Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-38
Application of Perturbation Theory Anharmonic Oscillator

We are studying perturbation theory we have developed the rudiments of time independent perturbation theory already. And we have discussed one very, very simple example which we are going to rehash today. Now we go on to another example which is the next step once again it is going to be quite easy and this is that of anharmonic oscillator.

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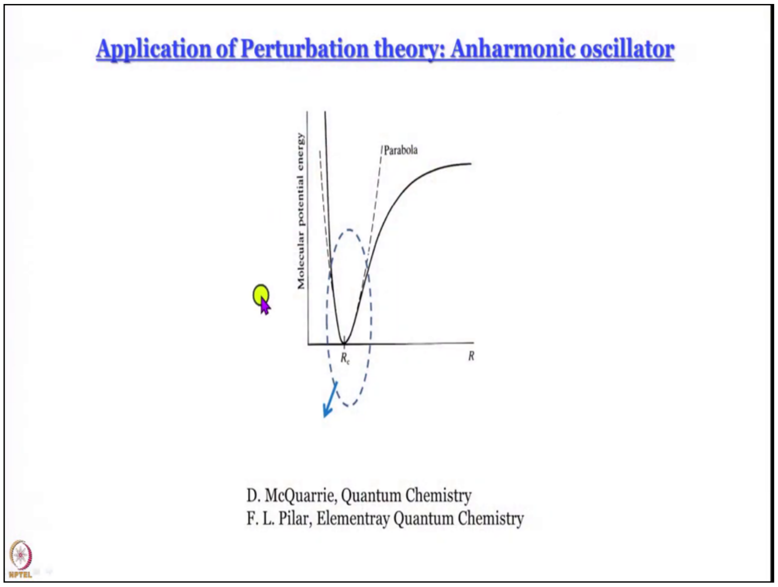

Application of Perturbation theory: Anharmonic oscillator

D. McQuarrie, Quantum Chemistry
F. L. Pilar, Elementray Quantum Chemistry

Now we have learnt earlier in this course that one can talk about vibration of diatomic molecules and one can model them using the simple harmonic oscillator model. And we know that we can solve Schrodinger equation exactly for this kind of system simple harmonic oscillator and we know what the solutions are we are going to revise once again today. But then we also understand that this simple harmonic oscillator with parabolic potential cannot really be the complete picture.

Because if you think of interaction of two atoms we are talking about diatomic molecules and if you want to plot their potential energy we very well know what it is going to be when the two atoms are very far away from each other the interaction energy is zero. As they come closer and closer and closer nucleus of one experiences the electron of the other they attract each other so there is a decrease in energy stabilization until an optimum point beyond which the two nuclei discover each other and there is very, very strong internuclear repulsion because of which the energy rises sharply.

So this is the actual potential energy curve and so far we have worked with the idealized potential energy curve which is a parabola which is all right for small displacements about the equilibrium position. But there is no reason why we should be satisfied with that it is not going to work in many, many practical examples and also this is a chance to develop our theory our understanding of the theory and make it adaptable to more complicated problems.

So that is the scope of discussing application of perturbation theory in describing an anharmonic oscillator anharmonic oscillator means one that is not actually parabolic rather for longer distances it curves downwards and goes to 0 asymptotically.

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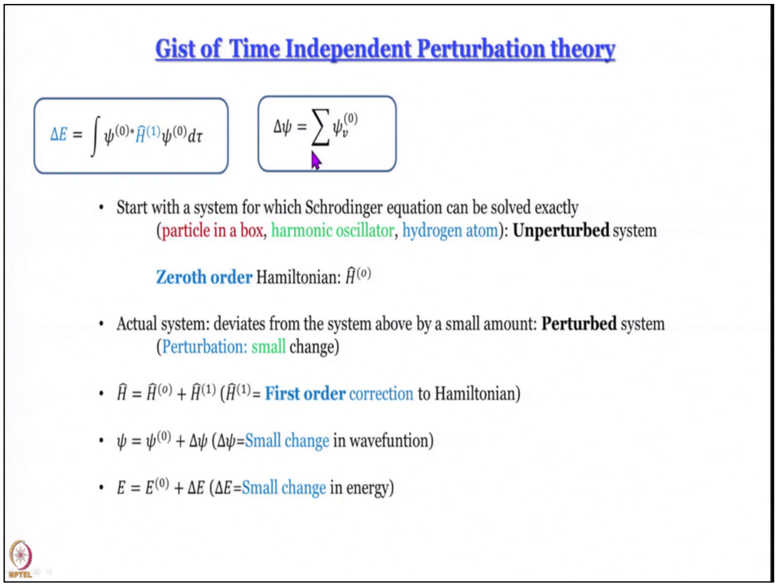

