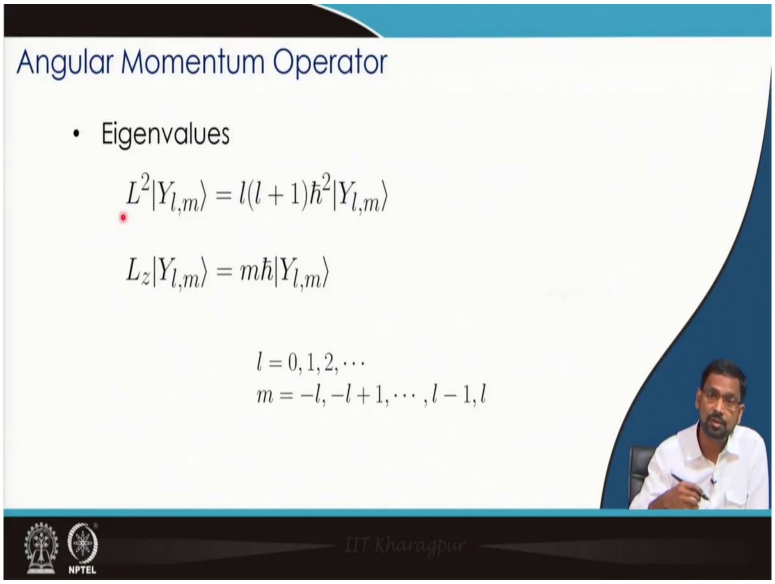

Angular Momentum Operator

- Eigenvalues

$$L^2|Y_{l,m}\rangle = l(l+1)\hbar^2|Y_{l,m}\rangle$$

$$L_z|Y_{l,m}\rangle = m\hbar|Y_{l,m}\rangle$$

$$l = 0, 1, 2, \cdots$$
$$m = -l, -l+1, \cdots, l-1, l$$

The spherical harmonic eigenfunctions ($Y_{l,m}$) have got two indices l and m. You remember when we talked about particle-in-a box or harmonic oscillator, the wave functions depend on a single index – a single quantum number. But here since we are constructing simultaneous eigenfunction of L^2 and Lz, we end up in having two quantum numbers (l and m).

$$L^2|Y_{l,m}\rangle = l(l+1)\hbar^2|Y_{l,m}\rangle$$

$$L_z|Y_{l,m}\rangle = m\hbar|Y_{l,m}\rangle$$

When L^2 acts on spherical harmonics, the outcome or the eigenvalues are depend on l. When Lz acts on spherical harmonics, the outcome depends on m. Here, l is the leading quantum number or independent quantum number and l can take values 0, 1, 2 … for orbital motion. Once l gets defined the value of m follows. So, m is not an independent quantum number, it is the trailing quantum number, it is the dependent quantum number, it depends on the value of *l*. If *l* is defined, then *m* can take certain possible values, i.e., *m* goes from -*l* to +*l* in the step of 1. So, if *l* = 0, then *m* = 0. When *l* = 1, *m* = -1, 0, +1.

The same algebra of angular momentum can also be used for spin or spin angular momentum. Spin also has similar properties like angular momentum operator. Both orbital angular momentum and spin can be expressed with the spherical harmonic functions, except for the fact that when we are talking about an electron spin, the leading quantum number *l* (or *s* for spin) is ½. In that case, $m = (= m_s) = -1/2$ and $+1/2$.

