Quantum Chemistry of Atoms and Molecules
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Lecture-36
Introduction to Perturbation theory

In a discussion of many electronic atoms we have said already that here. We have a situation when you cannot solve the Schrodinger equation directly like we could do it for hydrogen atom or rigid rotor or harmonic oscillator or free particle or particle in a box. So that is why it is cliche that the quantum chemistry are often teased by other people saying that these people have only one equation and they do not even know how to solve it.

Of course that does not make too much of a sense as a way of pulling each other legs. But one thing that has come out very clearly is that we will not be able to do a very, very rigorous solution of Schrodinger equation for systems here on. So, we need approximation methods and we have already used one approximation that is orbital approximation. And that is how we have sort of circumvented the problem that is there of electron-electron repulsion by considering effective nuclear charge and shielding constant.

We have been able to reach a situation where we can still use the same wave functions 1S, 2S will not the same but modified 1S, modified 2S, modified 2P so on and so forth that is we have been using. Here just orbital approximation again is not enough. We need to now indulge in we need to engage rather detailed discussion of more thorough approximation methods of quantum mechanics.

You will see when you do that this concept of shielding and all the come anyway. Only thing is that when you talk about wave functions. We enter a little more abstract domain you might be able to come back 1S, 2S etcetera later on but at least during the course of this discussion. Sometimes you might actually lose the memory of this good old orbital's have generated with talk in terms of both general wave functions.

So, there are two kinds of approximation techniques that are very popular in quantum mechanics one is perturbation theory the other is variation theory. These two theories are used to perform approximation. And to start with we are going to talk about perturbation theory.

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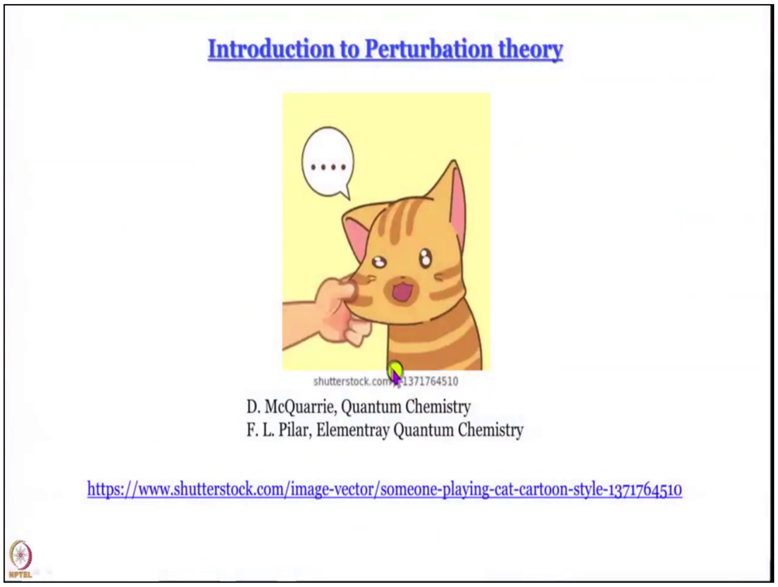

So, now you might be wondering in all this discussion where does this cartoon of a cat getting its cheek pulled by somebody comes in. Well we will see in the course of our discussion but before we get into it just so that we; do not forget please have a look at the cat what has happened ah the cat this is the cat unperturbed cat and what the owner or whoever it is has done is that is tucked at the cheek.

So only this cheek portion is distorted a little bit rest of the cat is what it was before its cheek was pulled, please remember this then ah unless I forget all about this we will come back to this analogy later on. But now we start slowly talking about perturbation theory we wish to introduce ourselves to this technique.

