Quantum Chemistry of Atoms and Molecules
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Lecture-54
Electronic Wave functions of He Atom

This is where we are stopped we had written an expression for energy of helium atom in terms of the spin orbitals and the Hamiltonian actually I should have written it using power point like I do but then is too tedious.

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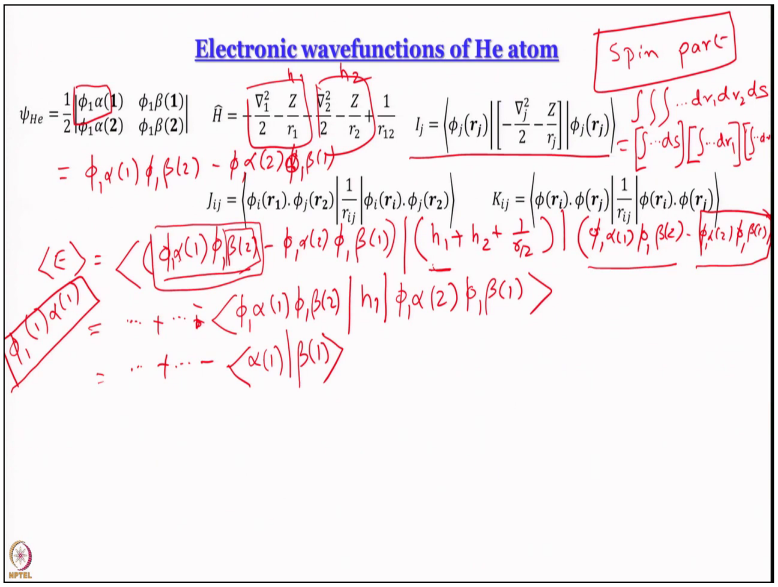

Electronic wavefunctions of He atom

Spin part

$$\psi_{He} = \frac{1}{2}\begin{vmatrix} \boxed{\phi_1\alpha(1)} & \phi_1\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) \end{vmatrix} = \phi_1\alpha(1)\phi_1\beta(2) - \phi_1\alpha(2)\phi_1\beta(1)$$

$$\hat{H} = \underbrace{-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}}_{h_1} \underbrace{-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}}_{h_2} + \frac{1}{r_{12}}$$

$$I_j = \left\langle \phi_j(\mathbf{r}_j) \middle| \left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j} \right] \middle| \phi_j(\mathbf{r}_j) \right\rangle \quad \iiint \ldots dr_1 dr_2 ds = \left[\int \cdots ds\right]\left[\int \cdots dr_1\right]\left[\int \cdots dr_2\right]$$

$$J_{ij} = \left\langle \phi_i(\mathbf{r}_1).\phi_j(\mathbf{r}_2) \middle| \frac{1}{r_{ij}} \middle| \phi_i(\mathbf{r}_i).\phi_j(\mathbf{r}_2) \right\rangle \qquad K_{ij} = \left\langle \phi(\mathbf{r}_i).\phi(\mathbf{r}_j) \middle| \frac{1}{r_{ij}} \middle| \phi(\mathbf{r}_i).\phi(\mathbf{r}_j) \right\rangle$$

$$\langle E \rangle = \left\langle \left(\boxed{\phi_1\alpha(1)\phi_1\beta(2)} - \phi_1\alpha(2)\phi_1\beta(1) \right) \middle| \left(h_1 + h_2 + \frac{1}{r_{12}} \right) \middle| \left(\phi_1\alpha(1)\phi_1\beta(2) - \boxed{\phi_1\alpha(2)\phi_1\beta(1)} \right) \right\rangle$$

$$\boxed{\phi_1(1)\alpha(1)}$$

$$= \cdots + \cdots - \langle \phi_1\alpha(1)\phi_1\beta(2) | h_1 | \phi_1\alpha(2)\phi_1\beta(1) \rangle$$

$$= \cdots + \cdots - \langle \alpha(1) | \beta(1) \rangle$$

So I decided that I should subject you to my bad handwriting at least once sorry about that. Now let me do something let me try and expand this a little bit not all little bit. So, let me what are we trying to do here we are trying to say what is the role of this spin part of the wave function. We have already given you the answer the expression for energy but there, there was no spin part only the spatial part of the orbital was there.

So we are going to convince you now that that is we ok can take care of the spin part or rather the spin parts sort of take care of themselves we will see how. Now here when we expand what will the first term be for the first term I can take this and h 1 and this so the first time is going to be something like integral phi 1 alpha 1 phi 1 beta 2 h 1 operating on the same wave function phi 1 alpha 1 phi 1 beta 2 plus there will be more terms we will perhaps write 1 or 2 of those.

