Approximate Methods in Quantum Chemistry
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Lecture 04
Exactly Solvable Models – I

Hello students! Welcome to this lecture. In the previous lecture we discussed about the principles and postulates of quantum mechanics and in this lecture would start looking at some exactly solvable models in quantum chemistry.

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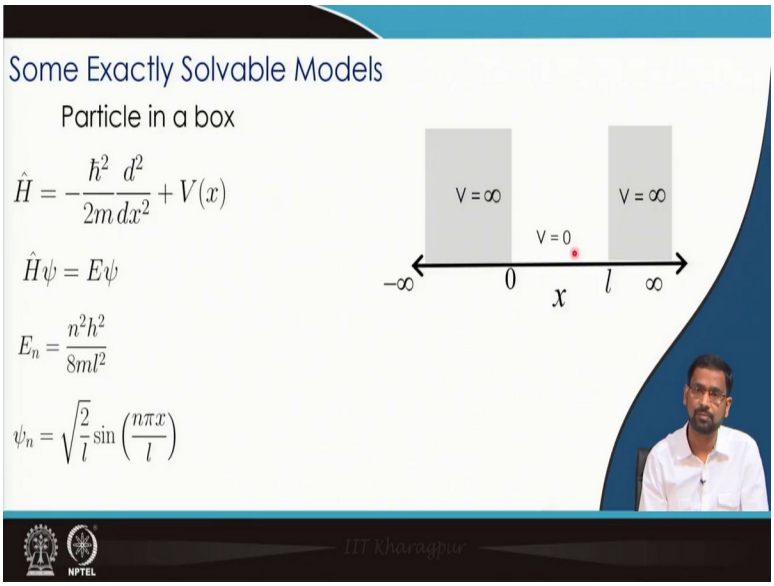

The first problem that we are going to discuss is the 'particle-in-a-box' problem. The particle in a box problem is quite a relevant problem in chemistry. You can imagine it by considering an electron confined to the nuclear environment in an atom or in a molecule. Consider an electron experiences an infinitely high potential barrier to escape this box (i.e., the molecule). We can define our potential in this manner. Along x-axis, between x=0, and x=l, the electron or the particle experiences zero potential and outside (i.e., x=-infinity to x=0 and x=l to x=+infinity), the particle experiences an infinitely high potential. This creates a box between x=0 and x=l that the particle can never escape.

We want to solve this problem quantum mechanically. The first step is to write down the corresponding Schrödinger equation and to do that we require the definition of the Hamiltonian operator. The Hamiltonian operator will have a kinetic energy contribution and some potential energy contribution.

Who can contribute to the kinetic energy? Whenever we have a particle which has got a mass and which is moving with some velocity, it has a kinetic energy. In the current problem, we have got a particle (consider mass m). The corresponding kinetic energy operator can be expressed in terms of the momentum operator ($p_x = i\hbar \frac{d}{dx}$), as $p_x^2/2m = -(\hbar^2/2m)\frac{d^2}{dx^2}$.

What is the potential energy? In the system, all interactions (such as interaction between particles, or interaction of particle with external field, etc.) contributes to the potential energy. In particle-in-a-box problem, outside the box the potential is infinite and inside the box potential is 0. So, *V* takes a very simple form: it is either infinite or does not exist.

With this Hamiltonian I can write down the corresponding Schrödinger equation. I am sure you have already solved this equation in your earlier quantum mechanics course. We are not going to derive the solution, rather we are going to use the results (that is the eigenvalues and the eigenfunctions)

$$E_n = \frac{n^2 h^2}{8ml^2} \qquad \psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

Apart from the constants (*h* = Planck's constant, *m* and *l* are constants for a specific problem), we see that the eigenvalues and eigenfunctions depend on parameter *n* (the quantum number) that goes from 1, 2, 3 and so on so forth.

