Quantum Chemistry of Atoms and Molecules
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Lecture-43
Variation Method

In the next few classes we are going to talk about variation method which as we will see is a very powerful approximation method and goes way beyond the scope of perturbation theory. And this variation method is completely based on what you see in the cartoon here.

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Variation method

https://www.kissclipart.com/

It is completely based on the fact that we cannot do better than the best we are going to learn today something called the upper limit theorem which says that no matter what you do in variation method the energy you calculate will be little more than or at best case scenario which is almost impossible to reach equal to the n ground state energy of a system. You can never get by this variation method and energy that is lower than the ground state energy low energy is good right low energy means stabilization when we are talking about ground state.

So what will say what we see is that the calculated energy by this method will always be greater than mostly greater than the ground state energy or it will provide an upper bound for the energy that is what allows us to have sort of a free hand with clear playing around the system and trying to get the correct result. And this is something that we are going to demonstrate today with an example and then we are going to prove this upper bound theorem upper limit theorem.

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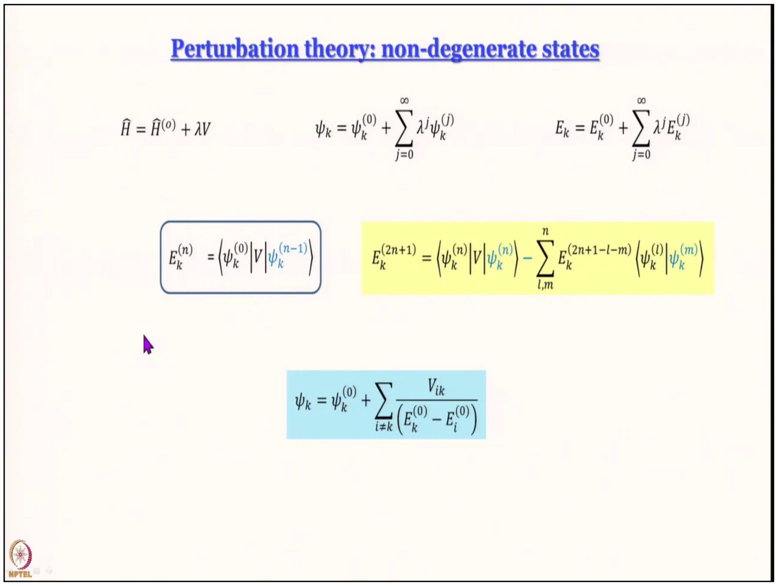

Perturbation theory: non-degenerate states

$$\hat{H} = \hat{H}^{(0)} + \lambda V \qquad \psi_k = \psi_k^{(0)} + \sum_{j=0}^{\infty} \lambda^j \psi_k^{(j)} \qquad E_k = E_k^{(0)} + \sum_{j=0}^{\infty} \lambda^j E_k^{(j)}$$

$$\boxed{E_k^{(n)} = \left\langle \psi_k^{(0)} \middle| V \middle| \psi_k^{(n-1)} \right\rangle} \qquad E_k^{(2n+1)} = \left\langle \psi_k^{(n)} \middle| V \middle| \psi_k^{(n)} \right\rangle - \sum_{l,m}^{n} E_k^{(2n+1-l-m)} \left\langle \psi_k^{(l)} \middle| \psi_k^{(m)} \right\rangle$$

$$\psi_k = \psi_k^{(0)} + \sum_{i \neq k} \frac{V_{ik}}{\left(E_k^{(0)} - E_i^{(0)}\right)}$$

But before that let us not forget what we have studied we have studied perturbation theory for a non degenerate state 1 can represent the wave function as a wave function which is called an unperturbed wave function this is essentially the wave function of a system which is exactly solvable and we have studied many such examples harmonic oscillator rigid rotor hydrogen atom and then we say that the perturbation is small.

So you can write the part wave function of the perturbed system as the unperturbed wave function plus a correction term. Similarly you can write an expression for energy Hamiltonian is written as unperturbed Hamiltonian plus lambda into V we have talked at length about why this is a good formulation energy of the nth order correction is given by this integral and we have said that we can work out even 2n + 1 with order correction.

And from this expression we actually obtain a nice expression for the perturbed wave function also.