Gist of Time Independent Perturbation theory

$\Delta E = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$

$\Delta\psi = \sum \psi_v^{(0)}$

- Start with a system for which Schrodinger equation can be solved exactly (particle in a box, harmonic oscillator, hydrogen atom): **Unperturbed** system

  Zeroth order Hamiltonian: $\hat{H}^{(o)}$

- Actual system: deviates from the system above by a small amount: **Perturbed** system (Perturbation: small change)
- $\hat{H} = \hat{H}^{(o)} + \hat{H}^{(1)}$ ($\hat{H}^{(1)}$= **First order** correction to Hamiltonian)
- $\psi = \psi^{(0)} + \Delta\psi$ ($\Delta\psi$=Small change in wavefuntion)
- $E = E^{(0)} + \Delta E$ (ΔE=Small change in energy)

But before that let us once again remind ourselves what we have learnt about perturbation theory. We have learned that you always start with a system for which Schrodinger equation can be solved exactly. In the case we are going to discuss today that system is going to be harmonic oscillator. This is an unperturbed system and the Hamiltonian of the unpartnered system is called the zeroth order perturbation. 0 means 0 perturbation no perturbation has come and the actual system and harmonic oscillator for today is something that deviates from the system by a small amount, please remember small amount.

It is very important to understand that perturbation theory does not work for large deviations from the unperturbed system. So, this perturbed system that we are trying to build a description of should deviate from the unperturbed system only by a very small amount then we can write the Hamiltonian of the perturbed system as the zeroth order Hamiltonian for plus a first order perturbation term. We can write the wave function as the zeroth order wave function plus some delta Psi which is also due to first order perturbation.

And E we can write as E zeroth plus delta E where delta is a small change in energy because of the perturbation that we have introduced. Now here we write one because we could have or in some cases you have to talk about H second, H third so on and so forth. Second order third order perturbation might be required. In fact if you talk want to talk about I think the in fact anharmonic oscillator I do not have that data today.

But maybe next day I will just show that data to start with people have gone up to 13th order perturbation why? So, that we get a closer match to the experimental energies and but to start with let us stick to first order. For first order perturbation we have proved that delta E the change in energy due to first order perturbation is integral Psi 0 star first order correction to Hamiltonian operating on Psi 0 integrated over all space.

Please remember that these two wave functions are one and the same they are not different. And now something that I think I mentioned in the passing but we have not written anywhere it is better to write it at least once for most of the cases you can write delta Psi as sum over Psi 0 we are talking about the vibrational wave functions today that is why I have written V the thing is this small perturbation right.

So whatever wave function you generate is different from the original wave function by a very small amount. And remember these zeroth order wave functions constitute a complete orthonormal set that means if it was three dimensional space x y z complete set you do not need anything else. So something like that so some vector in this function space should we should be able to express any vector in this function space even though it has deviated little bit by a sum of these orthonormal vectors. That is the idea that is why you can conveniently write a linear sum of wave functions.

