# Quantum Chemistry of Atoms and Molecules

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## Lecture-46
## Secular equations in Variational calculations

I found this nice cartoon in republic of math which sort of depicts the state we are presently in so what we are doing is we are doing lots of calculations.

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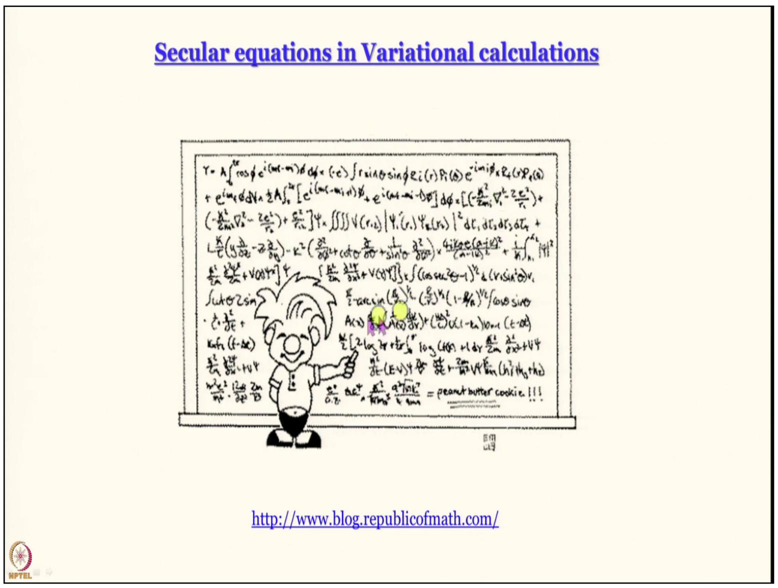


Humongous amount of calculations right in fact so humongous that we are not even doing it that is I am not doing it I am telling you that you can do it by yourself right tedious big calculations but I mean if you are intimidated we are intimidated only by the volume the tools are not all that difficult. So, far what is present in this cartoon is looks much more intimidating. So, but then this is leading us to very important results that is why we are happy like this person right here.

What we want to see is can we now slowly move towards a situation where this boat full of mumbo jumbo falls into something that is systematic and easier to handle.

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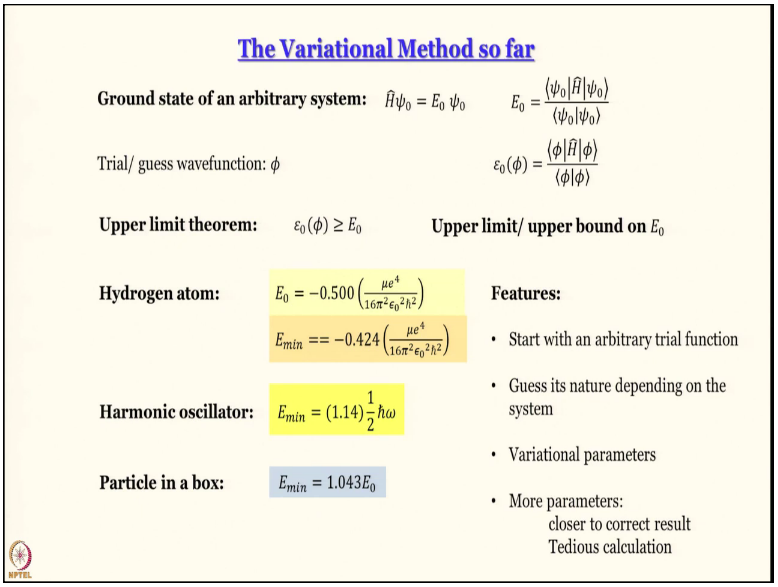


So to do that we once again recap what we have learned I will not say once again all these high equal to sign kind of thing but we have studied upper limit theorem we have used it and I will show you the results once again to refresh your memories. For hydrogen atom using upper limit theorem we have calculated a an energy and the peril of copy paste the second equal to sign is still there we have obtained the value of 0.424 whereas the actual value is 0.5 with minus sign for hydrogen atom.

