Quantum Chemistry of Atoms and Molecules
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Lecture-37
Scope of Perturbation theory

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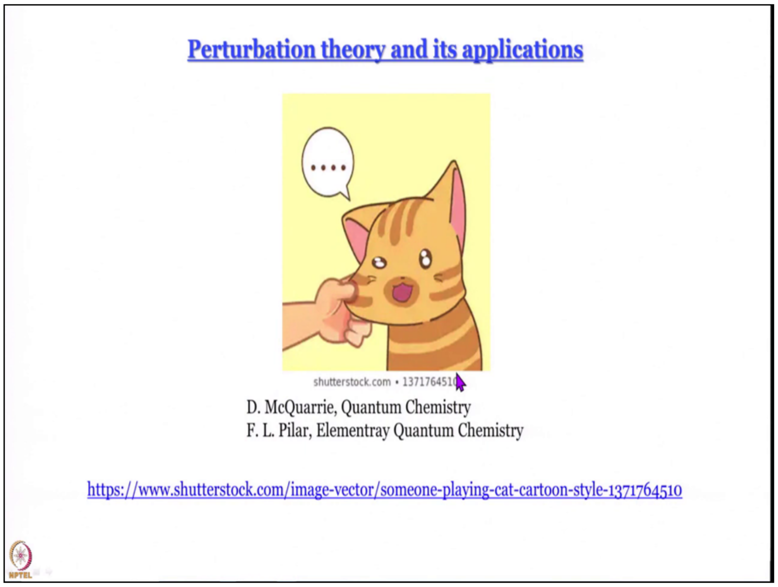

Perturbation theory and its applications

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We have been introduced to perturbation theory and we have discussed why I think this cat represents for perturbation theory nicely. Today we will complete our discussion will get an expression for the Delta E the first order correction to energy and will do a very, very simple example of an application of perturbation theory. Then for the next few models were going to talk about applications in progressively more chemical chemistry dated system.

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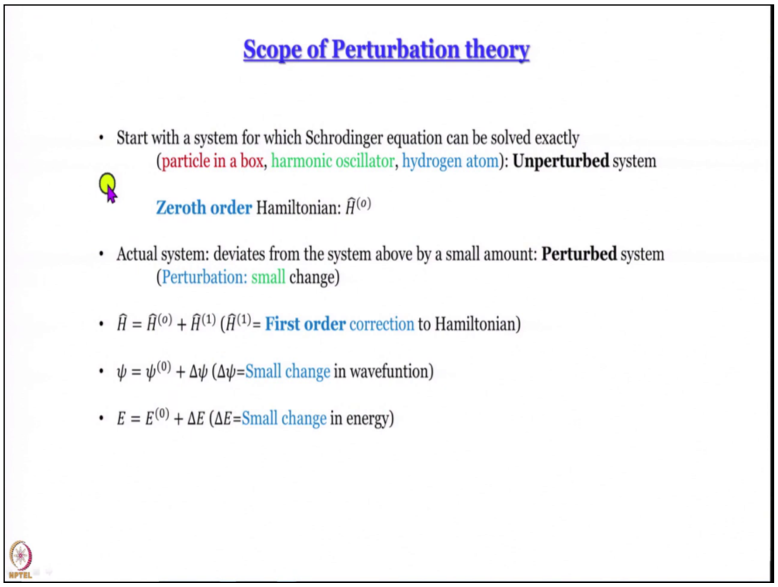

Scope of Perturbation theory

- 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 we do that status quickly recap what we have discussed already you are said that the scope of perturbation theory is that it works when the deviation from the unperturbed system is very, very small. We can write the Hamiltonian of the perturbed system as zeroth order of the Hamiltonian of class a first order correction. We write the wave function as 0th order wave function plus first order correction delta C.

We can write E as 0th order energy plus first order correction to energy delta E. before going further we make sense to say that this expression is of course incomplete. I might want to do I might want to invoke a second order third order perturbation. Sometimes it might be necessary.
In the next module we are going to discuss a case where first order perturbation with a certain kind of expression of a quantity just does not work either have to change that quantity or you have to invoke second order perturbation.