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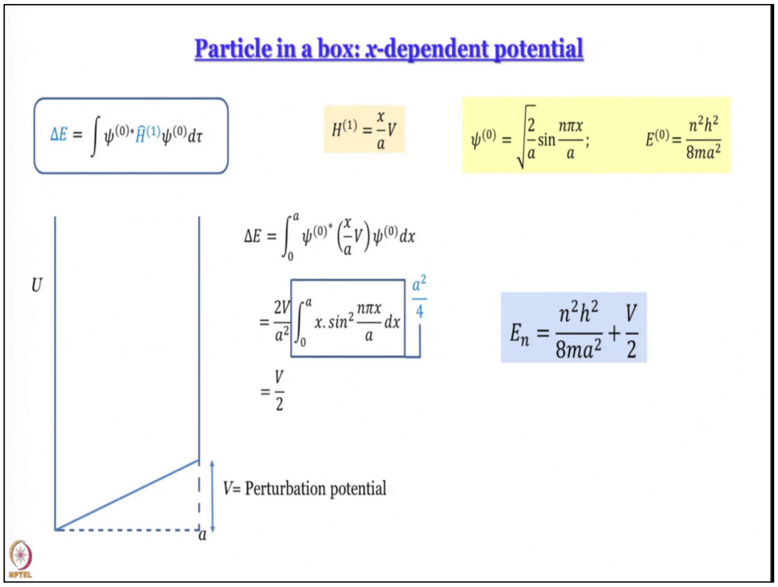

Particle in a box: x-dependent potential

$$\boxed{\Delta E = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau}$$

$$H^{(1)} = \frac{x}{a} V$$

$$\psi^{(0)} = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}; \qquad E^{(0)} = \frac{n^2 h^2}{8ma^2}$$

$$\Delta E = \int_0^a \psi^{(0)*} \left(\frac{x}{a} V\right) \psi^{(0)} dx$$

$$= \frac{2V}{a^2} \underbrace{\boxed{\int_0^a x.\sin^2 \frac{n\pi x}{a} dx}}_{\frac{a^2}{4}}$$

$$= \frac{V}{2}$$

$$E_n = \frac{n^2 h^2}{8ma^2} + \frac{V}{2}$$

Now with this background we have already discussed this particle in a box with a slanting bottom means when x equal to 0 potential energy is 0 when x equal to a potential energy is V. This is called the perturbation potential and we have derived that this first order correction to Hamiltonian well we actually used it, it is pretty straight forward from here its a straight line 0 at x equal to 0 V at x equal to a simply becomes x into V divided by a.

So you put this into the expression of delta E we use the wave functions of the unperturbed system and we got this kind of expression the delta E is V by 2. So, energy of the nth state is given by the energy of the unparalleled state this one plus V by two it is as simple as that. So, all energy levels are just offset upward by V by 2 that is all nothing else. So, this is it is not as if it has no application you can think of chemical systems where you can actually apply it. And most importantly it allows us to get comfortable with our theory due to its own simplicity.

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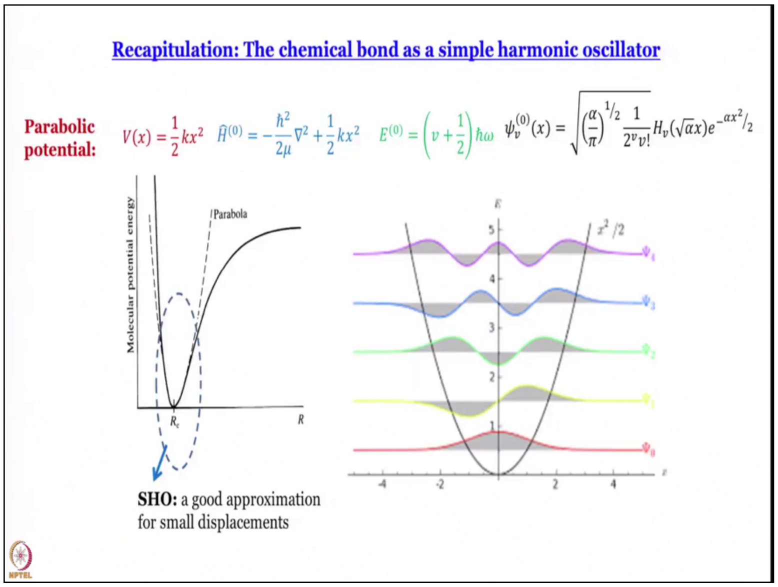

Recapitulation: The chemical bond as a simple harmonic oscillator

Parabolic potential: $V(x) = \frac{1}{2}kx^2$ $\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}kx^2$ $E^{(0)} = \left(v + \frac{1}{2}\right)\hbar\omega$ $\psi_v^{(0)}(x) = \sqrt{\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^v v!}}H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2}$

SHO: a good approximation for small displacements

Now let us go ahead and talk about anharmonic oscillator to do that let us recapitulate what we have studied about simple harmonic oscillators parabolic potential as I said V of x is equal to half k x square the unperturbed Hamiltonian is minus h cross square by two mu del square plus half k x square. And here I do not remember if I said this already if I have not let me say it once again please remember that when you have two bodies m 1 and m 2, mu is more like m 1.