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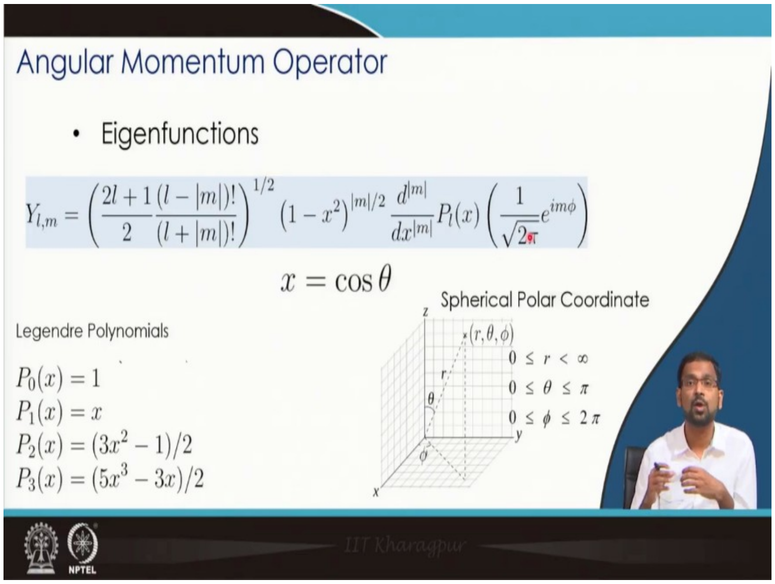

Angular Momentum Operator

- Eigenfunctions

$$Y_{l,m} = \left(\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right)^{1/2}\left(1-x^2\right)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right)$$

$$x = \cos\theta$$

Legendre Polynomials

$$P_0(x) = 1$$
$$P_1(x) = x$$
$$P_2(x) = (3x^2 - 1)/2$$
$$P_3(x) = (5x^3 - 3x)/2$$

Spherical Polar Coordinate

$0 \le r < \infty$
$0 \le \theta \le \pi$
$0 \le \phi \le 2\pi$

When a particle shows a circular motion, for which we are discussing angular momentum, working with Cartesian coordinate system is not advisable. Instead, the spherical polar coordinate makes life much simpler. Let us define the spherical polar coordinate (see the diagram in the above slide screenshot). The three orthogonal coordinates in the spherical coordinate system are the radial coordinate (*r*) that determines the radius of the sphere, the two angular coordinates $\theta, \wedge \phi$. θ is defined as the angle that *r* vector makes with the z-axis. If you make a projection of the point to xy plane and measure the angle that this vector makes with x-axis that value represents the ϕ angle (see the diagram). As in the Cartesian system we have x, y, z, in spherical polar coordinate system we have *r*, theta and phi. While theta goes from 0 to π, phi can go from 0 to 2π. For each value of theta, I can move around the z-axis along xy plane and I can make 2π revolutions. If I do this for a fixed value of *r* the resulting structure that I would get will be a sphere. That is why this coordinate system is called spherical polar coordinate system as it traces a sphere when we scan through the theta and phi components for a given value of *r*. Here theta and phi are the two angular coordinates and *r* is the radial coordinate. For angular momentum operator we do not consider *r* dependence, we would mostly be interested in the results of the two angular coordinates.

Now, let us look at the form of the spherical harmonic eigenfunctions ($Y_{l,m}$), see above. There are several terms in the expression but we will break them down. The first term is the normalization constant and it depends on *l* and *m*. Once you define *l*, *m,* this term is a constant. The functional form of the eigenfunctions comes next.

Let us look at the last term, $e^{\Im\phi}$, which has phi dependence and depends on quantum number *m*. If m = 0, this term does not exist, if m = 1 or -1, this term is $e^{i\phi}$ or $e^{-i\phi}$. The $1/\sqrt{2\pi}$is the normalisation constant.

Now, let's see the middle terms that come from the theta part. Since *l* and *m* are inherently coupled, you see both *l* and *m* dependence here. This part contains a differentiation of the order *m*. The differentiation is of the Legendre polynomials. Some of the lower order Legendre polynomials are shown in the figure above. It is recommended that with the given polynomials, you write down these spherical harmonics for a few values, so, that you would appreciate the results well.

The eigenfunctions of the angular momentum operator are used in the results of particle-in-a sphere and in hydrogen atom problem.