So, is not necessary that first order correction is be all and end all of it. But for most of our purposes we will stick to first order correction.

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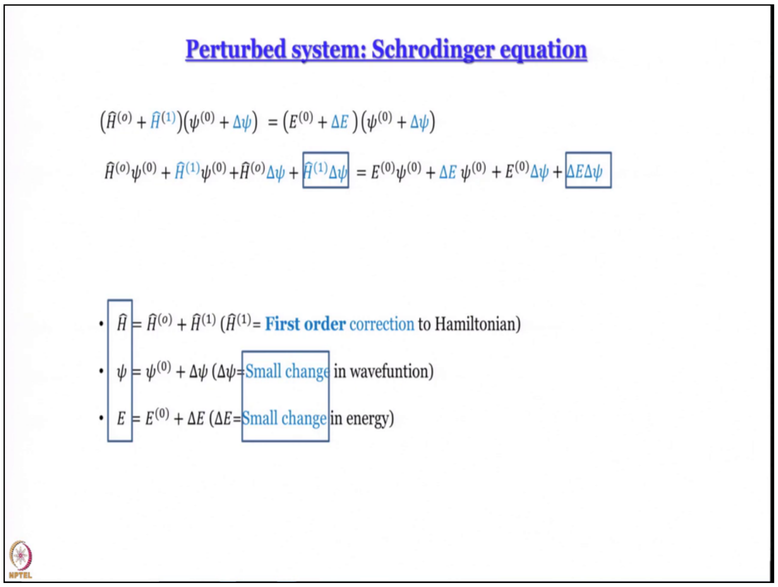

Perturbed system: Schrodinger equation

$$\left(\hat{H}^{(o)}+\hat{H}^{(1)}\right)\left(\psi^{(0)}+\Delta\psi\right) = \left(E^{(0)}+\Delta E\right)\left(\psi^{(0)}+\Delta\psi\right)$$

$$\hat{H}^{(o)}\psi^{(0)}+\hat{H}^{(1)}\psi^{(0)}+\hat{H}^{(o)}\Delta\psi+\boxed{\hat{H}^{(1)}\Delta\psi} = E^{(0)}\psi^{(0)}+\Delta E\,\psi^{(0)}+E^{(0)}\Delta\psi+\boxed{\Delta E\Delta\psi}$$

- $\hat{H} = \hat{H}^{(o)}+\hat{H}^{(1)}$ ($\hat{H}^{(1)}$= **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)

Then what we did is we set up Schrodinger equation in terms of a H hat Psi and E equal to this. Since Delta Psi and Delta E have small changes we figured that this is H 1 hat the first order correction to Hamiltonian multiply operating on Delta Psi and delta E multiplied by delta Psi remember it is an operator which cannot be multiplied by delta Psi it is operating on delta Psi. So, these two are products of small quantities they are 0 it is also said that H 0th operating on Psi 0 is the same as E 0th multiplied Psi 0 because that is your Schrodinger equation for the unperturbed system so they cancel each other.

We are left with H 0th – E 0th operating on Delta Psi plus first order correction to Hamiltonian operator on Psi 0 is equal to Delta E multiplied by the unperturbed wave function. Here we said that let us not forget that this unperturbed energy subtracted from the unperturbed Hamiltonian is in itself and operator in this case is operating on Delta Psi. The problem with that is that we do not know what happens when it operates on delta Psi.

We perfectly know what happens when it operates on 0th order wave function because H 0th is equal to E 0 multiplied by Psi, H 0th minus E 0th is operating a Psi 0 is equal to 0. So, since some then we know replace by delta Psi by Psi 0th then we know how to go about this, that is what essentially trying to do. To do that first of all we have to multiply by Psi 0 star and integrate all space. This is the expression we get.