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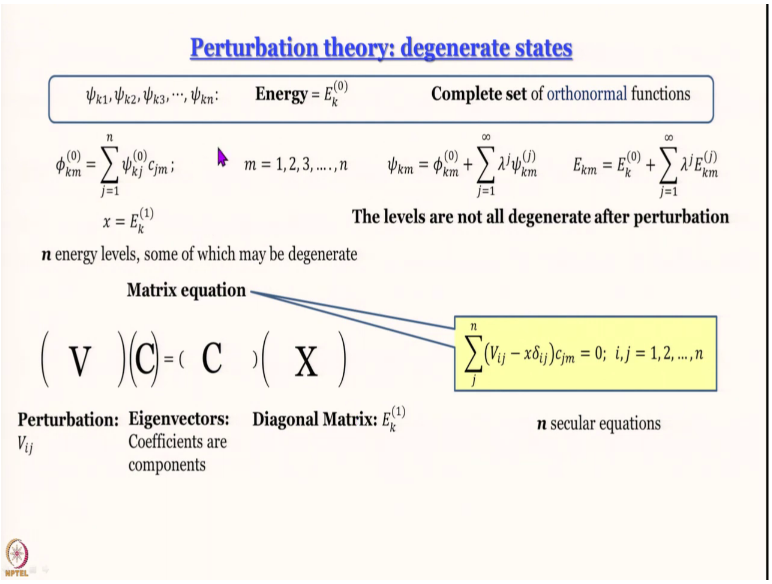

Perturbation theory: degenerate states

$\psi_{k1}, \psi_{k2}, \psi_{k3}, \cdots, \psi_{kn}$: **Energy** = $E_k^{(0)}$ **Complete set** of orthonormal functions

$\phi_{km}^{(0)} = \sum_{j=1}^{n} \psi_{kj}^{(0)} c_{jm}$; $m = 1, 2, 3, \ldots, n$ $\psi_{km} = \phi_{km}^{(0)} + \sum_{j=1}^{\infty} \lambda^j \psi_{km}^{(j)}$ $E_{km} = E_k^{(0)} + \sum_{j=1}^{\infty} \lambda^j E_{km}^{(j)}$

$x = E_k^{(1)}$

The levels are not all degenerate after perturbation

n energy levels, some of which may be degenerate

Matrix equation

$$(\mathrm{V})(\mathrm{C}) = (\mathrm{C})(\mathrm{X})$$

$$\sum_{j}^{n} (V_{ij} - x\delta_{ij}) c_{jm} = 0; \ i, j = 1, 2, \ldots, n$$

Perturbation: V_{ij}

Eigenvectors: Coefficients are components

Diagonal Matrix: $E_k^{(1)}$

n secular equations

For non degenerate states the difference in our approach is that now you cannot really say that the perturbed wave function is some unperturbed wave function plus correction term because these unperturbed wave functions are all degenerate. So, you cannot say that I am taking psi k 1 and not psi k 3 so first of all we form a linear combination and then we try to look at what happens when we add a perturbation term to this linear combination of the complete set of orthonormal wave functions of the unperturbed systems that we take.

And we have seen cases in which the perturbed levels are partly degenerate we have seen cases in which the perturbed levels are completely non degenerate starting from a degenerate level. And we have said that this has many applications in chemistry like stark effects Zeeman effect d orbital splitting and so on and so forth. For degenerate case we have obtained at this matrix equation which gives rise to n number of secular equations.

And then we can work with the secular determinant and try to find the solution. So, this is what we have studied and perturbation theory itself is a rather strong approximation technique.

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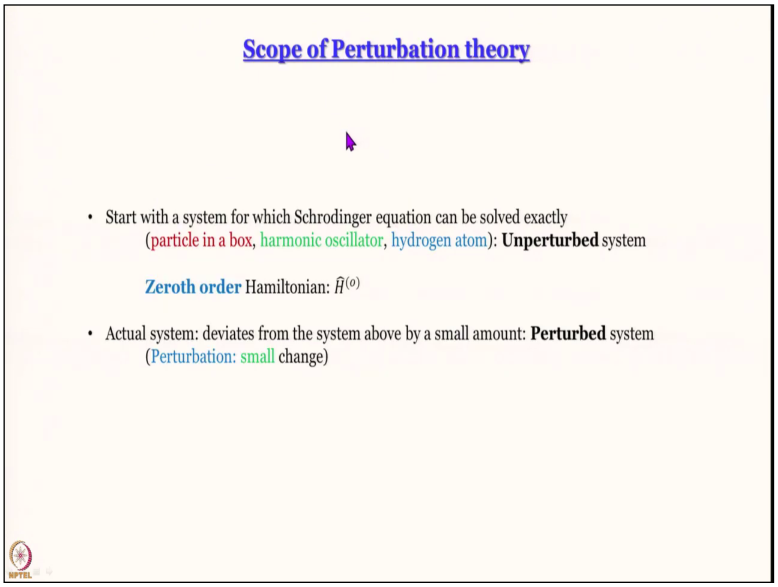

Scope of Perturbation theory

- 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)

The problem with perturbation theory is that its scope is rather limited this is something that we had shown you at the beginning of our discussion of perturbation theory. It works well when the perturbed system is close to an unperturbed system whose exact solutions are known. But there are many systems which are not so easily relatable to something that is exactly solvable. There are many cases in which the deviation if you want to call it a deviation is definitely much more than what the scope of perturbation theory can cover.