For harmonic oscillator we have a deviation of about 14% and for particle in a box using a weird wave function we have got a deviation of about 4%. So, the strategies or the features that we have seen so far is we start with an arbitrary trial function arbitrary in the sense that we do not know whether is a correct 1 but then there is a method in the madness as well we remember what we did for particle in a box or for simple harmonic oscillator we sort of realized that they have to be symmetric with respect to the midpoint and they have to become 0 somewhere or the other.

So I am not going to use something like E to the power alpha x square that is not even a good wave function so when I say arbitrary trial function it is arbitrary within a certain limit it is not a arbitrary-arbitrary completely using anything that is not going to work you still have to think before you decide which trial function you can use. So, we have to guess the nature depending on the system and this trial function has to be associated with variational parameters means parameters that we can vary.

And see how that variation affects the energy of the system and for which value of this parameter or parameters we get the minimum value of energy. So, the more parameters we use and this is something that will demonstrate today we will get closer to the correct result. Of course the downside of that is that the calculation becomes more tedious but then if you have sufficient computational power it is better to use as many parameters as you can there is no problem of over parameterization we are saved by the upper limit theorem great.

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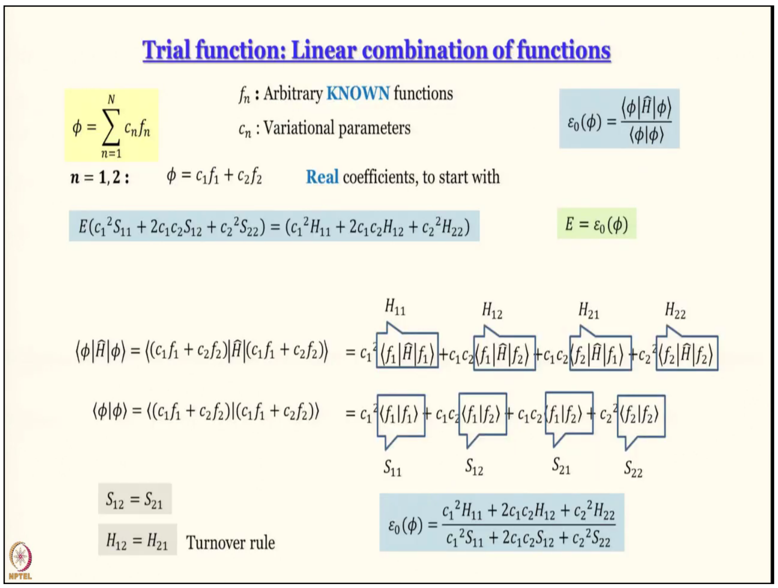


So what we will do now is we are going to use this trial function which is a linear combination of functions. So, let us say that we express this function of ours phi which is a wave function of the system as a linear combination of n number of some arbitrary but known functions are they orthonormal not yet and at the risk of boring you I am going to say this 3, 4 times more. Please remember right now we are performing a perfectly general discussion we know what the functions are they can be Gaussian functions with different full width of maximum and curvature and so on so forth.

They can be cosine functions sine functions combinations of them but I should know the functional form of f at least it is not completely arbitrary and then everything will converge at you know that will not happen. So, I start with capital n number of arbitrary known functions which are compatible with the system. And what I do is I use the coefficients as the variational parameters. We can always do it and again this is something that we have encountered in chemistry I am not sure whether I have referred to it earlier in this course but even if I have I do it again.

See I request you to think of something that we studied in solutions in the chemistry of solutions thermodynamics. Remember we talked about activity and we said that concentration usually especially for more concentrated solutions concentration is not a good enough parameter you have to use activity. Activity is equal to concentration to activity coefficient right. So, the thing is this what does that mean so we are pretending as if part of the concentration actual concentration is not available for doing the reaction right because law of mass action says that whatever mass of the reactant there is that is going to participate in that reaction that is going to govern the rate of reaction and so on and so forth.

Why are we using a fraction of the mass by invoking this activity coefficient because the problem is not with concentration to be honest the problem there is that these ions especially cannot move as fast in solution in the presence of other ions as they would in their absence? So, consider sodium chloride solution this is a sodium ion and there is well 1 excess of chloride ion around it right. So, now when the sodium ion moves it has to overcome the drag by the what we call negatively charged cloud that is why it is actually running slower.