On right hand side we get Delta E multiplied by the integral of the 0th order of wave function and unperturbed wave function and its Complex conjugate is integral of course is equal to 1. So right hand side gets cleaned up to; gets only delta E. In the left hand side we now trying to find out what would be this expression here.

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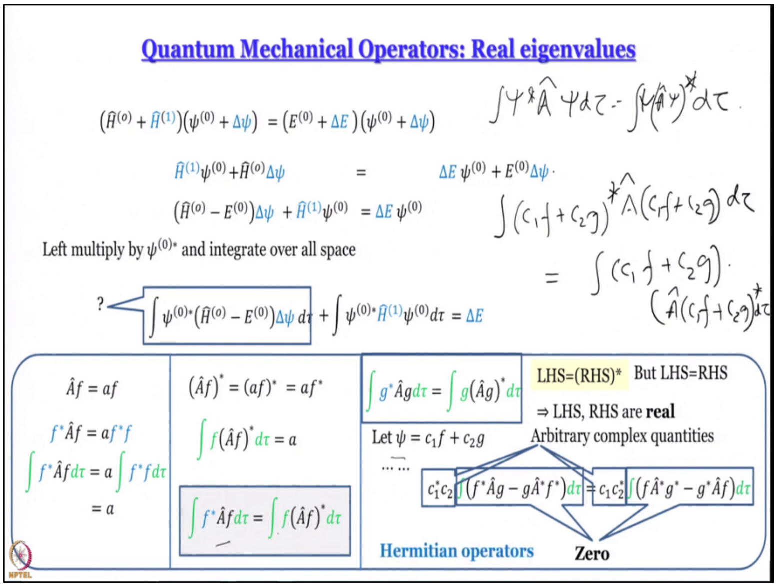

Quantum Mechanical Operators: Real eigenvalues

$$\left(\hat{H}^{(o)} + \hat{H}^{(1)}\right)\left(\psi^{(0)} + \Delta\psi\right) = \left(E^{(0)} + \Delta E\right)\left(\psi^{(0)} + \Delta\psi\right)$$

$$\hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(o)}\Delta\psi = \Delta E\,\psi^{(0)} + E^{(0)}\Delta\psi$$

$$\left(\hat{H}^{(o)} - E^{(0)}\right)\Delta\psi + \hat{H}^{(1)}\psi^{(0)} = \Delta E\,\psi^{(0)}$$

Left multiply by $\psi^{(0)*}$ and integrate over all space

$$? \quad \boxed{\int \psi^{(0)*}\left(\hat{H}^{(o)} - E^{(0)}\right)\Delta\psi\, d\tau} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau = \Delta E$$

$$\int \psi^{*}\hat{A}\psi\, d\tau = \int (\hat{A}\psi)^{*} d\tau$$

$$\int (c_1 f + c_2 g)^{*}\hat{A}(c_1 f + c_2 g)\, d\tau = \int (c_1 f + c_2 g)\left(\hat{A}(c_1 f + c_2 g)\right)^{*} d\tau$$

$$\hat{A}f = af$$

$$f^{*}\hat{A}f = af^{*}f$$

$$\int f^{*}\hat{A}f\, d\tau = a\int f^{*}f\, d\tau = a$$

$$\left(\hat{A}f\right)^{*} = (af)^{*} = af^{*}$$

$$\int f\left(\hat{A}f\right)^{*} d\tau = a$$

$$\boxed{\int f^{*}\hat{A}f\, d\tau = \int f\left(\hat{A}f\right)^{*} d\tau}$$

$$\boxed{\int g^{*}\hat{A}g\, d\tau = \int g\left(\hat{A}g\right)^{*} d\tau}$$

LHS=(RHS)* But LHS=RHS

⇒ LHS, RHS are **real**

Let $\psi = c_1 f + c_2 g$

…… ……

Arbitrary complex quantities

$$c_1^{*}c_2\int\left(f^{*}\hat{A}g - g\hat{A}^{*}f^{*}\right)d\tau = c_1 c_2^{*}\int\left(f\hat{A}^{*}g^{*} - g^{*}\hat{A}f\right)d\tau$$

Hermitian operators

Zero

To do that this is where we have got so far. We remember that quantum mechanical operator, but must necessarily have real eigen values. Because one of the central themes of quantum mechanics is that the eigenvalues of quantum mechanical operators are the values of the observable this operator stand for. You cannot have a physical observable with an imaginary value. If you are asking what is the position and if I say the position is root phi into i what is that mean?