But before that let me try to see and I let me try to make sense of this integral. So, remember this integral is really not a single exponent a single integral right. So, what are the parameters here there has to be something in terms of there has to be dr 1 there has to be dr 2 and there has to be ds spin also so it is actually triple integral. So, in principle I should be able to separate it out into a product of maybe 3 integrals can we do that let us see.

So first of all I can take this spin part out I hope you I understand what I am talking about this here is really integral, integral, integral whatever we have in terms of dr 1 dr 2 ds I can say. So I want to write it as integral of the spin part ds multiplied by integral of the r 1 dependent part with respect to dr 1 and integral of the r 2 dependent part dr 2 is just that we are using bracket notation nothing else. So, we can take the spin part out and write a an integral for itself that will be integral alpha 1 alpha 1 star alpha 1 over all space that is gone.

Because remember what is this phi 1 alpha 1 it is really phi 1 one alpha 1 that means electron number 1 has alpha spin and resides in spatial orbital phi 1. This has gone out. Next what do I have the spatial part also I have coordinates of your well no I mean that is all there is 1 more not special part. I have another spin part that is beta 2 yeah beta 2 and beta 1 beta 2 and beta 2 my handwriting is so bad that I myself am getting confused.

So can blame you for getting confused here sorry about that so this is what we are talking about beta 2 and beta 2. So, second integral that comes out is beta 2 beta 2 beta 2 in bra beta 2 in ket. What remains a special part is phi 1 1 h 1 operating on phi 1 1, how did I get this? Phi 1 1 from here let us not forget that what we have written here this phi 1 alpha etcetera these are spin orbitals so they are products of a spatial part and a spin part right. So I have to write 1 in brackets in both.

So now just look at these look at these integrals spin wave functions are normalized this is equal to 1 this is equal to 1 and this what is this, this is equal to i yeah j equal to 1 r j this small j is equal to 1 minus del j square by 2 minus z by r j this is equal to h 1 as we have defined and that operates on phi 1 j. So, this is basically I 1 so the first term remember we are only writing the first term now first term becomes I 1 from here neglecting the we are not really working with the normalization constant we are just working with the remaining wave function that is fine.

So you see that we are actually getting those integrals which do not contain the spin parts. The spin parts sort of take care of themselves by normalization right normalization that is all. Now what more can we do here let us take something else what is the second integral going to be? Second integral is going to be say I will take this 1 minus phi 1 oh no what am I writing here; so we will write here; so second 1 will be minus phi 1 alpha 2 phi 1 beta 1 h 1.

Then I take this minus so minus minus will become plus and the integral will be something like phi 1 alpha 2 phi 1 alpha 2 phi 1 beta 1 what did I say I will take h 1 or h 2, let us take h 1 h 1 phi 1 alpha 2 phi 1 beta 1 I hope it is not very difficult to see that by similar treatment we are going to get I 1 once again right. Because what you have you will have phi 1 1 h 1 phi 1 1 same thing. Again you have alpha 2 alpha 2 that is 1 beta 1 beta 1 that is 1 so again you will get I 1 from there.

So you see how this expression I 1 comes in this in the expression for how this integral I 1 comes in the expression for energy? Now let me clear this up a little bit well all the terms are there I am just not writing all the terms I am trying to just expand and see what happens. Now let us take a different combination of terms we have already written 2 terms. So, I can write something dot dot dot plus dot dot dot what we have got I 1 I 1 third 1 let us take this let us take h 1.

And let us take the second term because that also has to be done right a plus b well a minus b into a minus b how much what is it yeah a square minus a b minus b a minus b square that is the kind of thing we are doing here. So, what will that integral be now, plus integral alpha phi 1 alpha 1 phi 1 beta 2 h 1 and now taking the second one so see this will not be plus this will be minus and the second one is phi 1 alpha 2 phi 1 beta 1.

Now let us see if things get more interesting so I am not writing the first terms whatever terms are there only this term I will focus on what will happen I can bring out phi 1 phi 1 1 h 1 then phi 1 2 right. So, what I get here is well even before going there here we have alpha 1 and here you have beta 1 so you get alpha 1 you get beta 1 multiply them together and integrate over all space what do you get you get zero because they normalize.

So what I am trying to say is that lot of these terms actually become equal to 0 right. And then when you go a little further when you expand upon this r ij term you are going to get what is called this j ii j 11 term iI equal to j here so there is no problem you just can take this j 11 right. So, this is how you can expand see just for helium it is so long that we are not having the patience to work it out. So, imagine what it will be for an n electron atom where n is a large number is going to be huge.