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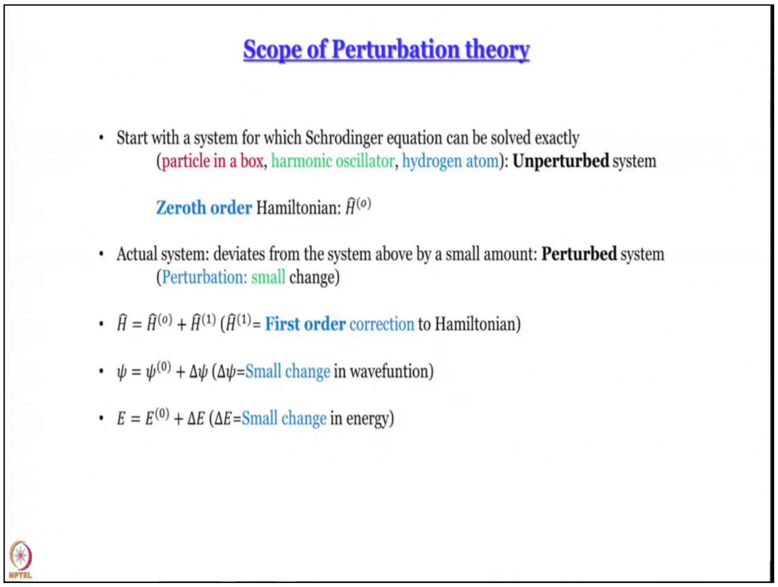

So, first thing I want to say is what is the scope of perturbation theory? Perturbation theory is an approximation that you cannot use anywhere and everywhere. If it was then you would not need the more rigorous variation method later on. So, in perturbation theory what happens is you start with a system for which you can have exact solution of Schrodinger equation. For example as we said particle in a box, harmonic oscillator or hydrogen atom and these systems from where we start this systems for which exact solution of Schrodinger equation can be obtained.

These are called unperturbed systems. So, what exactly is the formal definition of perturbation will come to that shortly. But we start with an unperturbed system for which we are able to solve Schrodinger equation without much hassle ah we can solve it exactly. Then the Hamiltonian for such an unperturbed system is called the 0th order Hamiltonian what is the meaning of 0, 0 means there is no perturbation. ah

Exact solution is there. This is how we write it H hat for a Hamiltonian operator and we write a 0 superscript in bracket which means 0th most of the time I will try to say H 0th by mistake I can say H 0 please ah do not get confused about it what when I write this H 0 or H 0th what I mean is the unperturbed well 0th order Hamiltonian of the perturbed system. Next we try to build a description of the actual system by considering a small deviation from this unperturbed system from which we get started.

And this word small is big in this context it is very important to remember that perturbation is a small disturbance but we call this a perturbed system. But please do not forget that perturbation is a small change. If the base value is 1 lakh, then it is if the deviation is by 100 it is not if the deviation is by 20000 then perturbation theory would not work and you will see shortly why it would not work. It is important that we never forget that the scope of perturbation theory is an extremely small ah I will not say minuscule but small deviation from the unperturbed system.

Please remember this perturbation is not very, very ah big change and that is what brings us back to that cartoon of the cat. Remember the entire cat was exactly the same only a small portion of the cheek that was pinched by two fingers of this ah owner of the cat only that portion got distorted rest of the cat was the same. So, you might call that a distortion but if the entire cat was caught and elongated by some way that would definitely not be distortion and that would definitely not be perturbation that would be a very major distortion.

Perturbation theory would not work in situations like those. So, once again let me emphasize in different colors perturbation is a small change very, very important ah not a small point at all great. So, now what we do is we write the Hamiltonian of the perturbed system as H 0th plus H first but H first this term is the first order correction to Hamiltonian. Psi of the perturbation system is written as Psi 0 plus you can write Psi first but generally we write delta Psi.

But delta Psi is a small change in wave function and E also is E 0th plus delta E where delta E is a small change in energy. so, if the so called perturbed system has an energy well if the perturbed system has an energy of 10 units and the so called perturbed system has an energy of say 50 units then perturbation theory will not work you cannot really work like this because delta E is going to become greater than E 0 or even comparable to E 0 or even a sizeable portion fraction of E 0 then perturbation theory will not work.

