Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-51
Hartree - Fock Equations and Self Consistent Fields

We are inching towards the climax of this very interesting discussion about many electron atoms and to keep things simple our discussion has been limited to helium and that is how it is going to be for this course. We have talked about variation method we have talked about perturbation theory. Today and may be in a couple of more modules or 1 more module we are going to talk about Hartree-Fock equations and how Hartree-Fock equations are handled by using something called self consistent fields.

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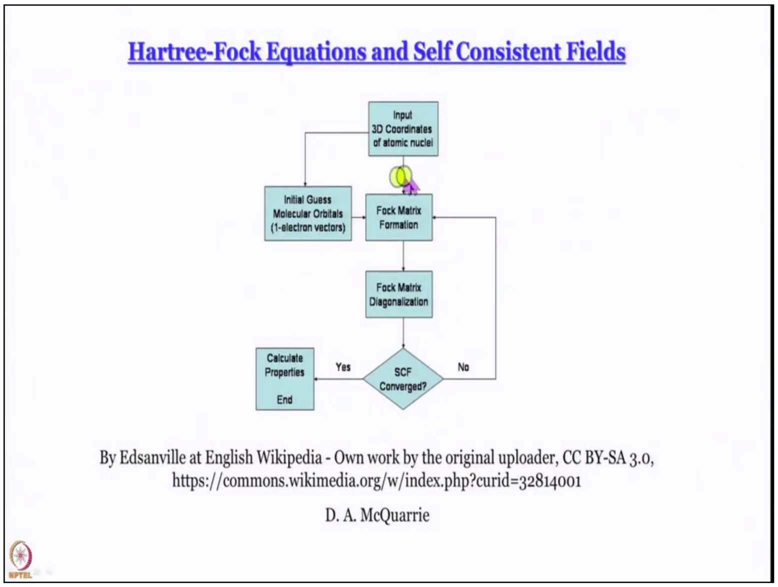

Hartree-Fock Equations and Self Consistent Fields

Input
3D Coordinates
of atomic nuclei

Initial Guess
Molecular Orbitals
(1-electron vectors)

Fock Matrix
Formation

Fock Matrix
Diagonalization

SCF
Converged?

Yes

No

Calculate
Properties
End

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D. A. McQuarrie

And what you see here is from wikipedia its an algorithm of how this self consistent fields are used to handle Hartree-Fock equations. So, we will slowly see how it makes sense what I would like you to note now is that it is an iterative method. You have to go around do the calculations again and again and again and then keep improving your results; that is in a very, very simple manner how it works.

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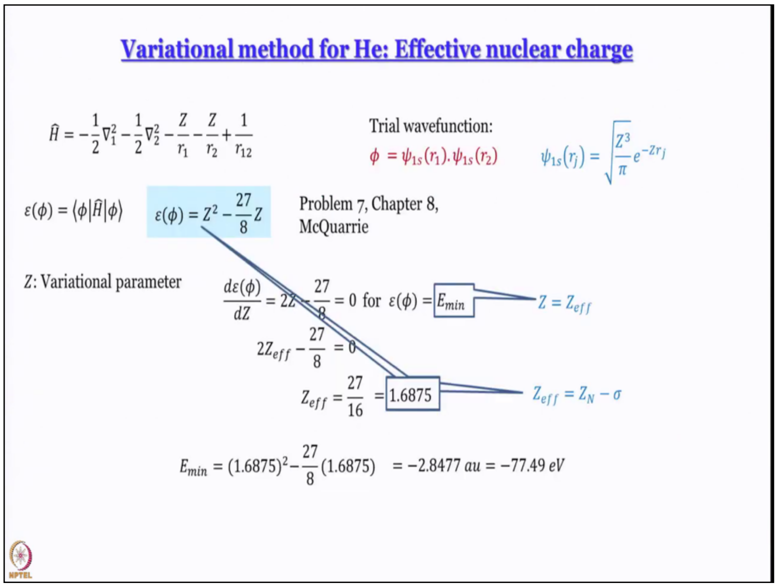

Variational method for He: Effective nuclear charge

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

Trial wavefunction:

$\phi = \psi_{1s}(r_1).\psi_{1s}(r_2)$ $\psi_{1s}(r_j) = \sqrt{\frac{Z^3}{\pi}}e^{-Zr_j}$

$\varepsilon(\phi) = \langle\phi|\hat{H}|\phi\rangle$ $\varepsilon(\phi) = Z^2 - \frac{27}{8}Z$