It means it is not in real space. So, that cannot be the case if I ask what is a momentum and you say 0.32 multiplied by Omega or 0.32 - 5.6i what kind of momentum is that? Momentum positions are to be real quantities. So, eigen values must be there for quantum mechanical operators using this we have got this expression here. Integral f star A hat f d tau is equal to integral f multiplied by A hat f star d tau.

So what you see is what we are trying to do is we are trying to interchange the basis. Here at least they have been able to interchange this complex conjugate and a function by itself. Left multiplication here is a complex conjugate left multiplication here is by the actual function but our job is not done because here the two functions of different if something like integral f star A hat g d tau. Here we have integral f star A hat g d tau. Here we have integral f star A hat f d tau. We have somehow bring in a g here.

Then we know what this is going to be and that is what we proceed to do from here. Since we need a g let us simply write this same expression in terms of g without any loss of generality. I am talking about the function how does it matter if you call it A for if you call it g or if you call it phi or whatever you want to call it a rose called by any other name as just sweet. So we write this but then there is a reason why we have written it is not just; we want to bring in a different function here.

And to do that what we do if we take a linear combination of f and g, can we take Psi is equal to c1 multiplied by f + c2 multiplied by g why because we want an integral f star a head g d tau this linear combination will enable us to do exactly that. We are going to jump step because this lengthy if you want you can do it yourself. You not have to remember anything as long as we understand the logic we are good.

So now see this f is any general function right instead of f I might as well write Psi. Second write integral Psi star A hat Psi d tau. Let me write what happens when I take Psi and put it here in this equation I get integral Psi star A hat Psi beta is equal to integral Psi A hat Psi the complex conjugate of the whole thing d tau it is simple as that. What is Psi? Psi is a linear combination of f and g so what are you doing you are just write that instead of this I will write integral c1 f plus c2 g star A hat operating on c1 f plus c 2 g d tau is equal to integral c1 f plus c2 g multiplied by A hat operating on c1 f + c2 g full star d tau.

And then what we do is we expand this that is the step that I want to skip. It is not all the difficult also A hat operating on this linear side. What will it be? It will be c1 multiplied by A hat f + c2 multiplied by A hat g it is simpler it is linear operators is it not. And then you just open this up. So this way just do it using values of f and g and put in these expressions also it is a little tedious but not impossible to come to this expression.

C1 star c2 multiplied by integral of multiplied by f star A hat g minus g into A hat f star d tau is equal to c1 c2 star multiplied by integral g star – g star A hat f integrated over all space. See we are almost there a look at this integral instead of Psi 0 I write f instead of delta Psi I write g integral f star A hat g star a hat g getting to the functional form that we require. But before we get there it is important to now develop an understanding of the situation and that is where we are going to embark upon or where we going to reach very important property of quantum mechanical operator let us see.

See first of all this left hand side here is the complex conjugate of the right hand side see c1 star c1 c2 c2 star f star A hat g A hat star g A hat star f star g star A hat f. So, right and left inside a complex conjugate of each other point number 1. Point number 2 is well it is an equation of course LHS equal to RHS what are we saying here? You are saying that LHS is RHS are complex conjugate of themselves. That is going to happen only when LHS and RHS are real otherwise impossible.

Something similar also comes when you talk about called hermitian matrix. So LHS and RHS have to be real it is as simple as that. Now see this c1 star c1 c2 are perfectly arbitrary constants and I have not told you that this is phi and ci or other way round or anything. So naturally since these are arbitrary complex quantities we should expect that c1 star c2 in the general case is going to be complex. Multiplying two complex numbers either c1 star and c2 both are to be real or c2 as to be the complex conjugate of c1 star then only this c1 star c2, c1 c2 star going to be real, but that is not the case.

