Quantum Chemistry of Atoms and Molecules

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Lecture-12
Harmonic Oscillator: Part 1

So for in this course we are talked about free particle. We have talked about particle in a box and then we talked about tunneling. Today we move to another system which is very important from the point of view of quantum mechanics and this system is that of a harmonic oscillator. We will take 2 or 3 modules to complete the discussion. So, today we are just going to introduce ourselves to the problem.

And we are going to learn a very important concept called ladder operator. A harmonic oscillator of course is something that all of us are familiar with from; once again class 11 and 12. We know harmonic oscillator is an oscillator that obeys Hook's law. What is Hook's law? F equal to - kx or can write - kx equal to m d2x dt2 where x is a displacement from mean position and we might remember the classical examples of harmonic oscillator.

A pendulum of a clock is a harmonic oscillator provided angular displacement is not more than 4 degrees and there are many such examples. And oscillatory motion is very closely related to circular motion. And that is why we get results that look very, very similar to what we get in circulatory motion. And we get to work with things like frequency of Oscillation and so on and so forth things if you encounter in rotational motion.

So, as usual your first going to remind ourselves of the classical picture of harmonic oscillator and then will going to the quantum mechanical description. So let us get started.

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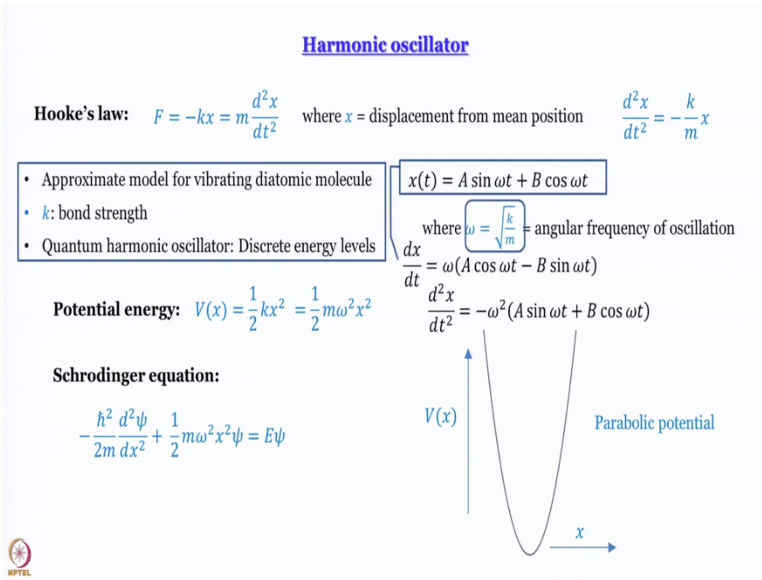

Why should we start? Why should we discuss Harmonic oscillator in Quantum chemistry course anyway. The biggest reason from the point of view of a chemist is that harmonic oscillator provides an approximate model for a vibrating diatomic molecule. And then if you do that then this k that is there the force constant is basically tells us how strong is a spring is if it is for spring. So what we do this, we approximate be chemical bond between two atoms in a diatomic molecule.

To, start with as spring with a spring constant k, so automatically k becomes Bond strength, so if you can determine k quantum mechanically or spectroscopically then we get to know the bond strength, which is a very important parameter for the most fundamental important parameters of chemistry. Now when we try to talk about molecules of course, the classical description is not going to be complete and we have to discuss Quantum harmonic oscillators.

So whenever we go from classical to Quantum regime, we find that several difference is coming discrete energy levels coming, will talk about wave functions and we see we get one more very interesting concept that comes up. Before going there let us develop the treatment the little bit. First of all let us simplify this Hook's law a little bit and let us rearrange and write d2x dt2 is equal to -k by m x, now this is a differential form which we can differential equation form, which we can try to solve.

And trail solution that we use is x of t is equal to A Sin Omega t + B cos Omega t once again this Sin Omega t cos Omega t is reminiscent. Offer to get in circular motion. Omega here is root over k by m and that as we might know is angular frequency of oscillation. To see whether this is a valid solution or not what will do it will differentiate twice and see what we get. So let us find dx dt. What is dx dt? We have A Sin Omega t + B cos Omega t so when you differentiate Sin Omega t with respect to t omega comes out and Sin Omega t derivative is cos omega t.

And the second term + B cos Omega t once again Omega comes out and cos omega t when you differentiate it gives you - Sin Omega t. So, what you to get is omega multiplied by A cos Omega t - B Sin Omega t and since we are talking about eigenvalue equations is very obvious that this is not an eigenvalue equation. So, this function that you use is not and eigen function of the first derivatives. What about the second derivative because second derivative is what we are interested in we want to solve this differential equation.