So for such system we have this elegant method that we are going to discuss now the variation method.

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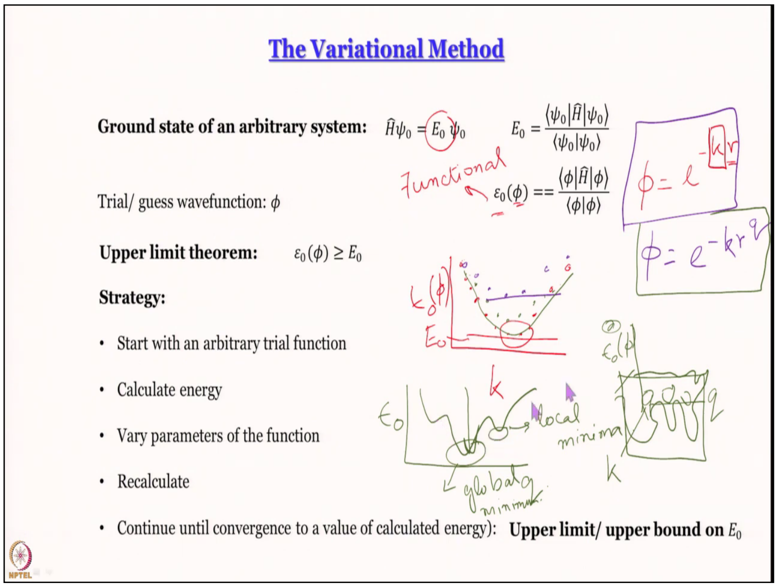

The Variational Method

Ground state of an arbitrary system: $\hat{H}\psi_0 = E_0\,\psi_0$ $\quad E_0 = \dfrac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}$

Trial/ guess wavefunction: ϕ $\quad$ Functional $\quad \varepsilon_0(\phi) == \dfrac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$

$\phi = e^{-kr}$

$\phi = e^{-kr^q}$

Upper limit theorem: $\varepsilon_0(\phi) \geq E_0$

Strategy:

- Start with an arbitrary trial function
- Calculate energy
- Vary parameters of the function
- Recalculate
- Continue until convergence to a value of calculated energy): **Upper limit/ upper bound on E_0**

Now why is variation of; what why is it called variational method of all things we will see. But to start with let us say we have an arbitrary system and the ground state of that arbitrary system is associated with this Schrodinger wave equation H psi 0 equal to E 0 psi 0. all right Right now we are going to talk only about ground states. So, why what is the meaning of arbitrary system? The meaning of arbitrary system is that we do not know what the form of this wave function is, we have no idea.

So how do we go about handling such a system? How do we try to find out the energies of such an arbitrary system that is what variational method allows us to do. So, we start with this thing that we know expectation value of the ground state energy, what would that be? That would be integral psi 0 star H hat psi 0 divided by integral psi 0 star psi 0 if psi 0 is not normalized. So, this is a general expression if psi 0 is normalized of course the denominator will be equal to 1 but then we work with this general expression to keep things as broad as possible.

Now what we say is we do not know what the wave function is right but let us make a guess. Let us assume some kind of a wave function and that is called the trial or guess wave function. Now at this point of time if this might sound to be too much of a story what is going on here I do not know wave function but I will guess how will I guess you see we are going to before trying to prove variation theorem will actually show you an elegant example where we actually know the solution and we will see that this variation method allows us to guess of a wave function that gives good enough values.

So with a little bit of experience we will be able to guess it is not so difficult. And as you will see this guess wave functions need not be well for systems where you can solve it exactly this guess wave functions need not be exactly the same as what you are going to what you get by exact solution but you can still get the correct energy that is the interesting part. You do not have to do you do not have to get the right result in the right way.

You can get the right result using a wave function that whose mathematical form is not the same as the exact wave function if it is possible to obtain. However it still lets you go close to the energy and energy finding energy is the real problem in quantum mechanics that is what you are worried about all the time no matter what we do. Remember this Hamiltonian is the energy is the quantum mechanical operator for energy.