That would be very, very specific case. We are we have written a general discussion. So, the arbitrary complex quantities these are contest complex quantities. So what about the rest? Remember the left hand side let us work with the side first. Left side is real. Left side is made up of two factors. The first one is c1 star c2 and second one is this f star integral second is the integer. Similarly right hand side is c1 c2 star multiplied by another integer.

Each is real. In the left hand side focusing their c1 star c2 we said in the general case has to become complex which means that the integral either has to be its Complex conjugate. It is the product of the integral and c1 star c2 is real. Either the integral has to be a complex conjugate of c1 star c2 but if that is the case once again generality is lost. It is a specific case. We do not want to talk about specific cases. We want to see if there is something that is absolutely general.

Similarly on the right hand side also the same thing will happen. So what is the only other situation in which we have a complex number multiplied by a quantity and the product is real unless the second quantity is a complex conjugate of a complex number. The only other option you have is that the second quantity is 0. Anything multiplied by 0 is 0 why this is not because 1 by 0 anything real or imaginary does not matter.

Multiply by 0 you got to get 0. So the general solution is that these integrals on the two sides must be equal to 0. Integral A star A hat g minus A hat star g star d tau must be equal to 0 similarly integral f multiplied by A hat star g star minus g star A hat f d tau is also equal to 0. Well there are too many f, g and star here, please do not get scared. Please do not get confused. Stop the video here if you are not understood replay.

Reply as many times as you need and it will sync. It will sync in faster if you do it by yourself something that you are saying in almost every module please make sure that in addition to hearing what I am saying you write down the same thing so that you practice. So, this is 0 let us clean up things a little bit and before doing that this is actually the definition of hermitian operators. An operator that satisfies this condition that is integral is 0 is called hermitian operator.

And hermitian operators as we see have real eigenvalues. This is the definition. Do not say that hermitian operator’s definition is that they have a real eigan value that is a coronary. This is really the definition we of the sort of back calculated, starting from the real eigen functions. We have shown that the operator has to be hermitian. This integral has to be equal to 0.

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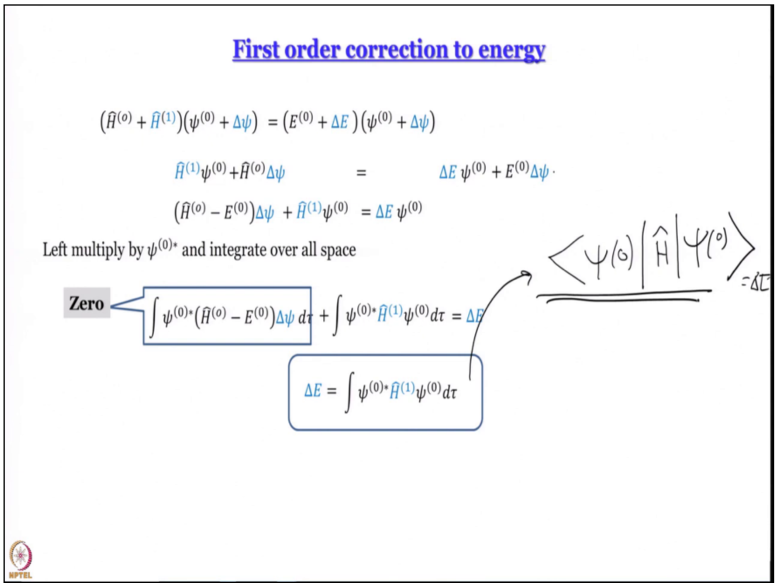