So ah what will do for the rest of this module is that will try to build a ah an expression for this delta E. And delta Psi I am telling you now maybe when we talk about ah anharmonic oscillator later we will come back to this in a little more detail this delta Psi or Psi you can say is written as a linear combination of these Psi 0's. Remember the wave functions the eigen functions of

Hamiltonian of the unperturbed system constitute a complete set of orthonormal vectors. I do not recall now whether we have formally discussed what a complete set is but let me tell you what it is. Let us think of ah real space; the space we live in x y z three vectors unit vectors along x y z they are enough to ah describe the location of anything any point in this space. So, x y z or i j k if you want to put it that way constitutes a complete set.

If I only take x y then it is not a complete set for three dimensional space it is a complete set for x y space. So what kind of a space you are choosing when I space I do not mean physical space I mean hyperspace that will decide what the dimensionality of this; ah what is the required dimensionality for completeness. No vector that is required to define ah anything in that function space as it is called is left out that is what complete set is.

All the vectors that are required to define the function space fully is are there. So, that is a complete set. So, since these ah 0th order wave functions form a complete orthonormal set what we can do is ah see we are talking about very small ah distortion. So, we can say that ah even the perturb wave functions are roughly going to be in that hyperspace that function space.

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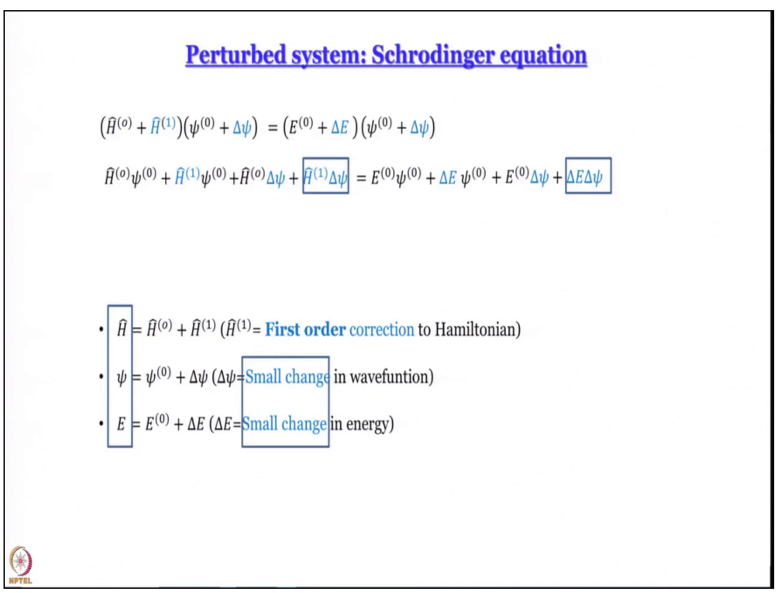

So, ah whatever is the ah wave function the water wave function we should be able to write it as a linear combination of all the ah wave functions orthonormal wave functions in for the unperturbed systems. So, essentially you are going to write this Psi as sum over I Psi I 0th but we will worry about that later on we are not talking about wave functions just as yet. ah Right now for the rest of the module and maybe there will be a spill over to the next module we are talking about your ah delta E.

How do we find the ah small change in energy. So, let us proceed and by doing that we are going to again ah perform a formal discussion of a fundamental aspect of quantum mechanics that we had ah perhaps should have done earlier generally in classes it has done earlier. But we wanted to get straight into the chemistry that is why we did not now we need it so we are going to discuss that very fundamental aspect of quantum chemistry properties of quantum mechanical operators also in the course of this discussion.

So that is a ah something additional something extra that we get to discuss here,. let us get ahead. So, ah what we do now is unfortunately I have gone a little far I do not know why? So, yeah this is what it is so this is what we have for the perturbed system we have the new Hamiltonian H hat new wave function Psi, new energy E and they all differ from the original unperturbed values by small amounts.