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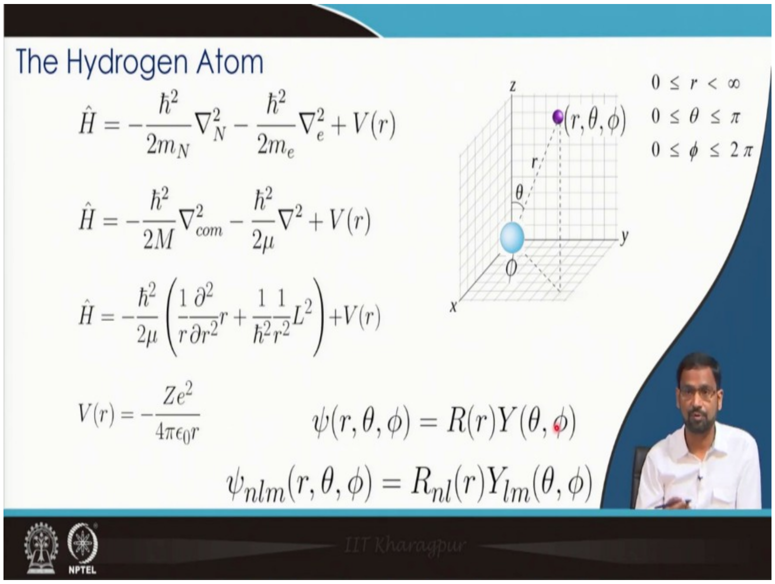

The Hydrogen Atom

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

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{com}^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{\hbar^2}\frac{1}{r^2}L^2\right) + V(r)$$

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

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

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

$0 \le r < \infty$

$0 \le \theta \le \pi$

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

Now, let us consider the next exactly-solvable system, that is the hydrogen atom. When you consider a hydrogen atom, we have a central nucleus around which an electron moves around. It is convenient to express this system in the spherical polar coordinate system introduced earlier. Apart from the two angular coordinates (theta and phi), we now have the radial coordinate that can change, which determines the radial distance of the electron from the central nucleus, which can vary from 0 to infinity.

Now, if we want to solve this problem quantum mechanically, the first step is to write down the Hamiltonian. The Hamiltonian has the kinetic energy (of nucleus and of electron), and the potential energy of interaction between electron and nucleus (see the above figure).

The kinetic energy operators are expressed he as the Laplacian (noted by nabla symbol or inverted delta). The Laplacian is given by $\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}$ in the Cartesian system, which can also be expressed in the spherical polar coordinate system. The potential energy is due to interaction of the positively charged nucleus with the negatively charged electron which can be expressed as a Coulomb potential.

In the Hamiltonian we wrote down, we have got two independent particles: the electron and the nucleus. There is a straightforward way with which we can convert these two-particle systems into two effective one particle systems. I can rewrite this Hamiltonian operator in a slightly different way, where the first term shows not the kinetic energy of the nucleus rather the kinetic energy corresponding to a fictitious particle with mass capital M, which is the sum of the mass of two systems m_1 plus m_2 in this case mass of nucleus plus mass of electron. The second kinetic energy term corresponds to an effective particle of reduced mass μ, the Laplacian is not of the electron coordinate, rather the separation between the nucleus and the electron.

The first term involves the movement of the centre of mass. It essentially means that if I move my hydrogen atom from one place to another, what would be the effect? I know it does not matter, as long as the internal coordinate (nucleus-electron separation) does not change. Leaving aside this overall translational motion, I am left with the second and the third terms, which actually depend on the separation between the electron and nucleus.

Since mass of electron is much smaller than the nuclear mass, the sum of the two will be close to the latter. Hence, the centre of mass will be very close to the nucleus. Thus, you can effectively call the first term as the kinetic energy of the nucleus. Look at the second term. The second term, represents the reduced mass which is going to be very close to the mass of the electron. Again, the second kinetic energy term is the electron kinetic energy. But the advantage is that now, the two kinetic energy terms are decoupled and hence can be treated separately.