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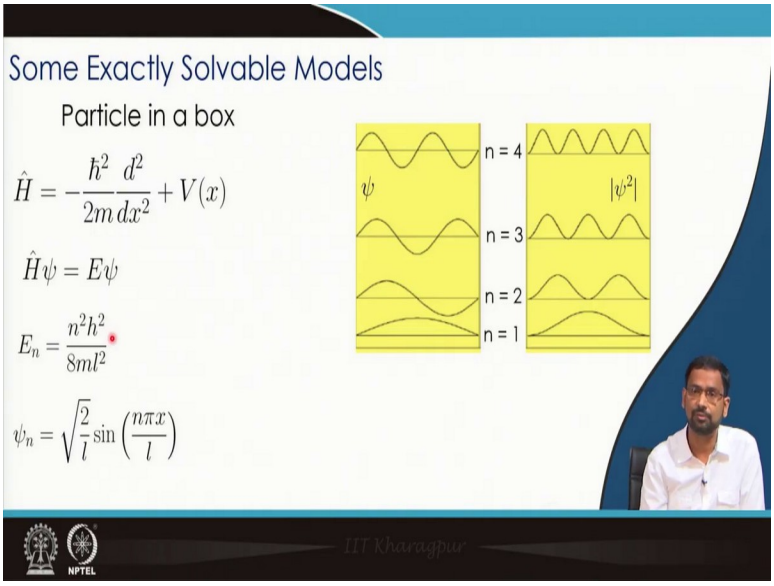

The eigenvalues or the energy has n^2 dependence. The energy spacing (see the slide screenshot) keeps on increasing for increasing n. The energy also depends on the mass and the length of the box. When the mass is very large or the length is very large then you see the En value becomes very small. When En itself becomes very small the spacing between two energy levels becomes even smaller. This means, that when mass and length are very large the spacing between two neighbouring energy value becomes negligibly small. So much so that the quantised nature of these energy levels loses meaning and the energy levels appear continuous. That means when mass is large, length scale is large, we are actually entering the classical realm. In classical world there is no such quantization of energy level. It is a phenomenon that is strictly observed in the quantum world. This is an example of quantum to classical correspondence.

Now let us consider the wave functions $$\psi_n = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)$$

The factor under square root is the normalization constant. Apart from that you see a *sine* function that depends on the quantum number n (apart from other constants like, pi, x and l). In the figure above, the wave functions for different values of n are plotted. You can observe that as I consider larger values of n, I am trying to fit a greater number of periods of the *sine* function into the same length of the box, which results in a greater number of nodes (places where the wave function as well as the probability of finding the system becomes 0).

It is a common feature that you would see in most quantum mechanical systems that higher energy states typically correspond to a greater number of nodes. Now, in addition to the wave function, we can also discuss the probability density of the corresponding eigenfunctions.

So far, we discussed the case where the potential outside the box is infinite. So, outside the box the wave function is always 0. That makes sense because the particle never escapes the box. But that is true only when we have infinitely high wall, but if we have a finite barrier there is a chance of leaking of the wave function or the tunnelling, where you would see that the wave function slowly decays outside the box. Tunnelling is a purely quantum mechanical phenomenon. For a free particle, where V=0 everywhere, there is no boundary.

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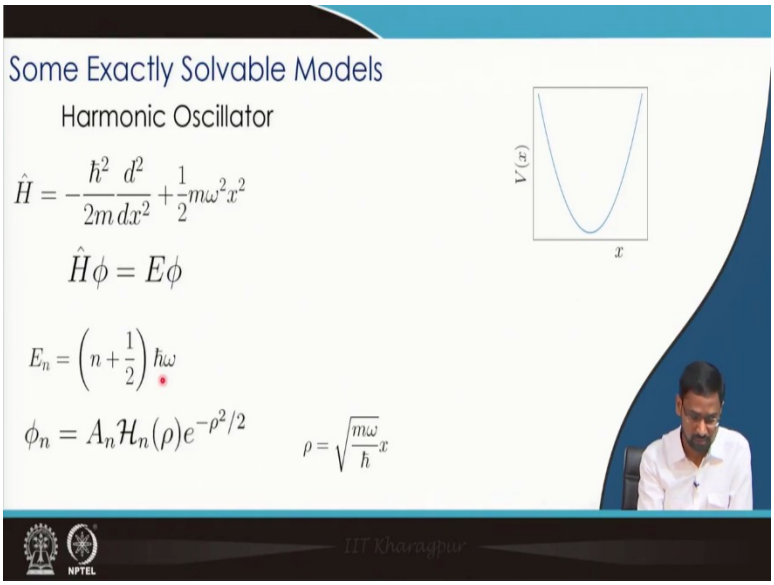