If you differentiate once again, what will we get the first term A cos omega t - Omega A Sin Omega t and Omega multiplied by this omega already gives you -omega square. Second one gives us Omega multiplied by B Sin Omega t and minus sign is already there. So now omega square comes out and d2x dt2 turns out to be omega square minus omega square multiplied by A Sin Omega t + B cos Omega t see what happened you got back x of t in this equation.

First of all is an eigenvalue equation. Secondly, if you compare this equation with this equation, it is very clear that -k by m is equal to minus omega square or Omega is equal to root k by m. This is something that comes from classical mechanics. We want to go into the quantum world. Then what we need to do if we need to write Schrodinger equation. For that, we need to remember that potential energy in this case is going to be half kx square.

So this is a parabolic potential. Let us also remember that a relationship between Omega the frequency of oscillation frequency of oscillation and the force constant k, so instead of k we might as well write something in omega. We write half m omega square x square that is your potential energy. So now we take this and plug it in Schrodinger equation. The first term of the Hamiltonian remains the same is the kinetic energy operator.

In case of potential energy we are going to write half m omega square x square. So, here is what we get – h cross square by 2 m d 2 Psi by dx2 + half m omega square x square Psi. Now it might be worthwhile to here that usually what we do if we do not work with m, we work with reduced mass because it is the two body problem when you talk about oscillator is a diatomic molecule HCL the other two atoms and moving with respect to each other and it is difficult to formulate the problem that way.

So what we do it reduce it and instead of m we write ad mu the reduced mass and that is what we worked with but for now will just we write m whenever the need arises will switch conveniently to mu and I am not going to the detail of it because that we must have done earlier in Physics classes.

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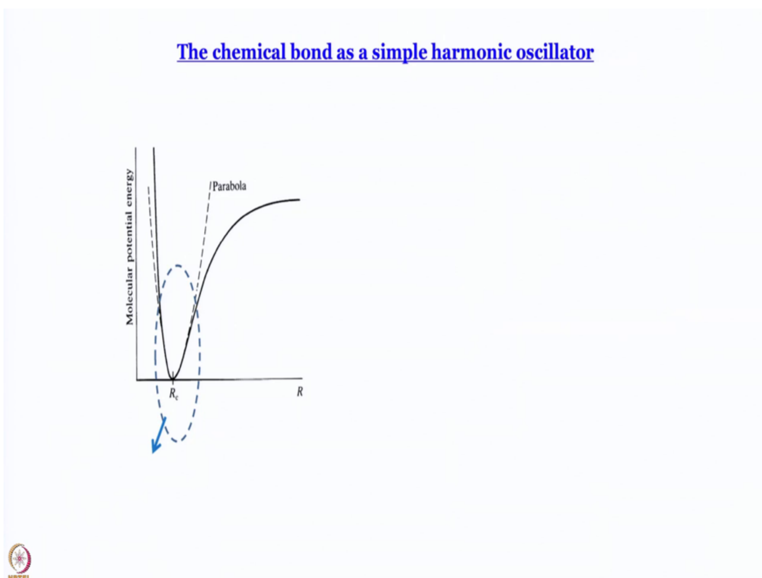

So, now before going further let us discuss a little bit about why a simple harmonic oscillator would be a more or less valid model for chemical bond. We know from; once again class 11, 12 knowledge that a potential energy surface for diatomic molecule is something like this is not really a parabola when the two atoms very far away from each other. Then the interaction energy is 0 and then when they come closer than the attractive forces predominate and then energy goes down until a minimum point equilibrium bond length.

After which the energy increases sharply due to internuclear repulsion. So, it is very clear that this curve that we have drawn solid curve is definitely not a simple harmonic oscillator. But if I try to draw a simple harmonic oscillator and superimpose with it you can see that from for small displacement from the mean position that 2 curves are more or less super imposable from here to here 2 curves are more or less the same.

And remember simple harmonic motion requires very small displacement from mean position anyway. So if you are going to work with small displacement from mean position then simple harmonic oscillator model might be a valid model. So that is the premise within which we are going to work for now. Later on when you want to do Spectroscopy not in this course, when you want to Spectroscopy then you consider anharmonicity of the oscillator.

But let that be the story for another day whoever is interested can go to the lectures on our molecular Spectroscopy course, which are now freely available on YouTube. So, simple harmonic oscillators is a good approximation for small displacement.