But since we do not have any easy way of handling this running slower business we use this coefficient and pretend as if not all of the concentration is available for doing the reaction right. Similarly it is very highly possible that actually you should play around with the function itself like what we did earlier for particle in a box remember we had this x to the power alpha kind of thing perhaps that is the right thing to do but we do not know what the right thing to do is?

So we just compensate for that like we did for activity in case of activity and activity coefficients we can consider we compensate for that by bringing in this coefficient for each of these functions and we say that this coefficient is the variational parameter. So, basically we make this problem a mixing problem when I take a linear combination its as if I am mixing functions right I cannot mix functions with hand but I can add them right. I can so coefficients they tell me what is the; contribution or concentration of each function in the function that I synthesize.

So, I am playing around with the composition of the function by setting c n to be the variational parameters then we can use with we can work with fixed functions fn right. So, and we will see an example of that when we talk about this particle in a box problem and to keep things simple we start with real coefficients but that is really not a mandatory. You might as well work with complex coefficients it will take care of itself and also to keep things simple we start it with a 2 component system.

Let us say only 2 functions contribute to phi so n equal to 1 and 2 right N equal to 2 in that case what is phi phi then will be equal to c 1 f 1 + c 2 f 2 what is f 1 what is f 2 it is something I have decided that this is f 1 that is f 2 I have not revealed yet and phi is the wave function I try to synthesize. So, now this is what we want right epsilon 0 how do we get it? Let us try to evaluate the numerator first integral phi star h phi is h known yeah h would better be known for a system right h is known.

So what I do is in ket vector in sorry bra vector I write c 1 f 1 + c 2 f 2 which really means its complex conjugate in the gate vector I write c 1 f 1 + c 2 f 2 itself and now I have 2 terms in the vector 2 terms in the ket vector. So, I am going to get actually if I open it out I am going to get a sum of 4 different integrals multiplied by appropriate coefficients. Let us see let us take the first term of the vector first term of the k vector what do I have c 1 f 1 left multiplying h operating on c 1 f 1.

So since H is linear c 1 is going to come out and I am going to get c 1 square outside the integral inside the integral I have integral f 1 star h f 1 this c 1 square multiplied by integral f 1 star h f 1. So, this is the first term I get. What is the second term? The second term I can take between this first term of bra vector and second term of ket vector if I do that I get c 1 from raw vector c 2 from ket vector f 1 in the bra vector H operating on f 2 in the ket vector right.

Next I take the product of c 2 f 2 and H c 1 f 1 then I get again c 1 c 2 it does not matter whether I write c 1 c 2 or c 2 c 1 so I will follow the same convention multiplied by integral f 2 star H f 1 star is sorry not f 1 star f 2 star H operating on f 1 is there anything else yes there is something else c 2 f 2 multiplied by H c 2 f 2, so I bring that c 2 out and we get c 2 square multiplied by integral f 2 H f 2. So, see the first and the last integrals are similar in form they are integral f i H well integral f i star H f i right.

In the first case i equal to 1 in the second case i equal to 2 that is all. So, this I call H 11 and the second 1 is called H 12 so in general I can call these the h ii vectors in the case we are discussing I can take up only 2 values I equal to 1 or I equal to 2. So, this is what we get H ii next we focus on the other 2 well you understood where this i 11 came from right the index denominator well not denominator index or subscript of the function here in the bra vector you have f 1 ket vector of f 1.

So one from here one from here I call it h 11 here you have 2 in bra vector 2 in ket vectors h 22 so what will this 1 be we have f 1 in bra vector f 2 in ket vector. So, this will be H 12 this will be h 21 before I forget let me remind you that these are actually matrix elements. If you write an H matrix with these integrals then H 11 takes the 11 position h 12 takes E 12 position H 21 takes the 21 position h 22 takes the 22 position.