Now, let us focus on the second and third term, which depend on the internal coordinate (r). The Laplacian is shown in the spherical polar coordinate system, which has terms dependent on the radial and angular components. I am expressing the Laplacian in a simpler way. The first term contains only radial terms. The second term has r dependence apart from L^2 (the square of the angular momentum operator). Now our Hamiltonian of hydrogen atom actually has the L^2 term. Why is it so important? Because we already know its solution.

As it would turn out, when you do the derivation, you would see that the overall wave function has dependence on three different quantum numbers: l and m correspond to the two angular coordinates (exactly the way we discussed about the angular momentum operator). On top of it, we have got another quantum number n, the so-called principal quantum number. In this case, n

is the leading quantum number and l and m follow the value of n. The total wave function is given by the radial part (depends on n and l) and angular part (depends on l and m).

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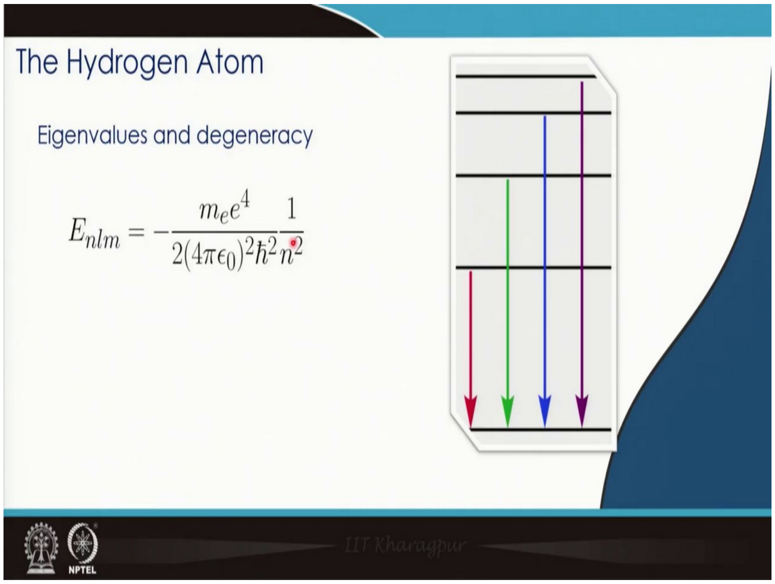

The Hydrogen Atom

Eigenvalues and degeneracy

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

We will come back to the explicit form of the wave function later. First let us look at the eigenvalues or the energies (E_{nlm}). Actually, when you check the expression, you would see that the energy depends on (apart from some constants), one quantum number n. The constant appearing in the energy expression is the Rydberg's constant, which is -13.6 eV. This constant is multiplied by $1/n^2$, where $n = 1, 2, 3\ldots$

The diagrammatic presentation of the energy levels is made in the above figure. Since the energy is inversely proportional to n^2, as you go higher, the separation between two neighbouring energy levels get reduced. But, one important thing that you should notice is the negative sign. The negative sign indicates that this is a stable situation, i.e., the electron is being attracted to the environment of the nucleus. When n is very large, suppose n is infinite, the energy value will come close to 0. What does that represent? That would represent that when n is very large, the electron has gone very far away from the nucleus. So, much so, that at one point the electron will lose any contact with the nucleus and in that case, we would call that it an ionized (free) electron. In that sense situation the electron becomes ionised, leaving behind the cationic nucleus. In that case, there is no interaction energy. This leads to a free particle. An electron which is free from the influence of the electron. But as long as it is under the influence of the nucleus, the energy is negative.

Additionally, we would also see that the energy depends only on n but not on l and m. This leads to degenerate states. This degeneracy and the form of the eigenfunctions is what we are going to discuss in our next class. Thank you for your attention.