So, the next thing that we will do is we are going to simply write the Schrodinger equation for the perturbed system.

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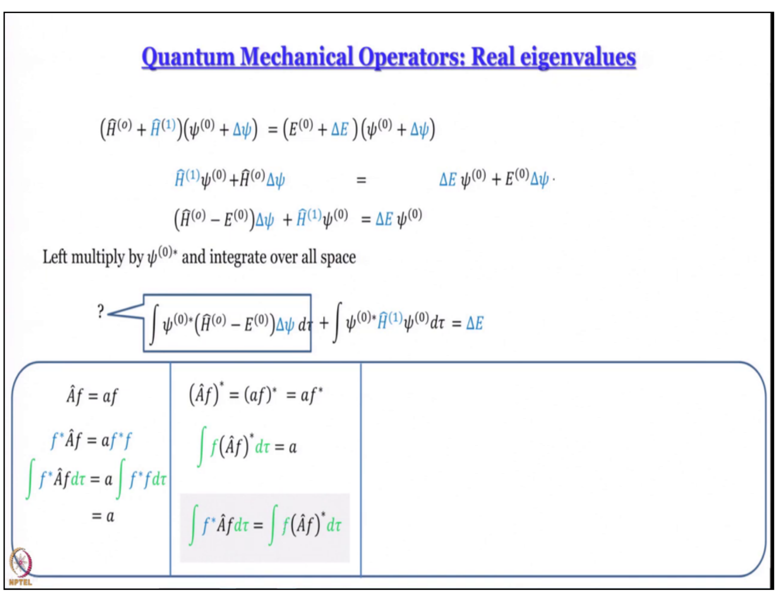

Schrodinger equation for the perturbed system and for that ah we are going to write the Schrodinger equation for the perturbed system and ah for that we are going to work with this H hat Psi and E. So, what is Schrodinger equation H Psi equal to E Psi simple, so instead of H we are going to write H 0th plus H first like this instead of Psi we are going to write Psi 0 plus delta Psi. Then right hand side is E Psi instead of E we will write E 0 plus delta E and that will be multiplied by Psi which is Psi 0 plus delta Psi simple as that.

So this here is our Schrodinger equation for the perturbed system great. So, now let us open it up a little bit let us open the brackets we are going to have 4 terms on the left 4 terms on the right and then as usually happens in physical chemistry many of these 8 terms are going to vanish thankfully and we will have a beautiful expression for delta E. So, now ah H 0th Psi 0 plus H first Psi 0 let us say these are the two terms. I have taken these two terms in the first place well this I do not even have to say it like this everybody can do it.

This third and fourth term will be H 0th delta Psi plus H first delta Psi simple. Right hand side similarly will be E 0th Psi 0 plus delta E Psi 0 plus E 0th delta Psi plus delta E delta Psi we have got our 8 terms. Now let us see how many of these are going to become 0. First it is very simple but let me once again ah emphasize the point that is not small the point that the changes are small delta H is small delta Psi is small.

So what happens when you multiply a small quantity by another small quantity 10 to the power minus 3 is a small quantity 10 to the power minus 5 is another small quantity multiply you get 10 to the power minus 8 which is ah smaller than each of these small quantities whose product we have taken. So, delta E delta Psi is going to be really very small and therefore we are going to neglect it. Remember we are approximating we are learning approximation methods.

Here if we say that we will not neglect any terms then there is no point in doing this exercise. So, I am reminded of another clichaeye something that a very renowned quantum chemist had told a student the student did not want to do approximation. So, the ah professor said see, there is an ant crawling on the table I want you to work out the time that the ant will take to go from this side of the table to that.

So you have to consider that the table is stationary and then you have to work out the velocity of the ant and work it out. Now if you say the table is on the surface of the earth the earth is rotating about its axis and revolving around the sun the entire solar system is moving and the galaxy is moving as well. So, then you have so many terms in the equation then before you can even write it the ant would have crossed the table.