Now, let us look at another exactly solvable model, i.e., the harmonic oscillator. In chemistry we can use harmonic oscillator in many cases. The harmonic oscillator model can be considered wherever the system oscillates around an equilibrium position. If you have a system and you do something to it and then it starts oscillating forward and backward around the original position or the equilibrium position, that is a system where we can use harmonic oscillator model. In chemistry where can we use? Consider a bond vibration. From microwave spectroscopy, for example, we can know the equilibrium bond distance. But then we also know that at a finite

temperature, the system undergoes internal motion along the normal modes of vibrations, which can be probed by IR spectroscopy. The atoms in a molecule show a harmonic movement around their equilibrium position, for example, a bond stretching and shrinking. Hence, molecular vibration is a popular place where harmonic oscillator results are used. In fact, we explain infrared spectroscopy or vibrational spectroscopy by using the eigenfunctions and eigenvalues of harmonic oscillator problem.

In the harmonic oscillator model, we have a particle of mass *m* that goes around the equilibrium position along x-axis. The motion can be towards the positive side or negative side of x = 0. The potential is given as a harmonic oscillator potential ($V = (1/2) k x^2 = (1/2) m \omega^2 x^2$), where *k* is the force constant corresponding to the harmonic oscillator with the angular frequency (ω). In harmonic oscillator model, we have a soft potential that slowly increases from x=0. In case of particle in a box, we had hard potential, which is either 0 or infinite. But both the models are one-dimensional models involving a single particle. The kinetic energy has the same form as we had in the particle-in-a box problem.

With the given Hamiltonian, we can write down the Schrödinger equation. The solution of harmonic oscillator problem is perhaps a little more complicated than the particle-in-a-box problem. But nevertheless, it is rather straightforward. We are not going to do the derivation to get to the results. Instead, we are going to use the final results, i.e., energies and the wave function.

Let us, first consider the energies.

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

The energy depends on the frequency corresponding to the harmonic oscillator (ω), which is going to be different for different systems. If you have a harmonic oscillator with very large value of omega, the energy and the energy difference will be accordingly large. Apart from this, the energy has *n* (quantum number) dependence.

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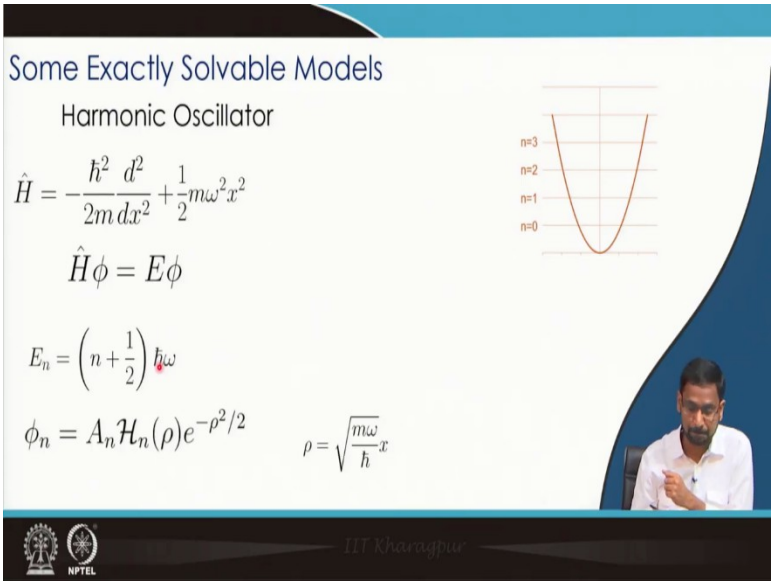