If m 1 is a smaller mass mu is always like the smaller mass when you talk about relative motion it is like the smaller mass plus half k x square this is your unperturbed Hamiltonian for simple harmonic oscillator, energy of which we know is V plus half multiplied by h cross omega. You can change this to h omega because h cross h by 2 pi omega is nu into 2 pi. So, this 2 pi that 2 pi cancel and you can write h nu did I say h omega that is wrong sorry about that.

So, h cross omega is the same as h nu and remember h nu what it is I think all of us know. And this here is the wave function of a simple harmonic oscillator some constant multiplied by a hermite polynomial multiplied by a Gaussian function. So, this is how they look and I hope you have figured out why it is that it is ok for these wave functions to go out of this potential energy surface its fine that is how we get it great.

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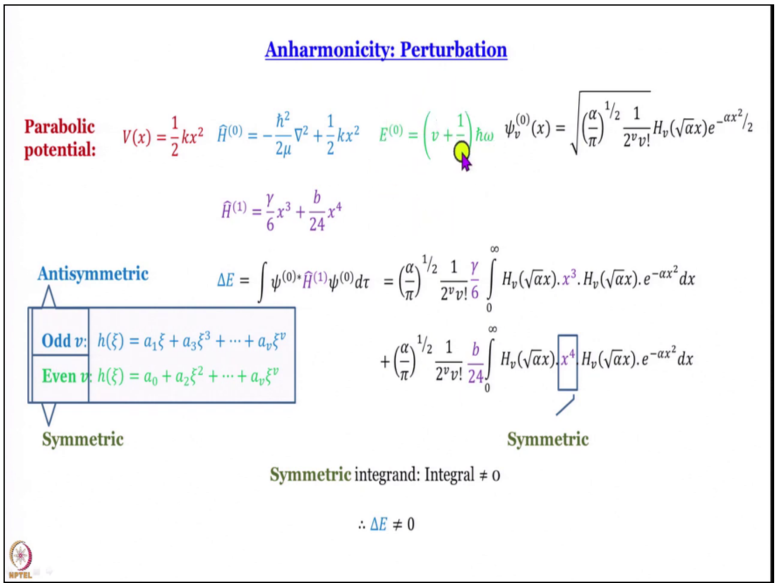

Anharmonicity: Perturbation

Parabolic potential: $V(x) = \frac{1}{2}kx^2$ $\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}kx^2$ $E^{(0)} = \left(v + \frac{1}{2}\right)\hbar\omega$ $\psi_v^{(0)}(x) = \sqrt{\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2^v v!}} H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2}$

$$\hat{H}^{(1)} = \frac{\gamma}{6}x^3 + \frac{b}{24}x^4$$

$$\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}d\tau = \left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^v v!}\frac{\gamma}{6}\int_0^\infty H_v(\sqrt{\alpha}x).x^3.H_v(\sqrt{\alpha}x).e^{-\alpha x^2}dx$$

$$+\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^v v!}\frac{b}{24}\int_0^\infty H_v(\sqrt{\alpha}x).\boxed{x^4}.H_v(\sqrt{\alpha}x).e^{-\alpha x^2}dx$$

Antisymmetric

Odd v:	$h(\xi) = a_1\xi + a_3\xi^3 + \cdots + a_v\xi^v$
Even v:	$h(\xi) = a_0 + a_2\xi^2 + \cdots + a_v\xi^v$

Symmetric

Symmetric

Symmetric integrand: Integral ≠ 0

$\therefore \Delta E \neq 0$

Now we are going to consider an harmonicity as a perturbation. So, let us bring in a perturbation term how do we do it? Well without even thinking much one thing that one can do is that where will the perturbation come not kinetic energy in the potential energy. So potential energy already is a polynomial of second order and it is usually possible to express this kind of quantities as a polynomial of whatever order we want.