But we just demonstrated I hope this demonstration was not confusing for you, you just try to work it out yourself.

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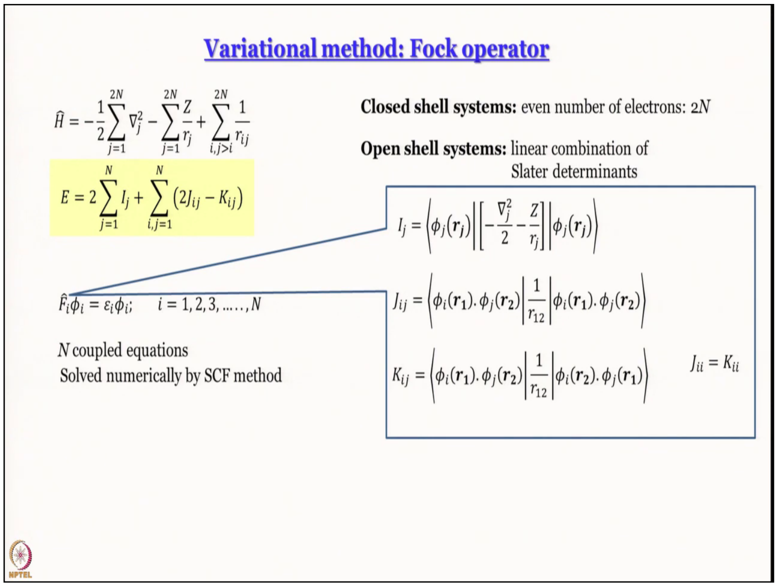

Variational method: Fock operator

$$\hat{H} = -\frac{1}{2}\sum_{j=1}^{2N}\nabla_j^2 - \sum_{j=1}^{2N}\frac{Z}{r_j} + \sum_{i,j>i}^{2N}\frac{1}{r_{ij}}$$

$$E = 2\sum_{j=1}^{N} I_j + \sum_{i,j=1}^{N}\left(2J_{ij} - K_{ij}\right)$$

$$\hat{F}_i\phi_i = \varepsilon_i\phi_i; \qquad i = 1, 2, 3, \ldots\ldots, N$$

N coupled equations
Solved numerically by SCF method

Closed shell systems: even number of electrons: $2N$

Open shell systems: linear combination of Slater determinants

$$I_j = \left\langle \phi_j(\mathbf{r}_j) \middle| \left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j}\right] \middle| \phi_j(\mathbf{r}_j) \right\rangle$$

$$J_{ij} = \left\langle \phi_i(\mathbf{r}_1).\phi_j(\mathbf{r}_2) \middle| \frac{1}{r_{12}} \middle| \phi_i(\mathbf{r}_1).\phi_j(\mathbf{r}_2) \right\rangle$$

$$K_{ij} = \left\langle \phi_i(\mathbf{r}_1).\phi_j(\mathbf{r}_2) \middle| \frac{1}{r_{12}} \middle| \phi_i(\mathbf{r}_2).\phi_j(\mathbf{r}_1) \right\rangle \qquad J_{ii} = K_{ii}$$

You will be convinced that you will be able to write the expression of energy in terms of these integrals. For helium what happens? For helium first of all I will write this I 1 so I 1 plus I 2 but I 1 plus I 2 are one and the same right so you can write what expression you get from there and here you will write k i j equal to j ij where well again i and j are 11 so you can write 2 j 11 minus j 11 that will be 1 j 11 and then you can substitute you will get the expression for energy for helium.

But the story does not stop here we have learnt variational method. So, we know that this expression that we have got now we have to minimize we have to find the minimum value of the energy that we get from this expression right. How do you do that in variation method you just minimize it right and when you minimize you end up getting equations like this, you get a fock operator this is called a fock operator I will show you the fock operator or maybe I will not I will tell you what fock operator is made up of.

If you want to know the form you are welcome to consult Macquarie's book or Pillars book it is written there well Pillars book not very sure Macquarie is book definitely so f i operating on phi i gives me epsilon i phi i that is the kind of equation that will get. So, these f i's are made up of these integrals essentially it is something like an expression analogous to the expression of Hamiltonian but with the functions in it you just expand it.

And how many n values are there, there are well 1 2 3 4 5 6 up to n i values are there not m right so that is the number of orbitals that are there. Remember we have said that we have n orbitals and we can we can put in maximum of 2 electrons in them. So, we can accommodate 2 electrons in this n number of orbitals. So, what we get then is this, this kind of equations using fock operator for this again this is like an eigen value equation fock operator operating on a wave function gives me back the wave function multiplied by epsilon i I get n number of equations.