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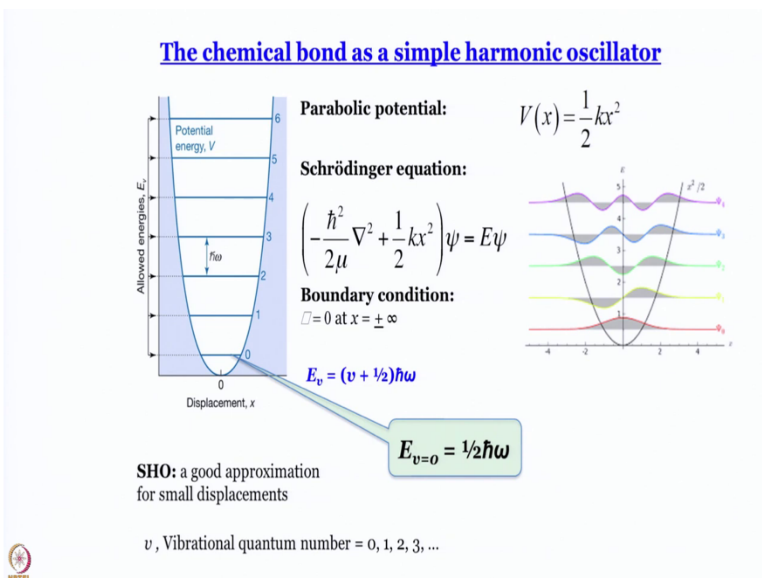

You work with the parabolic potential we write it Schrodinger equation as already done in fact we have written it in a little more complicated form that will come back later. And then when we solve it was always with boundary condition, sorry Psi not coming here. And this is actually Psi,

Psi is 0 at x equal to plus minus infinity to remember the conditions that arose from Born interpretation the system cannot exist beyond x equal to plus minus infinity, right?

So for continuity like in particle in a box the boundary condition is Psi equal to zero at x equal to plus minus infinity not a; wherever this potential energy surfaces and as we are going to see later on right now. What I am doing right now is I am sort of putting the cart before the horse and giving you a brief summary of the results. Later on will actually arrive at that reason why I want to do this is that we are going to do a little bit mathematical manipulation.

I would not like us to get lost while doing that. I like everyone to know what lies there at the end because the end result is what is of use as application in chemistry. So, let me give you the end result first so that even if you get confused while we go to the next discussion, it is not so much of a problem to understand the application. So, when you work it out; we will see that energies is quantized. Energy E V is equal to V + half into h cross Omega, Omega one second is angular frequency of oscillation and V is the vibrational quantum number ranges from 0 1 2 3 4 and so on and so forth.

So this is what you will get will get discrete energy levels and they are going to be equi spaced that is very easy to see. You just workout for E V +1 is going to be subtracted E V from E V +1 will always get h cross Omega in a simple harmonic oscillator. Quantum harmonic oscillator we get equispaced energy level and energy gap between the two; between two successive levels is always h cross Omega that is 1 quantum of vibrational energy.

Now we will of course get wave functions will work all this out right I am only giving you the summary of the answers. We will work out and will get see that we get wave functions that look somewhat similar but not exactly similar to what we get for particle in a box, but in every major departure from particle in a box you see that some wave function is there outside the potential energy surfaces as well, and I like you to take this as an exploratory question.

I like you find out may be post on the forum why you think the wave function exists outside the potential energy surface as well of course it dies down fast but let that be homework for you that is one thing. The second thing is that as I said vibrational quantum number ranges from 0 to infinity. So, the lowest energy, you can get when you put V equal to 0 is half h cross Omega. you see vibration energy for Quantum harmonic oscillator can never be settled. Quantum harmonic oscillator can never be rest.

Even if you lower the temperature to 0 Kelvin you get a minimum energy of half h cross omega this is called this zero point energy. This is a very major departure from a classical harmonic oscillator. Classical harmonic oscillator can actually be stationary. Quantum harmonic oscillator cannot be stationary why because it does then its position is determined completely uncertainty in position is 0. What is the position x is equal to 0 it will be in equilibrium position.

And what is the uncertainty in momentum that also is 0 because it is not vibrating anymore. So delta p is equal to 0 and x is equal to 0 is not allowed; it is not allowed because of Uncertainty principle that is why Quantum harmonic oscillator can never be at rest zero point energy is there. When we talk about rigid rotor later, you see that a rigid rotor can be at rest even quantum rigid rotor and we will discuss why that is the case. Why the departure from Quantum harmonic oscillator.