First order correction to energy

$$\left(\hat{H}^{(o)} + \hat{H}^{(1)}\right)\left(\psi^{(0)} + \Delta\psi\right) = \left(E^{(0)} + \Delta E\right)\left(\psi^{(0)} + \Delta\psi\right)$$

$$\hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(o)}\Delta\psi = \Delta E\,\psi^{(0)} + E^{(0)}\Delta\psi$$

$$\left(\hat{H}^{(o)} - E^{(0)}\right)\Delta\psi + \hat{H}^{(1)}\psi^{(0)} = \Delta E\,\psi^{(0)}$$

Left multiply by $\psi^{(0)*}$ and integrate over all space

Zero

$$\int \psi^{(0)*}\left(\hat{H}^{(o)} - E^{(0)}\right)\Delta\psi\, d\tau + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} d\tau = \Delta E$$

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

$$\underline{\underline{\left\langle \psi(0) \middle| \hat{H} \middle| \psi^{(0)} \right\rangle}} = \Delta E$$

So let us clean up things now and write this integral f star A hat g – g multiplied by A hat star f star d tau equal to 0. So what we can do is we can expand the left hand side and get 2 terms and since one has minus sign we can take it to the right hand side that way we get integral f star a hat g d tau is equal to g multiplied by A hat star g star d tau and that is a happy situation why, because look at this Psi 0 star let us say there is f H 0th – E0th that is your let us say A hat and this is g.

The problem we have here is that g that is delta Psi is not an eigen function of H 0th – E 0th. But Psi 0 is an eigen function so we can somehow take this delta 0 here and bring this Psi 0's here then that is happy situation. I mean ok if you bring Psi 0 star also that not have ok this equation is what allows me to do that. As an operator operating on a function left multiplied by another function. But it says is that within the integral sign you can just interchange the two functions.

Instead of f star now f star will come here, and g will go there. So this is what we get. So using this expression we get delta Psi star multiplied by H 0th – E 0th, H 0th complex is ok E 0 complex is E 0th complex is E 0th complex H 0th complex does not make a difference H 0th – E 0th operating on Psi 0 d tau. So, this expression here gets transformed this integral here gets transformed to another integral where we have this problematic delta Psi star factor multiplying an operator operating on its wave function.

Now tell me what is the eigen value of this H 0th – E 0th operator for Psi 0 I can find eigenvalue and I can do it fairly easily. Remember Schrodinger equation for the unperturbed system unperturbed Hamiltonian operating on and perturbed wave function gives us energy of unperturbed system multiplied by unperturbed wave function. So, let us bring this to the left hand side we get H hat 0th Psi 0th - E 0th Psi 0th equal to 0.

Or we get and write like this H hat 0th – E 0th that is the operator we are working with operating on Psi 0th is equal to 0. So first thing we have done we have transform this integral to another one in which we are H 0th – E 0th operating on Psi 0 and we found that this H 0th – E 0th operating on Psi 0 is 0. So inside the integral we have delta Psi 0 multiplied by 0 integrated over all space. What will it be? Definitely it is going to be 0.

So now after all this exercise we are happy to see that even this problematic term is actually is 0 you do not have to worry about it. So finally we get an expression for the first order correction to energy and expression is Delta E equal to integral unperturbed wave function multiplied by the first order correction term to Hamiltonian operating on the unperturbed wave function integrated over all space. Another way of writing it in Dirac notation that is often done as we have discussed a little bit is we can write the same thing as Psi 0th H hat Psi 0th integrator over all space this is your delta E.

I think we are now familiar with this expression that should be no problem. So you got an expression for the first order correction to energy.