So, these are matrix elements, since I have forgotten to write this here, let me at least write by hand. So, these are matrix elements forgive my bad handwriting. So, now let us quickly write an expression for integral phi star phi d tau yeah so again substitute c 1 f 1 + c 2 f 2 for phi in both bra and ket vector open now up this is what you get. Once again you have c 1 square multiplied by we call this s 11 integral f 1 star f 1 we call it s 11.

This integral f 2 star f 2 d tau is called s 22 and these 2 are called s 12 and s 21 respectively now this s does it ring up bell I mean I am sure most of us would have studied some quantum chemistry course somewhere. When we talk about bonding this kind of expressions are often encountered and this s is used for overlap integral. Please remember that these are not overlap integrals here because when you talk about overlap integrals the convention is you talk about 2 different atoms here we are discussing the same system.

We are not even talking about any atom or anything right now same system. So, let us just call this s 11 they are going to evolve into overlap integrals later on when you talk about molecules. So, we have ended up and once again do you see that s 11, s 12 s 2 and s 22 they are again matrix elements of the capital S matrix not very difficult to understand. So, it is trivial and it is very easy to see that s 12 has to be equal to s 21 it should also be very easy to see that H 12 equal to H 21 why because we know turnover rule right.

Now right so we can easily write integral f 1 star H phi 2 is equal to integral f 2 star H phi 1 remember H is a hermitian operator even though we do not know what the wave function is we know what H is and even if you do not know what H is H has to be a hermitian operator by definition. So, turnover rule is applied and h 12 is going to be equal to h 21 so that is an important observation in the H matrix the corresponding of diagonal elements are equal to each other H 21 equal to H 13 23 is equal to h 32 so on and so forth.

So if you substitute this what do you get c 1 square multiplied by h 1 one + c 1 c 2 multiplied by H 12 + H 21 so H 12 and H 21 are 1 and the same so I get 2 into H 12 or 2 into h 21 is fine that multiplied by 2 c 1 c 2 + c 2 square multiplied by integral f 2 star f 1 so sorry what am I saying I just say that once again what I am trying to do is I am trying to write an expression for epsilon 0 5 while doing that I am just simplifying it and we are writing this expression here I get c 1 square multiplied by H 11 + c 1 c 2 multiplied by H 1 2 + H 2 1 in brackets since H 1 2 and H 2 1 are 1 and the same I can write 2 c 1 c 2 h 1 2.

And the last term is c 2 square multiplied by H 22 1 thing I want to remind you is that these are numbers are not they right these are integrals and they are integrals that we should be able to evaluate we are going to choose the functions that way so these are all numbers c 1 the coefficients are actually the parameters here. Similarly in the denominator I get c 1 square s 11 + 2 c 1 c 2 s 1 2 + c 2 square s 22.

Now what will do is just to get into the same convention as that of the textbook I am going to replace epsilon 0 phi I by E. So, I get E multiplied so I am basically bringing the denominator up in the numerator of the left hand side so E multiplied by c 1 square s 11 + 2 c 1 c 2 s 1 2 + c 2 square multiplied by s 22, c 1 square s 11 + 2 c 1 c 2 s 1 2 + c 2 square s 1 2 this is your left hand side.

Right hand side will be equal to same as numerator c 1 square multiplied by H 11 + 2 c 1 c 2 H 12 + c 2 square multiplied by H 22 what do I do next what do I want to do I want to find the minimum value of energy for that I have to differentiate with respect to the variation parameter and equate to 0. So, when I differentiate left hand side equal to 0 what do I get in the I get 2 terms essentially right it is a differentiation of product remember. So, the first term I am going to differentiate this function.

And in the second term I am going to keep the function intact and differentiate with respect to E sorry sorry so I differentiate with respect to alpha all the time gamma what is the parameter sorry c 1 all the time since it is a differentiation of products first of all I differentiate this function that I have keeping E constant then I differentiate E with respect to c n keeping the function constant. I hope I did not confuse you too much.