For now the very important take home message is that for Quantum harmonic oscillator the lowest allowed energy is half h cross omega and we will work it out in the next module is called zero point energy as I said. Now let us come back to the earlier slide and let us start trying to find solutions for Schrodinger equation. This is our Schrodinger equation minus h cross square by 2 m remember m will be replaced by mu in due course d2 Psi dx2 + half m omega square x square Psi equal to E Psi.

There are 2 ways of finding solution of the Schrodinger equation for a harmonic oscillator. The first way is a power series method for brute force method, which is of use in many other applications as well. I am not very sure whether you want to do it here but will see. The method that will definitely workout is the algebraic method using ladder operators this is a fantastic method and it introduces us very important concept of ladder operator as you will see.

By the way the discussion and performing is from Griffiths quantum mechanics book. I find that this book is very nice reading as well. The treatment is nice and it is as if the author is talking to you. So, you get a good feeling if you read this book but you can study this from any standard quantum chemistry, quantum mechanics book that you are comfortable with ok. So let us go ahead and let us try to learn the algebraic method using ladder operators for finding solution of Schrodinger equation for a Quantum harmonic oscillator.

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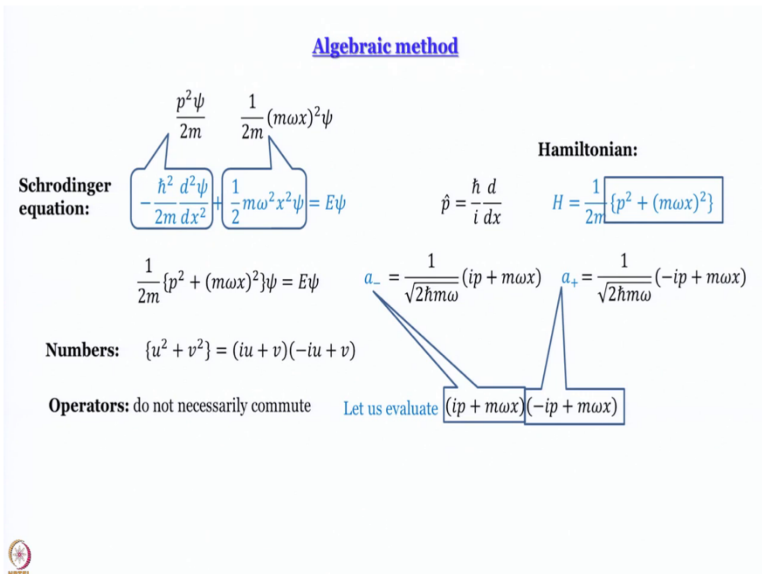

So, here is your Schrodinger equation, let us see if you can write it in little bit of simpler form. So, first of all if you get the kinetic energy term first 1 – h cross square by 2 m d 2 Psi dx2 here the operator involved here is minus h cross square by 2m d2x dx2 that is the kinetic energy operator as we discussed already. Of course here we are talking about motion in 1 dimension only.

So that is why you do not have this del 2 del x2 del 2 del y2 del 2 del z2 business. Now kinetic energy is directly as direct relationship with linear momentum and as you know linear momentum operator is h cross by i d dx or you could write – ih cross ddx right of course kinetic energies p square by 2 m. So, you can write this kinetic energy operator –h cross square by 2 m d2 d2x in terms of this p hat operator. And of course is going to p square by 2 m so I can write the first term on the left hand side of the Schrodinger equation as p square Psi by 2 m.

For the sake of convenience I am not writing the hat anymore, but please do not forget that p here is actually an operator is not a number p square Psi by 2m is the first term and while writing a second term what will do it eventually want to write it in some simple form right. So look at the second term your omega square and x square and we have m so it can very easily come m Omega x whole square if I divide it by another m.

And the good thing is that if I do that the second term will also have 2m in the denominator the first term already has 2m in the denominator so I can take it out outside bracket. So, what I will do is I will write the second term as 1 by 2 m multiplied by square of the product m Omega x that operating on Psi. So, I have just re written in the 2 terms on the left hand side of Schrodinger equation. So now taking 1 by 2m outside the bracket the equation becomes 1 by 2m p square please do not forget the p is an operator plus m Omega x whole square so this together is the Hamiltonian operator that operating on Psi gives us E Psi.

I am operator, operator so many times because it is important that we do not forget that you are not dealing with numbers are dealing with operator even x here is really the position operator is the different method that when position operator operates on the wave function. It gives you the eigenvalue of position multiplied by the same wave function. So, now see this is our Hamiltonian 1 by 2m multiplied by p square + square of m Omega x.