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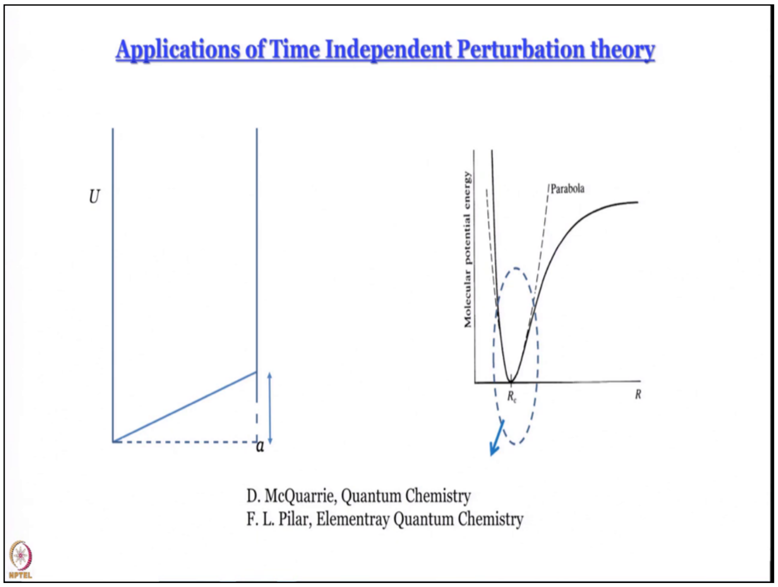

Applications of Time Independent Perturbation theory

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Now to conclude our discussion let us think of applications of this simple perturbation theory in some systems. Now before that for further record this is what time independent perturbation theory because you are working with time independent wave function. We are not working with time dependent wave function. Time dependent because you are working with stationary structure when we worked with; when you talk about Spectroscopy at that time will be imperative that to use time dependent perturbation theory.

But if you understand time independent perturbation theory, time dependent perturbation theory is actually child's play not difficult at all. So you go to see its application today we are going to talk about this kind of a system if particle in a box with a slanting bottom. And the next module we are going to discuss what is called an anharmonic oscillator and that is where we see what kind of problems we face if you do not define our perturbation properly or if we try to stop at too low level of correction.

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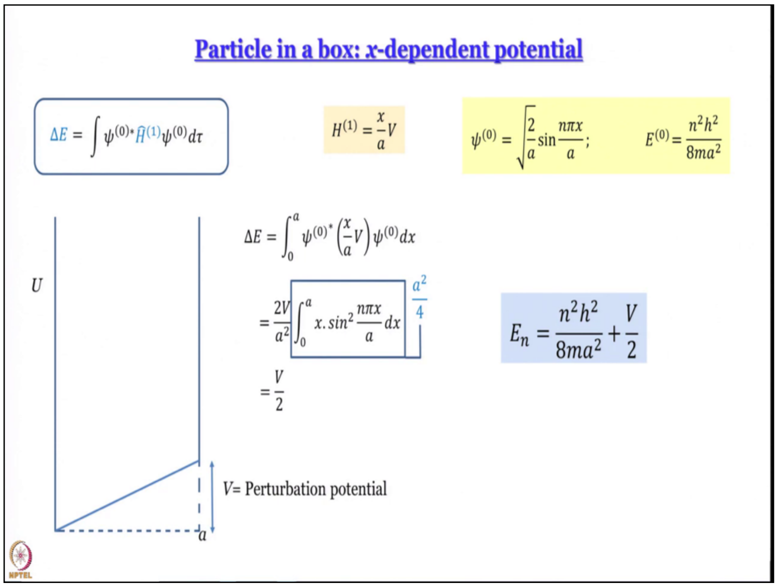

Particle in a box: x-dependent potential

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

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

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

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

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

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

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

V= Perturbation potential

So, let us start so what we are doing is we want to talk about particle in a box with slanting bottom which means a particle in a box within X dependent potential. So, to start with what will be the unperturbed system our good old particle in a box where V is equal to 0 for all values of X within 0 and a where 0 and a are the limits of the box and outside it is infinity. So for such a system for a particle in a box with infinite height of the walls the wave function as we discussed is root over 2 by a sin n Pi X divided by a.

An energy is n square h square divided by square 8 m a square simple. Now we want to bring in the perturbation to the system to arrive at our box with slanting bottom. So this is the perturbation we bring. So, let us say at multiplied by X equal to a the perturbation potential is V. Remember what you are trying to do is? We are trying to get an expression for the first order correction to the energy brought in by the slanting bottom.