Unlike particle-in-a-box where the minimum value of the quantum number n=1, here in the harmonic oscillator case, the lowest value of the quantum number is n = 0, when the energy is $(1/2)\hbar\omega$, also called the zero-point energy. Thus, the energy of the lowest state which is not 0. But that means even when the system is in its ground state still has got some energy and that energy is the zero-point energy. Now, as I use higher values of n, the energy increases ($(3/2)\hbar\omega, (5/2)\hbar\omega, (7/2)\hbar\omega$ … for n = 1, 2, 3, … respectively. The separation between two consecutive energy levels is going be $\hbar\omega$. In IR spectrum we observe the n = 0 to n = 1 transition, so that the IR band appears at energy $\hbar\omega$.

In harmonic oscillator all the states are bound states, that means no matter how much you distort this system from the equilibrium position, either right-hand side or left-hand side, the harmonic potential remains harmonic, which is an elastic potential. But in real life application (bond vibration, for example), the harmonic oscillator is a severe approximation and we often incorporate anharmonicity. I am sure you must have encountered this in your spectroscopy course.

Now, let us consider the eigenfunctions. The eigenfunctions of harmonic oscillator are slightly more complicated than the eigenfunction a particle in a box. Before we introduce the

eigenfunctions, let us learn about a transformation of the coordinate x (which is actually the displacement from the equilibrium position) to a dimensionless coordinate,

$$\rho = \sqrt{\frac{m\omega}{\hbar}}x$$

Here, m, ω are system specific constants. Normally, the harmonic oscillator eigenfunctions are expressed in dimensionless coordinate, so that you can switch from one molecular system to another molecular system and the expression remains the same, since the effect of the molecular environment gets incorporated by m, ω in the relation.

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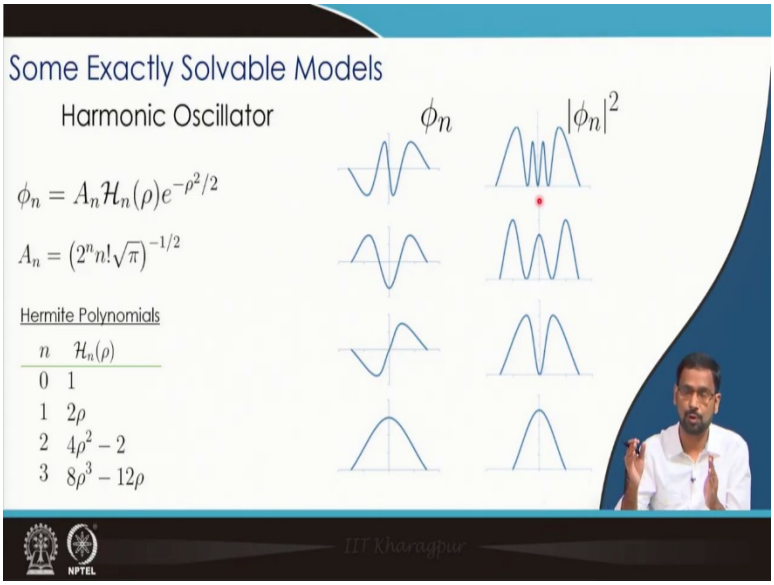

Now, let us look at this wave function $\phi_n$little closely. The eigenfunction has got three parts. The first one is A_n which is the normalization constant. In particle in a box problem the normalization constant was simply $\sqrt{(2/l)}$, independent of n. But here, the normalization constant depends on the value of n. The second term is the so called *Hermite polynomial,* a very useful polynomial popular in mathematics. You can always find in most quantum mechanics text books in the appendix. The 0^{th} order Hermite polynomial is simply 1. The first order Hermite polynomial is $2x$

or 2ρ (ρ is the dimensionless coordinate) and the higher order polynomials are given in the above figure. The third component of this harmonic oscillator eigenfunction is the Gaussian function $(e^{-\rho^2/2})$. The Gaussian function is an even function but the Hermite polynomials polynomial of order *n* is odd for odd values of *n* and even for even values of *n*. Therefore, the eigenfunctions of harmonic oscillator have definite parity, they are either even functions or odd functions, depending on the value of *n*. Having a definite parity is very useful in evaluating different properties of the harmonic oscillator.