Now look at this part p square + omega x whole square if there is some way of factorizing it would be of course if there are numbers and it is very easy because it is in the u square + v square form and we know that u square + v square can easily be factorized as iu + v multiplied by –iu +v square, u square – v square everybody knows that involves all real numbers. If I have u square + v square you can still factorize it by using the imaginary number iota i u + v multiplied by –iu + v just check whether this is ok or not.

I will give a second for that, alright fine let us go ahead. So, now the issue is the square is a not number as I said these are operators and the problem with operators is that if they are numbers then u into v would be equal to v into u commutation relations would hold uv equal to vu or uv –

vu is equal to z. Operators however, do not necessarily commute and here we are working with the momentum operator and the position operator.

We are going to show you in the next module that these 2 operators definitely do not commute. If the operators commute then some special property arises again let us again check out there, but operators do not necessarily commute. So it is not easy to factorize this u square + v square kind of expression into two products. But what will do is we will still try and see what is the form of this kind of product? We will take i into p + m omega x and will take minus Psi into P + m omega x multiply them together and see what we get.

And what we get is going to make our life a lot more interesting as for as your harmonic oscillator is concerned. What will do it will try to evaluate ip + m omega multiplied by - ip + m omega x. To do that what we will do is we are going to write this in a little simplified form once again, remember ip + m omega x is an operator in itself p is an operator x is an operator so the linear sum is also an operator and same holds true for – ip + m omega x.

What will do is we will construct an operator out of ip + m omega x and we are going to call it a minus. Similarly we are going to construct an operator out of minus ip + m omega x and we are going to call it not very difficult for you to guess now a plus. Now why this is called a minus and why that is called a plus you will see but for now let me just tell you what the form of the operated is a minus is actually 1 by square root of 2 h cross m Omega multiplied by ip + m Omega x.

Where did that 1 by 2 root over 2h cross m Omega come from it came from hindsight we are not the first people working. It has been done many times and people who did it for the first time actually found out that the subsequent result becomes simpler and more meaningful if we use this factor of 1 by root over 2h cross m Omega as if you see further then that is because we stand on the shoulders of Giants as take the advantage of standing on the shoulders of Giants that is where this factor comes from.

That does not falling from sky if you did for the first time you perfectly justified in not even writing this factor we write it because we know where we get it. Right similarly. If a plus is 1 by root over 2h cross m Omega multiplied by - ip + m Omega x. So, did you find the factors then what we want to do if you want to work out the product? Remember this is the operator once again, I am repeating many times because is a concept that often does not sync in if I just say once and go ahead.

So if we; there are two ways in which we can work out the product of a minus and a plus. We can either workout a minus a plus or we can work out a plus a minus. Remember that operator that is on the right operates first on the function operator on the left operates next. So, what we will do is we are going to evaluate a minus and a plus.

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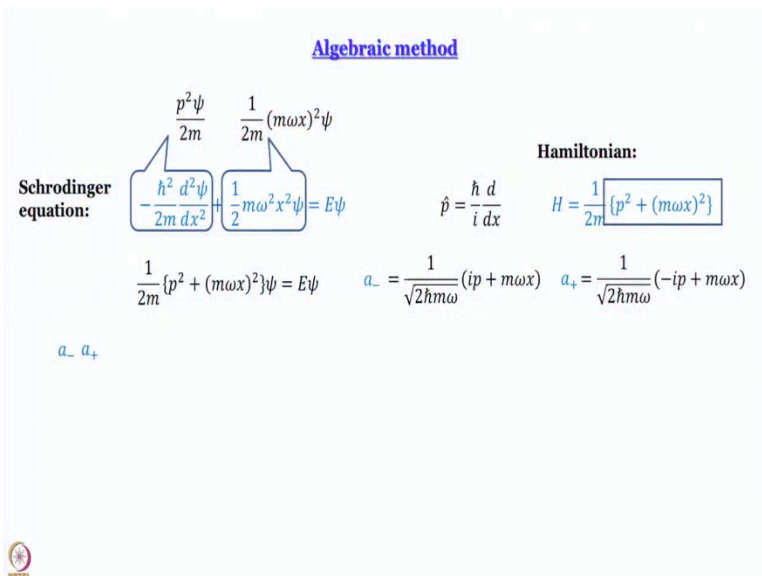

I request you after the module to evaluate a plus a minus yourself because we will use a plus a minus as well. So this is what we want to do now. Let us take a break come back and start right from here in the next module.