So we do not want our ant to cross the table before we can write all the terms this is an absolutely justified approximation delta E and delta Psi within the ambits of perturbation theory are very small. So, the product is even smaller so we are going to neglect this no problem with that. If we cannot do it then we cannot use perturbation theory we need something else. And there are situations that we are going to encounter where that is the case.

But then what it means is that you need something else you need some more rigorous theory you cannot use perturbation theory there. You cannot use an easy theory and not invoke the approximations that you need to make for it to be applicable. So delta E delta Psi is equal to 0 is anything else equal to 0 do you have any other quantity any other term where the quantities are both small h 0 Psi 0^{th}, no, h one at Psi 0th well h 1th it is very small but not necessarily Psi 0 H 0 delta Psi again delta Psi is small not necessarily definitely not H 0.

E 0 Psi 0 if you neglect that then that means energy of the unperturbed system is 0 not a general case delta E Psi 0th once again similar thing. So, wherever you have this ah blue terms multiplied by black ones you cannot neglect them. But here what about this one blue into blue H first multiplied by delta Psi, delta Psi is small and the perturbation is also small. So, the contribution of the perturbation to the Hamiltonian is definitely going to be small so we can neglect this H first delta Psi as well.

Out of the 8 terms that we have 2 of them are neglected because they are ah not; they are very, very small you do not have to worry about them let us see this. Immediately that brings us to another interesting situation now we have 6 terms instead of ah 8 can we get rid of more terms here let us see what is the first term? H 0th operating on Psi 0^{th} what is the first term on the hand side? E 0 multiplied by Psi 0 black and black, black and black.

So H 0th operating on Psi 0 and E 0s multiplied by Psi 0 are they related to each other these are Hamiltonian wave function and energy of the unperturbed system. Of course the Schrodinger equation H 0 Psi 0 is equal to E 0 Psi 0 that is the ah Schrodinger equation for the unperturbed system. So, this term on the left hand side is the LHS of ah Schrodinger equation for the unperturbed system.

This term on the hand side is equal to hand side of Schrodinger equation for the unperturbed system they are equal to each other and so ah they cancel each other is great. Starting from 8 terms we now have 4 terms. We have 4 terms starting from 8 terms. Now we have ah first order Hamiltonian first order correction to Hamiltonian operating on 0th order wave function plus 0th order Hamiltonian operating on delta Psi the change in wave function gives us delta E the change in energy multiplied by 0th order wave function plus 0th order energy multiplied by delta Psi.

Now our job is to try and make delta E as subject of formula and ah we have to see how we can simplify this further. Now one very simple technique ubiquitous technique we use every time in quantum mechanics whenever we have situations like this is to left multiply by an appropriate wave function and integrate over all space. When you do that many of the integrals become either 0 or 1 by virtue of orthonormalization orthonormal.

By virtue of wave functions being orthonormal and you get many useful new integrals. We are going to encounter many integrals of this kind later on exchange integral coulomb integral virus spectroscopy transition moment integral we have talked about transition moment integral very specially while discussing particle in a box. So, we are going to left multiply this but before that what we do is we bring this terms with delta Psi to one side H 0th minus E 0 delta Psi plus first order correction to Hamiltonian operating on Psi 0 gives us delta E multiplied by Psi 0 why are we doing this because we want to make delta E the subject of formula.

Now we will do what we are saying left multiply by the complex conjugate of the 0th order wave function and integrate over all space. When we do that what do we get? So the first term that we get is you multiply Psi 0 star left multiply this thing you get Psi 0 star multiplied by H 0 minus E 0 operating on delta Psi integrated over all space. Now ah do you see that H 0th minus E 0 is actually an operator H 0th is the unperturbed Hamiltonian operator and E 0 is just a number E 0.