It is just that the coefficients of higher order terms in the polynomial keep on decreasing otherwise it will be a divergent problem. So, the next term in the polynomial next time after x square will be something into x cube I might as well have written c into x cube or something like that I am using gamma by 6 because once again this has been solved results are known gamma by 6 is something that gives us nice results and this is the convention that is followed in the books anyway.

So first order perturbation to Hamiltonian is gamma by 6 x cube let us say. Now let us write the expression for delta E. We know what it is going to be integrals Psi 0 star in this case Psi 0 star and P 0 are the same multiplied by this first order correction of Hamiltonian operating on zeroth order wave function integrated over all space. So, let us write one by one what will I get first of all what will come out of the integral sign.

This constant here is under a square root, so from this Psi 0 zero star which is the same as Psi 0 we will get one square root of something term and from zeroth order Psi the second one will get another one. So, first constant that comes out of the integral sign is alpha by pi to the power half multiplied by 1 by 2 to the power V factorial V. Do we have to remember this for god's sake no please do not do not remember things that are not so easy to understand.

If required you can always look up a book or if it is a matter of examination we can always provide the values it is important to understand what is going on. So, this is what we have one constant has come out is there any other constant anywhere? Yes, so this is gamma by 6 that gamma by 6 will definitely come out, yes. Then we are left with an integral inside which we have this hermite polynomial multiplied by x cube multiplied by E to the power minus alpha x square multiplied by E to the power minus alpha x square.

So that is E to the power minus alpha x square sorry we have hermite polynomial multiplied by E to the power minus alpha x square by 2 and then there is an another one from this second Psi 0, so we will get product of two hermite polynomials and E to the power minus alpha x square by 2 multiplied by E to the power minus half x square by 2 is E to the power minus alpha x square that is sorted.

And in addition we have this x cube factor this is integrated over all space limit of x is going to be 0 to infinity. So, let us see hermite polynomial multiplied by x cube multiplied by another hermite polynomial the same harmonic polynomial once again multiplied by E to the power minus alpha x square dx. This is delta E what is the expression for this delta E you can find it out by put in putting in the different hermite polynomial expressions and seeing what you get.

At least now I am not going to do that we are going to remember some property of the vibrational wave functions of quantum harmonic oscillator. If you remember these are the expressions that we had obtained when we discussed harmonic oscillator. If you are a little rusty by now on harmonic oscillators I strongly advise that you go back and see those lectures and go through those notes and you might refresh your memory.

So if you remember we had come to understand that for odd values of V the hermite polynomial is a 1 multiplied by Xi + a 2 multiplied by Xi plus so on and so forth a v e f Xi to the power v where v has to be odd, v is odd. So, the even terms are missing. Similarly when v is even only the even power survive a 0 + a 2 Xi square plus well a 3 Xi cube Xi to the power 4 no cube so on and so forth. Last term is same but do not forget here v is even.

We know this, let us see if it is possible to use the knowledge of what odd and even v's are to figure out at least whether delta is going to be 0 or not right. We keep doing that all the time in quantum mechanics that is what we will do. Now when we talked about particle in a box remember we talked about symmetric and anti symmetric wave functions. Symmetric and anti symmetric with respect to inversion we replace x by minus x Xi by minus Xi does the wave function change sign or does it remain the same.

If it remains the same then it is symmetric, if it changes sign then it is anti symmetric. So, you can see here what we have Xi so replace Xi by minus Xi what do you get minus Xi, Xi cube replace Xi by minus Xi will get minus Xi cube. So, this for odd v's it is not very difficult to understand that the hermite polynomial is anti symmetric with respect to inversion. Similarly for even values of v you only get things like Xi squares Xi to the power 4 so on and so forth.

So if you replace Xi by minus Xi square of minus Xi is the same as square root of Xi so this is symmetric with respect to inversion. And whatever it does not matter please see that what we have here is a product of the same hermite polynomials actually square of harmite polynomial. So, you multiply an odd anti symmetric function by an anti symmetric function what do you get you get a symmetric function.