So we start with some trial and or guess wave function even though even if this sounds like very strange, please bear with me things will fall in place in a while not too long away. So, we have this trial or guess wave function phi. So, what I will do is I will define this thing epsilon 0 in terms of phi which has the same form as that of the eigen value of energy right. So, if I happen to be the correct wave function then epsilon 0 would be the energy right.

And now let me introduce a term before I forget and then I start using it arbitrarily later on this thing epsilon 0 is called a functional what is a functional? A function is a function of functions which means see phi is a function is not it epsilon 0 is a function of functions depending on what phi is value of epsilon 0 is going to change. So, energy is also functional of the wave function psi 0 this called a function or sometimes it is called a super function.

Super function or functional, a function of functions for now just the name is enough may be later on we might use this in a little more elaborate manner. But for those of you who are who have a little more exposure to how quantum chemical calculations are done you might be familiar with the term density functional theory. So, here for the first time we encountered that functional; functional is a function of functions epsilon 0 is a functional it is a function of the wave function phi.

Well now hold on here I said wave function what is the meaning of that well let us not say that let us just say phi is a function. So, epsilon 0 is sort of the average value with respect to phi. We will see how this all falls in place. So, the upper limit theorem which is of central importance in variational method makes a an extremely profound important useful statement and the statement is this epsilon 0 which is a function of phi has to be greater than or equal to E 0 which is the actual energy of this arbitrary system.

I have said lot of things, so let me just do an executive summary to make sure that we have all we are not left in the lurch. See I do not know what psi 0 is but psi 0 is the actual wave function even though I do not know it, it is there right maybe there is some way of finding it or maybe there is no easy way but I do not know how to find it and right now I do not bother right. But energy should be measurable I do an experiment I should be found able to find energy.

So that energy is related to the wave function like this it is the expectation of value of the energy integral psi 0 star a psi 0 star H psi 0 divided by integral psi 0 star psi 0 theta. What I am saying is if I write a similar expression in terms of some trial guess wave function anything suppose the correct wave function is E to the power minus k r and I take something like E to the power minus k dash r r square then that phi is E to the power minus k k dot r square right.

And then using that and using having to Hamiltonian we should be able to write once I know the system Hamiltonian should not be difficult to write we might not be able to solve Schrodinger equation will still be able to write the Hamiltonian. So, now if I take this some guess wave function make the Hamiltonian operate on it left multiply by phi star integrate over all space divided by integral phi star phi then I get this epsilon 0 phi.

What upper limit theorem says is that this epsilon 0 phi can never be less than the ground state energy E 0 and as we will discuss shortly that opens up tremendous possibilities and we will see how. So, the strategy of any variational calculation is this first of all gives a function. Assume some kind of a function how to guess a function well with experience looking at the system thinking what the system is like you we should be able to figure out some sort of wave functions like we are going to discuss discuss a particle in a box.

In one of the later modules you will see how we take how we select a function which sort of makes sense on the face of it. So, start with such an arbitrary trial function then calculate this energy when I say energy I mean epsilon 0 phi. Then you vary the parameters of the function if it is E to the power minus k r square then keep on changing the value of k what will happen value of energy obtained or whatever this functional is epsilon 0 energy like functional that is going to change.

Then calculate again so keep on calculating and see whether the value of this epsilon 0 is decreasing. Then continue until the value converges to some particular value and that would be the upper limit or upper bound to this actual energy E 0. Let me in spite of my poor artistic skills let me just try to draw something and see whether I can make it a little clearer. Let us say I have this phi which is equal to E to the power minus k r to the power what will I write q.

So let us say I am talking about phi which is dependent only on the radius vector r. Now k is a parameter that I can play around with q is another parameter that I can play around with these are called variational parameters. So, what I do is I have epsilon 0 and let us say I first play around with k maybe I will make the situation little simple starting right away with 2 parameters might be a little confusing so I will remove this q.

Let us say it is E to the power minus k r then the only parameter that I have is k. So, I will just fix some value of k. Let us say I fix k is equal to 100 or something find out what is epsilon 0 phi. So, whatever it is I plot then I change the value of k to say 99 I find I look for the I calculate the value of epsilon 05 I see that it has gone up then I change it to say 98 and then again I see its going up that means I am going in the wrong direction.