To do that we need to know what the first order correction to Hamiltonian is. First order correction to Hamiltonian will be of course the potential energy. What is the potential energy? It is equal to 0 for X equal to 0 it is equal to capital V let us say for X = a. So, what you have is a straight line going through the origin very simple. First order for any value of X is going to be x divided by a multiplied by V it is quite simple not difficult at all.

Ok X divided by a multiplied by V, V is the value at a. So, we take this expression for the first order correction to Hamiltonian and we plug it into the expression for delta E. This is what we get and of course to use expression for Psi 0th as well. So, delta E turns out to be a Psi 0th star which is the same as Psi 0 because Psi 0th is real wave function multiplied by X into V divided by a multiplied by Psi 0 integrated over all values x from 0 to a as simple as that.

Here this V is a constant is not it, a is also constant. V and a can come outside integral and what do we get here Psi 0th is is root over 2 by a sin n Pi X by a and there are two of them so I get 2 by a from there as well as. So, what come outside the integral is 2 by a multiplied by V by a some like that. So, 2V divided by a square that comes out inside your left with integral 0 to a X into sin square n Pi X by a dx.

Of course you can work this out yourself and integration not a very difficult one but standard integral we know the solutions already. We are going to just put the value from the compendium. The value of the standard integral turns out to be a square by 4. So the value for delta is that we have is 2V divided by a square multiplied by a square by 4 that turns out to be V by 2. So if see how simply how easily we have been able to find out the value for the first order correction to energy of the system even without working out what the wave function actually is.

This is the beauty of approximation method. We do not have to know the wave function to get the energy we can get the energy first then worry about the wave function. So let me just write this remember energy in particle in box is quantized. We said earlier that E 0th order energy for nth level is n square h square by 8 m a square. Now in the perturbation system this correction term of a by 2, so this is the expression for the energy of the nth energy level E n is equal to n square h square by 8m a square plus V by 2.

So what has happened to the energy level of particle in a box because of this slanting thing? What has happened is that every energy level as simply got offset by V by 2 what is V? V is the perturbation potential at X equal to a. So, energy here is not X dependent. Potential energy is X dependent fine energy is not. It would have been a little unhappy situation it was but it is not.

So, it is a good thing that we see n square h square by 8m a square plus V by 2 this is what we get. Now see V would better be small right you can think of very large values of V. What about n square h square by 8ma square. We are talked about what kind of energy is there can be. If V is very large then of course this treatment is not even valid because that delta E into Delta Psi that you cannot equal to 0 anymore id delta is large.

So you have to work with these that are small enough. If V itself is close to infinity of course this treatment is not valid otherwise it is and you see an elegant and simple example of application of time independent perturbation theory to a simple model system. Next day next module you go on and discuss application of the same time independent perturbation theory to your anharmonic oscillator. Remember harmonic oscillator equiv space energy level so on and so forth,

We will discuss why it cannot be really be the case for diatomic molecules and has to be a; it has to look different. You have to bring in harmonicity, if you going to bring in the anharmonicity perturbation and I will get a correction term to the energy. While you do that you will come upon something interesting. After anharmonic oscillator you want to see how one can use perturbation theory to talk about Helium atom.

Remember where talking about helium atom 2 modules ago from there we have taken a sort of a break and we are learning for perturbation theory. Only because we can go by we have to go back to the same system and use it, this is not a digression. We are developing the tool. So, that we can use it in our atomic system, please do not lose the focus of what we really want to do after this but to get there must learn the workings of the theory.

And the best way of learning it is to make the theory work on model systems and while doing that we also get some interesting results that are relevant to molecules also. Even this kind of a slanting box can be there in conjugated molecules in which all atoms are not carbon and anharmonic oscillators and ubiquitous in molecular vibrators. That is the reason why you are doing this but do not forget that all this is really a part of a discussion of many electron atoms to understand which we are going to use this perturbation theory.