For n = 1, 2, 3, … as you go for higher *n*, you start seeing a greater number of places where the wave function becomes 0, i.e., a greater number of nodes. For *n* = 0, no nodes, *n* = 1 you have got one node and so on.

The probability density $|\phi_n|^2$ plots for different *n* are also shown. You can notice that for higher values of *n*, the probability builds up towards the sides (the boundary region, away from equilibrium) of the harmonic oscillator, also called the turning points (where the oscillator retraces its path and comes back to the equilibrium to follow the opposite side of the trajectory). This to-and-fro motion is restricted by the two boundary regions at the turning points. At those turning points, we see the probability getting accumulated. This is again an important concept that we often use in spectroscopy when we talk about vibronic transitions and the Frank-Condon factors.

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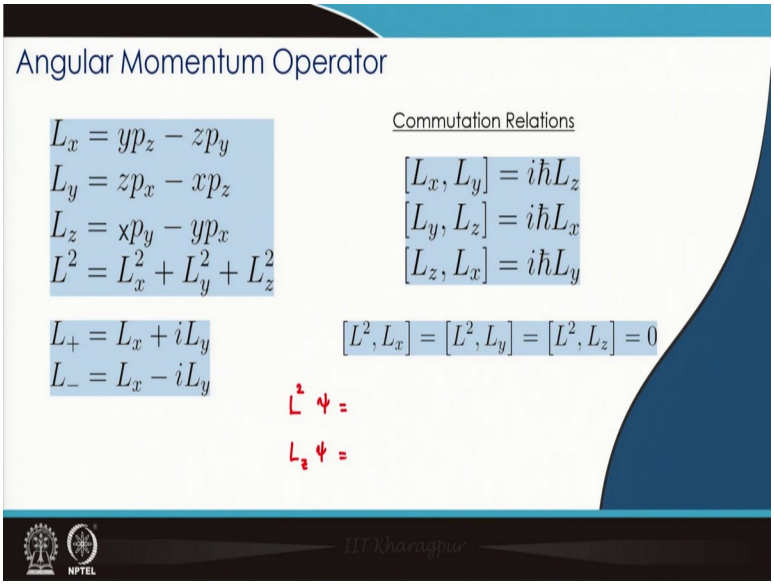

Now, before we go further looking for some other exactly solvable models, let us, discuss a very important operator and its eigenfunction. This operator is the angular momentum operator. Where do we need angular momentum operator? Whenever a particle shows a motion along a circular path, the angular momentum is better suited to describe the system.

From classical mechanics we know that angular momentum is given by the cross (or vector) product of *r* vector and the linear momentum vector, when the particle is moving around a circle of radius *r*. We can write $\vec{L} = \vec{r} \times \vec{p}$. In that case we can obtain the three Cartesian components of the *L* operator that is L_x, L_y, L_z (see the above figure). In addition to the individual Cartesian components we also define the L^2, L_+ and *L*- (the step-up and step-down operators). See their definition in the above figure.

The angular momentum operators are usually characterized by a very interesting commutation relation. The three Cartesian components of the angular momentum operator that is Lx, Ly, Lz do not commute with each other. If two operators do not commute then we know that they cannot have common eigenfunctions. So, that means if I know the outcome of Lx operator for a particular system precisely, I cannot know the same for Ly, because Lx and Ly do not commute. That means there will be some uncertainty. Apart from this, we know that these individual components *Lx, Ly, Lz* they commute with L^2 operator. Now, we have this interesting situation where Lx Ly Lz they do not commute with each other but each of these component commutes

with L square. So, that means if consider one of these pairs, say, L^2 and L_z, then you can see that we can construct simultaneous eigenfunction of these two set of operators.

The solution of angular momentum operator or the eigenfunctions of the angular momentum operator are obtained as a common complete set of solution for L^2 and L_z. What are they and what are their properties? These are some of the things that we would discuss in our next class. Thank you for your attention.