Because what am I looking for I am looking for an upper bound of this value E 0 right. So, if this keeps going up that means I am not going towards a 0 is it E 0 must be down somewhere the correct value E 0 must be somewhere down here because whatever epsilon 0 of phi I calculate this is just the upper bound. So, those values must be more than the actual value of E 0. So, I am going in the wrong direction. So, I started from say k equal to 100 I was decreasing I went from 100 to 98 to 97 and I see that the value of this epsilon 0 functional is going up.

So I am going in the wrong direction so from 100 what I will do is in the next step I am going to change to say 101 and then let us say I see it goes down that means I am going in the right direction. Change to 102 let us say it goes down right direction 103, 4, 5 let us say go from 105 to 106 and the value of epsilon 0 does not change maybe you have achieved convergence. Then let us say go to 107 and the value of epsilon 0 starts rising again what does that mean?

It means that the minimum value in epsilon 0 that I have got that is the closest I can get to the actual value of energy E 0 by this variation method. Now this diagram that I have drawn is a little too ambitious. So, what I have drawn is that I have g1 almost here that is not necessary it is also possible that maybe I will change the color of ink, it is very highly possible and in fact that is what happens most of the time that the minimum value that you get is nowhere close to E 0.

E 0 you might be able to find from experiment and that is a correct value that means that whatever trial function you have taken that is not sufficient. You need a more complicated function. So, suppose I started with phi equal to E to the power minus k r and I am not getting correct convergent I am not getting convergence or I mean I get it but the result I get is very far away from experimental values of energy. Then what I do is I introduce another parameter so I say that phi is equal to E to the power minus k let us say r to the power q or I can add another exponential decay whatever I want to do depending on what I think is correct.

Now suppose I have introduced q now what will happen for q equal to 0 no sorry for q equal to 1 I have already got this curve by changing all the k parameters values of the k parameter. What I can do is I can change the value of q to something else it was 1, I can change it to 2 let us say change it to 2 and now I get things that go down further then I am going in the right direction but suppose by changing 2 it went up that means I am going in the wrong direction with q.

So what you do is you play around with q and get the best possible curve for k c for which value of q you get right and that gives you the upper bound to the actual energy E 0 that is what we are looking for we can only get upper bound nothing else. So, now see if I have 2 parameters like this and this is a very favorite topic for very many different reasons then actually I am working in 3 dimensional space am I not.

The dependent variable is say phi well the dependent variable is actually epsilon 0 of phi that is what we are monitoring on one axis I can have k on the other axis I can have q and what you get is sort of a surface so horrible way to draw a surface but I have shown you nice figures right of surfaces. Remember the orbitals there we had made 3D plots will get something like that. Then what happens is that here I have shown you a very simple situation I have shown you that there is only 1 minimum that is not necessarily the case.

More often than not if I take let us say I am taking a section of this surface and looking only at variation of phi with q sorry epsilon 0 with q more often than not this epsilon 0 with q is something like this, so more than 1 minima. These minima that are not the deepest they are called local minima and this thing here is called the global minimum global minimum. So, what we are looking for is this we seek to find the global minimum because whatever epsilon 0 value that we get for the global minimum is the upper bound to the actual energy.

Now you might be a little confused here and you might be thinking what are we doing um I mean if you know the energy experimentally why do we even want to bother about this system well we only know the ground state energy right. So, there are other parameters that will get to understand if we can explore the system quantum mechanically we will get more information that is the whole idea.

And there are right now we have to establish the technique. Once it is done we might want to work with systems for which we do not have experimental values of energy also and then we might want to do predictive theory. But right now where we have reached is this, this here is the strategy that we start with some arbitrary function which will be associated with one or more parameters for some particular value or values of these parameters you calculate the energy then you play around with the parameters you vary them.

Now you see where the name variation comes from because you are varying the parameters that are associated with the wave function. So, we vary them and every time we vary we calculate the epsilon 0 value and we continue until we get the lowest value of epsilon 0 the upper bound to E 0. This is in a nutshell what you do in the variational method. And as we have discussed it is essentially a minimization problem you can say optimization problem.

We seek to find the minimum in the plot of epsilon 0 with each and every parameter here. So, even though I have done a very poor job of drawing it just imagine a surface, imagine a 3 dimensional surface in this case right it will have some hills it will have some troughs and we are looking for the deepest trough which is the global minimum that is what we seek to do in variational method.

So the major players here are the parameters associated with the wave function the variational parameters right. So, we play around with them and we see what happens. So, that is what we will do next we stop here now in the next module we will continue from here we will talk about a specific example that is hydrogen atom and then we are going to derive this upper bound theorem.