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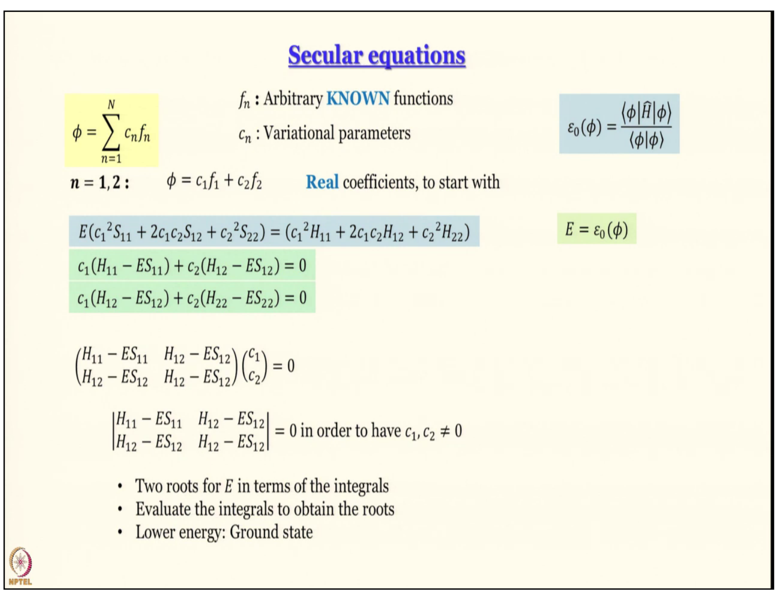

So when we differentiate with respect to c 1 what do we get with c 1 right. So, first of all let us keep E and differentiate this function here so I will get and I am differentiating with respect to c 1 right everything else is constant so here from here the first time I get 2 c 1 s 11 in the second term d c 1 is equal to 1 so I get 2 multiplied by c 2 multiplied by s 12, 2c 2 s 12. Similarly what I can do is I can do the other part second term there I do not have to differentiate the function I have to differentiate energy.

So when you do that we get del E del c 1 here I have to write del because there are 2 parameters c 1 and c 2. So, what do I do I just expand it a little bit first is equal to 2 c 1 H 11 + 2 c 1 H 12. So, I am now differentiating the right hand side. So, now see are you convinced that I differentiate the right hand side c 1 square H 11 you differentiate with respect to c 1 what do I get I get 2 c 1 multiplied by H 11 and remember what I said H 11 is a constant right its number plus how do I get 2 c 2 into H 12.

Because with respect we are differentiating with respect to c 1 so this becomes 1 and we are left with 2 c 1 s 12, now what about the third term, third term is c 2 square multiplied by H 22 with respect to c 1 c 2 is constant h 22 is a constant anyway. So, we do not worry about it it becomes 0. Moreover if you want to find the minimum then this del E del c 1 has to del c 1 has to be equal to 0 right. So, we said that to be 0 and this is what we get I said this to be just so this entire second term becomes 0 maybe I will just cut it out and see what happens.

Since this is 0, I just cut it out. So, now I have something on the left hand side E multiplied by 2 c 1 s 11 + 2 c 2 s 12 equal to 2 c 1 H 11 + 2 c 2 H 12 I can collect the terms in c 1 cannot I let us do that so we can write E multiplied by 2 c 1 s 12 + 2 c 2 s 22 is the same thing plus this is equal to 0 sorry what am I doing I think I have got the animation wrong sorry about that so differentiate with respect to 0 and then this is what you get right.

You get you just bring it to this side what happens this everything is multiplied by 2 so 2 cancels. So, c 1 multiplied by H 11 - E into s 11 this is what we get here and you could have put a minus sign in front of that it would have changed its equated to 0 anyway. Then terms in c 2 would be we are bringing to right hand side remember. So, c 2 multiplied by H 12 - c 2 well H 12 - E s 12 right that is what the coefficient of c 2 is on the left hand side c 2 multiplied by E multiplied by s 12 all right.

So from there we get this linear equation in c 1 and c 2 remember c 1 and c 2 are variables now I have 2 variables and so far I have only 1 equation I need 1 more I obtain the other 1 by differentiating with respect to c 2 and equating to 0 keeping in mind that del E del c 2 is 0 anyway. So, from here it turns out to be 2 c 1 H 1 2 + 2 c 2 H 22 that is your second equation in c 1 and c 2 what can I do from here?