You multiply a symmetric function by a symmetric function of course you get a symmetric function. So, what we understand here is that no matter whether v is odd or even no matter whether the hermite polynomial is symmetric or anti-symmetric the product is definitely symmetric. Why are we talking about this symmetry and all of a sudden just be there for a couple of minutes will reach, all right.

What else is there E to the power minus l alpha x square you replace x by minus x does anything change minus x whole square is equal to x square. So, even this factor is symmetric no problem with that what about x cube replace x by minus x it is not very difficult to see that x cube changes sign. So, this is an anti symmetric function. So, now you have three symmetric functions multiplied by an anti symmetric function what is the total integrant then?

Is it symmetric? Is it anti symmetric? It is not very difficult to see that the integrand is anti symmetric and as we have discussed earlier if the integrand is anti symmetric then of course the integral is 0 because if it is anti-symmetric then you just perform an inversion I becomes minus I. So, integral of I becomes minus integral of minus I but then the integral cannot change just because you have performed an inversion nothing has changed.

So if I equal to minus I then of course I equal to 0, so what we see here is that after doing all this we get the result that this x cube term yields a 0 value for delta E which means there is absolutely no contribution to energy. There is no change in energy due to perturbation if we stop at the x cube term. But then that is not a happy situation because perturbation is there, anharmonic oscillator is definitely different from a harmonic oscillator and we have experimental evidence.

So what we do is we look at the next term in the polynomial keep everything same add one more term x square here in the unperturbed Hamiltonian in the perturbation term we had incorporated the x cube term earlier. Now introduce x to the power 4 term you might ask why v by 24 let us not worry about it. Let us if you understand that this is a constant we are good. Now what we will do is we will take this and we will put it in once again in the expression for delta E.

Now of course we are going to get two integrals one containing x cube and the other containing x to the power 4. So, this is the first term right same as what we had got earlier and without much hassle we can understand that this entire term is actually 0 right that is why we are even talking about x to the power 4. What about the second one? Second one has x to the power 4 here. Now see this x to the power $ is symmetric right replace x to the power x by minus x, x to the power 4 is not going to change sign, so it is symmetric.

So what do we have here, the first hermite polynomial this hermite polynomial and that hermite polynomial no matter whether they are symmetric or not that product is symmetric this Gaussian factor is symmetric. Now x to the power 4 is also symmetric what does that mean that means the integrand the entire integrand is actually symmetric. So, the integral is non-zero and the contribution made to energy is also nonzero.

What one needs to do after this is just take this expression for hermite polynomial for v equal to 0 1 2 3 put them in and see what you get? You will get actual expressions for energy correction to energy and that is actually written by very I hope you understand that whatever expression you get is going to depend upon the vibrational quantum number v. So, in the expression of energy it comes as a next term in polynomial.

You might remember that the for the harmonic oscillator x this is the expression for energy. The correction term for energy turns out to be something in v plus half whole square. So, that is how we describe an anharmonic oscillator that is how we bring in anharmonicity as a perturbation. So, that then has allowed us to move over to a more realistic system. Before we close this discussion let me do something that is actually discussed in some other course.

But may or may be I would not let us not do that let me end with this; end this module with this brief discussion. This is only the tip of the iceberg we have just begun we have talked about time independent perturbation theory and we have seen how one can bring in anharmonicity as a perturbation to the unperturbed your harmonic oscillator system. One can perform a little more discussion on this as well.

And that is what we will do next day hopefully. It is just that we have to develop a concept of linear equations we have to understand what circular determinant is and then once we have done that we will perhaps discuss another very important system from the especially from the point of view spectroscopy, non rigid rotor. Will perform a brief discussion of that and then we are going to come back to where we had taken off a little bit.

Remember multi electron atom, helium atom we are going to see how perturbation theory is applicable to helium atom and we will see how far we can get using that. Once we are done with that we will learn another technique. The technique uses variation theorem and that will be a little longer discussion than perturbation theory and we will see how we can sort of get close to the actual value using variation theorem.

But before anything else in the next module I have to show you some experimental result and how we can approach it using this perturbation theory that we have discussed in the last few modules, thank you.