So ah an operator minus a number is also an operator. So, this H 0th minus E 0 is a quantum mechanical operator let us say A hat or something we are going to use this ah later. So, this is what we have the first term becomes integral Psi 0th multiplied by H 0th minus E 0 operating on delta Psi d tau looks quite formidable does not look like we can work this out but let us see ah whether things simplify a little bit.

Second term of course will be from here what do we have here first order correction to Hamiltonian operating on Psi 0th left multiply by Psi 0 star integrate over all space. We got the second term on the left hand side. What about the right hand side delta E remember is a number. So, delta E comes outside the integral then we have integral Psi 0 star multiplied by Psi 0 over all space this is what we get integral Psi 0 delta E integral Psi 0 star multiplied by Psi 0 d tau and that is a happy situation.

Because remember Psi 0th is ah normalized, if it is not normalized you can always normalize everything and will cancel the normalization constant will cancel. So, integral of Psi 0, Psi 0 over all space naturally is equal to 1. So, right hand side simply becomes delta E the question is what about the ah other two terms is there any way to find a simpler expression for the first term that we have here integral Psi 0 star multiplied by H 0th minus E 0th operating on delta Psi integrated over all space.

And to do this we are going to use a ah property of quantum mechanical operators. Remember quantum mechanical operators must have real eigen values that is where we are going to start from. Once again in case we lose track because of the sudden transition from perturbation theory to very basic quantum mechanics; please do not forget H 0th minus E 0th is an operator. It is operating on some delta Psi. So, we are trying to find a way of simplifying this integral.

We want to know what this integral is because then ah finding an expression for delta E becomes simple. So, ah we might as well write this operator as A hat and whatever we have here this delta Psi or Psi we can write it as f, f is a function. So, it has been said many times in this course that ah we are going to get eigen value equations whenever we have a quantum mechanical operator it operates on the wave function.

If the wave function has the information then it gives the information about the physical observable in the form of the eigen value. So, A hat f equal to a f is the eigen value equation that we get all the time. Now what we will do is something similar because we want this kind of an integral, integral some wave functions are multiplied by operator operating on some wave function. So, we will just go through the motion and ah do it.

We are going to left multiply by f star, so we get f star A hat f equal to a multiplied by f star f and then of course we are going to integrate. When we integrate left hand side becomes integral f star A hat f d tau is equal to a integral f star f d tau is a constant so it will go outside the integration ah sign as we have discussed already. So, we already know what integral f star f is overall space that is going to be 1 because f is normalized.

So right hand side simply becomes a. Now what we will do is since we have a complex conjugate of something here we are going to take complex conjugate of the terms on both the sides of Schrodinger equation that we have written in the general form. So, complex conjugate of A hat f on the left hand side should be equal to complex conjugate of a multiplied by f small a multiplied by f on the right hand side.

Now what we had done earlier when we had A hat f we had left multiplied by f star. Now we have A hat f whole star so we are going to left multiply simply by f because complex conjugate is already there. So you do that and do the integration ah you get what you get but before going there one thing that needs to be pointed out is right hand side is complex conjugate of a multiplied by f.

Now remember quantum mechanical operators have to have real eigen values. So, A star essentially has to be equal to a. It cannot be a complex quantity because the eigen value is supposed to be the value of a some physical observable it cannot be imaginary. So, it is ah complex conjugate must be equal to itself. So, we can happily bring a out here. So, this hand side becomes a f star. So, now we left multiply by f and integrate over all space this is what we get integral f A hat f whole star d tau is equal to a.

So we have two such expressions both are equal to a, how do we proceed from here? We can write equate the two left hand sides eliminate a and we get integral f star A hat f d tau is equal to integral f A hat f star d tau. Now ah we have something that is ah close to what we have here but not exactly the same. Because this expression if you see is something like f star a hat then g integrated over all space.

This one is integral f star A hat f integrated over all space they are not one and the same. So, we have to get from here to here we have to see whether we can get an expression where we have two different functions not the same one in this kind of an integral. So, that is what we are going to take up in the next module we stop here and will continue from here.