First of all I can try and focus on the coefficients and try to find expressions for the coefficients right because the simultaneous equations are in terms of c 1 as variable c 1 and c 2 as variable. Problem with that approach is that I do not know E yet so better find out E first. Let us learn that and then I will tell you that you can of course go ahead and find the coefficients but will not do that in this course that is all but it is very simple all right so here we are we have got an equation right we have got an equation and I hope it is not difficult to see that we can write it nicely as a matrix equation where the matrix elements are not H11 s 12 so on and so forth.

No rather they are H12 - E s 1 H 12 minus E s 12 what did I say H 11 minus E s 11 the second one is H 12 minus E s 12 third 1 is H 12 - c s 12, fourth 1 is H 12 - E s 12 that is the matrix. Now what are the possibilities now 1 possibility is that c 1 and c 2 is equal to 0 then we do not have to worry about anything the problem is if c 1 and c 2 are equal to 0 then what are we talking about here? Then I do not have a wave function no matter what f 1 and f 2 may be if c 1 equal to 0 c 2 equal to 0 the function vanishes phi does not exist I mean it becomes 0.

And wave function cannot be 0 everywhere that is 1 of the things that we learnt from 1 approximation. So, the other option is that this matrix equal to 0 so if you go a little further using Gammon’s theorem and all what it turns out is that this secular determinant, the circular determinant means the same matrix elements make up a determinant this time that is equal to 0 in order to have c 1 c 2 is not equal to 0.

What is the variable now in this case H 11 I can find out s 11 in principle I can find out the only variable here is E. So, if we set that secular equation to be 0 then we are going to get an equation in some nth order do you agree that well in this case we are going to get an equation of second order quadratic equation. So, if we solve these we will get 2 roots 2 solutions so use the smaller ones we first of all of course evaluate the roots and the root with lowest energy is the ground state energy.

This can be nothing with energy lower than down state is not it. So, that is what we get, fine, so, far for so much for secular equations for now.

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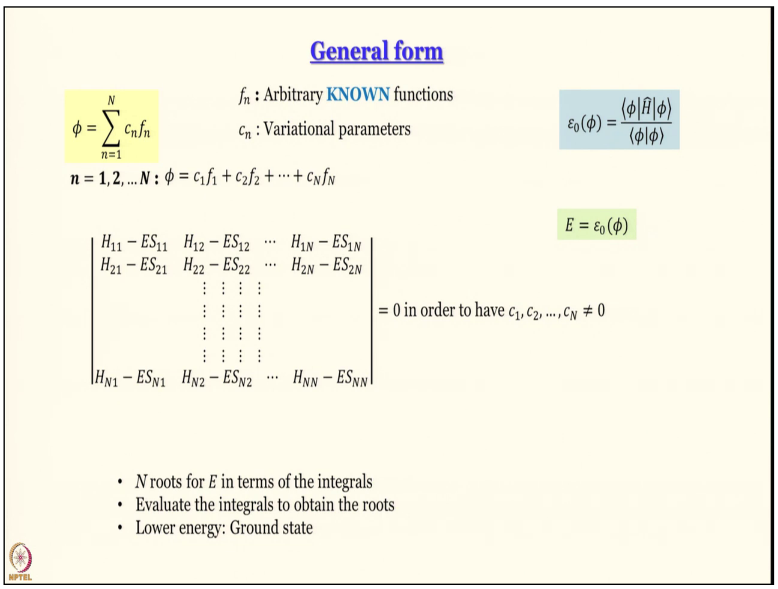


Well not really I want to show you the general form. The general form is for n number of terms this is what you will get H 11 - E s 1 H 12 - c s 12 why am I saying s 1 all the time. H 11 - E s 11 the 1 2 term is H 12 - E s 12 and so on and so forth up to H 1n - E s n 1 n. In the second term everything remains same just this subscript 1 becomes subscript 2 so on and so forth until in the capital Nth row the this subscript becomes capital A right so this has to be equal to 0 this is the equation that we need to solve.

So let us break now and let us come back and discuss very quickly in a short module how to tackle this particle in a box problem using secular equations.