And these are in coupled equations because these wave functions are not really independent of each other are they right they are not. So, what you do with these n coupled equations you solve them numerically by using your self consistent field method. What is the initial guess value that you use the initial guess value that you use is of your linear combination of Stator determinants. So essentially what you do here is that you write this expression get fock operator.

How do you get fock operator fix fock operator will also contain this phi's remember. So, it is not a simple differential equation it is exactly well very similar to what we have done earlier. So, to generate the fock operator you need the guess values and the guess values that you get are linear combinations of Slater equations I thought I have read them written below here looks like I did not write sorry about that.

So you start with this Slater determinants start with orbitals start with hydrogen atom orbitals ok saturated determinants involving hydrogen atom orbitals and construct the fock operator. Let the fock operators operate on the wave functions and write down the n coupled equations solve them numerically using the self consistent field method then you get the next set of these wave functions use this wave functions to generate the next generation of fock operators and then go on until self consistence is obtained and once again this becomes a computational problem.

That brings us to an end of the discussion that we wanted to perform and let us not pretend that we have discussed everything that is way beyond the scope of this course in fact the course has become much more than what I initially intended it to be. So, we are not going to go into further detail let us hope that we will be able to have another NPTEL course on advanced topics in quantum chemistry. If you are successful in that then we will start from here and talk about more advanced methods because you might remember I told you that a practitioner of quantum chemistry once told me that for him quantum mechanics begins where Hartree-Fock ends.

But for the purpose of this course it ends well at least for atoms it ends where Hartree-Fock ends the reason for doing this discussion in the first place is that we wanted to make certain points which are useful not only for these many electron atoms but also for molecules. Remember the course is quantum chemistry of atoms and molecules. So, the points that we have made in this discussion are these first of all you have to use approximation techniques and the techniques we have learnt are perturbation theory techniques and variation methods.

Using variation method you can get upper limits of energies using perturbation theory you can actually do an accurate calculation if you go to high level well higher order perturbation correction terms and provided the perturbation is does not change the system too much from the ideal system. And the problem here is that there has to be a system for which an exact solution of

Schrodinger equation must be there that requirement is not there in variation method that is why it is so popular.

But then you cannot do it at one go for most of the systems for initial systems that we tried for systems where we knew the exact solutions we did them at one go but then gradually we learned that the only way out the only way to tackle the problem of many electron atoms and systems as complex as these is to resort to iterative techniques. And the techniques that you use are called self consistent field methods in which you guess a wave function you construct an effective potential using those guess values of a function then find the solution of that equation.

Because the problems remember even though I am saying it many times I will say it again the problem with this kind of approach Hartree-Fock approach is that the operator itself contains the function. So, unless you start with some kind of a guess value of function you cannot really get going right. So, to get going we give some guess value and that guess value that guess cannot be any guess some sort of sense has to be there in the guess but eventually we have learnt that we do not have to stick to the exact solutions at all we can take anything.

So Gaussian exponential many things we talked about different kinds of orbitals and finally what we have shown you very sketchily is that by using this kind of SCF calculation using Hartree-Fock method using variational method one can get one can try and solve we get energy values for complex many item systems. What I am not going to say but I request you to read from Macquarie's quantum chemistry book or Prasad's book or Chandra's book any book that you like is what we have actually studied in class 11, 12.

Remember for many electron atoms we have talked about variation of ionization energy salt with variation we talked about variation of electronegativity so on and so forth. Actually when you do this kind of a an SCF calculation you get results by which you can get very, very close to the experimental values so this softwood variation where you see signatures of this main shell and subshell that can be actually modeled very nicely using Hartree-Fock method SCF calculations.

So I would like you to read that part because that is just story more of a story than what the story I told you over the last 2 modules. So, please read those by yourselves and refresh your memories and also understand to a little better extent I hope why you get that kind of a trend for many electron atom we are not going to discuss that explicitly here that brings us to an end of this part of the discussion that brings us to an end of the discussion of atoms.

But the concepts that we have generated here exchange integral coulomb integral and remember something called S integral of phi i phi j overall space, all these integrals are going to come handy in the subsequent discussion that we are now going to perform on quantum chemistry of molecules and there we are going to talk about 2 approaches valence bond theory molecular orbital theory.

I suspect all of you have heard of all this is just that we hope that we will be able to take our understanding to like one notch higher not complete but one notch higher than whatever it is at the moment right. So, next day we start talking about quantum chemistry of molecules.