Problem 7, Chapter 8,
McQuarrie

Z: Variational parameter

$$\frac{d\varepsilon(\phi)}{dZ} = 2Z - \frac{27}{8} = 0 \text{ for } \varepsilon(\phi) = \boxed{E_{min}}$$

$Z = Z_{eff}$

$$2Z_{eff} - \frac{27}{8} = 0$$

$$Z_{eff} = \frac{27}{16} = \boxed{1.6875}$$

$Z_{eff} = Z_N - \sigma$

$$E_{min} = (1.6875)^2 - \frac{27}{8}(1.6875) = -2.8477\,au = -77.49\,eV$$

So, far what we have been able to achieve is that by using a variational method for helium we have been able to reach what we have talked about earlier the effective nuclear charge. We had written down our Hamiltonian in atomic units and the trial wave function that we are using is very simple it is the same kind of a function that we had talked about earlier that we encountered during orbital approximation psi 1s is the same orbital that you get when you talked about hydrogen atom.

The only difference is that one of this Psi 1s wave functions is written in terms of the coordinates of electron number 1 the other is written in terms of coordinates of electron number 2 that is all. So, using this we defined this functional epsilon as integral phi h hat phi over all space in this case over r let us say or r theta phi whatever it. Now the thing is we used the atomic number z as a variational parameter and we did that consciously because we know that the atomic number seen by an electron in the presence of the other is less than the full value that is there.

So that is why we expect that the value of z will keep decreasing one way of doing it is taking z minus sigma the other way of doing it is by taking a fraction. So, here we are sort of taking it like a fraction but then of course we can subtract it from the original atomic number and get the effective atomic number get the shielding constant rather. So, this is a variational parameter so what we do is we minimize epsilon with respect to z and at the minimum value of it we say that z is equal to z effective.

So z effective turns out to be 1.6875 and hence 1 can calculate sigma and E min turns out to be minus 77.49 electron volt which is close to the actual value but well not close enough. If it was close enough then we could have closed the discussion right here.

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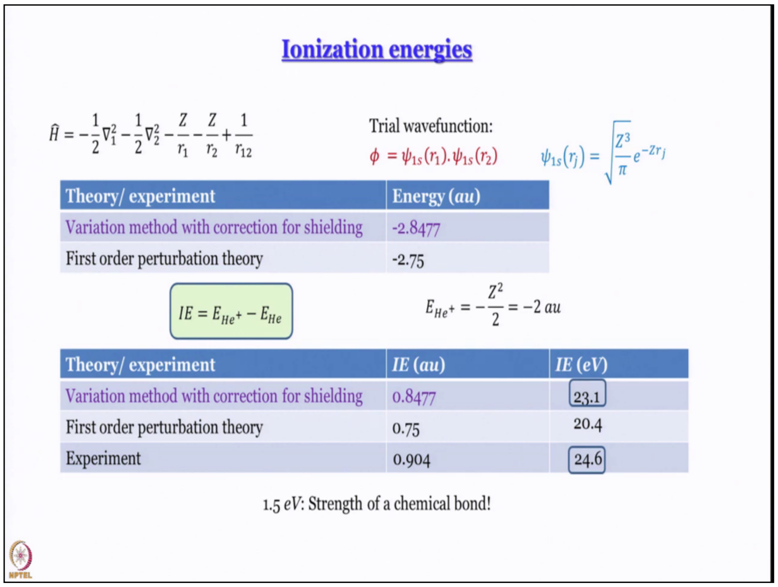

Ionization energies

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

Trial wavefunction:

$\phi = \psi_{1s}(r_1).\psi_{1s}(r_2)$

$\psi_{1s}(r_j) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr_j}$

Theory/ experiment	Energy (*au*)
Variation method with correction for shielding	-2.8477
First order perturbation theory	-2.75

$$\boxed{IE = E_{He^+} - E_{He}}$$

$$E_{He^+} = -\frac{Z^2}{2} = -2\ au$$

Theory/ experiment	*IE* (*au*)	*IE* (*eV*)
Variation method with correction for shielding	0.8477	$\boxed{23.1}$
First order perturbation theory	0.75	20.4
Experiment	0.904	$\boxed{24.6}$

1.5 *eV*: Strength of a chemical bond!

Next we said that it makes sense to look at ionization energies because when we look at ionization energies the fact that we do not really have an excellent agreement is highlighted little more. So, we see that the difference in the number that we get using variation method and the experimental number is about 1.5 electron volt which is sort of the strength of a chemical bond, so it is non trivial right. So there is room for doing better.

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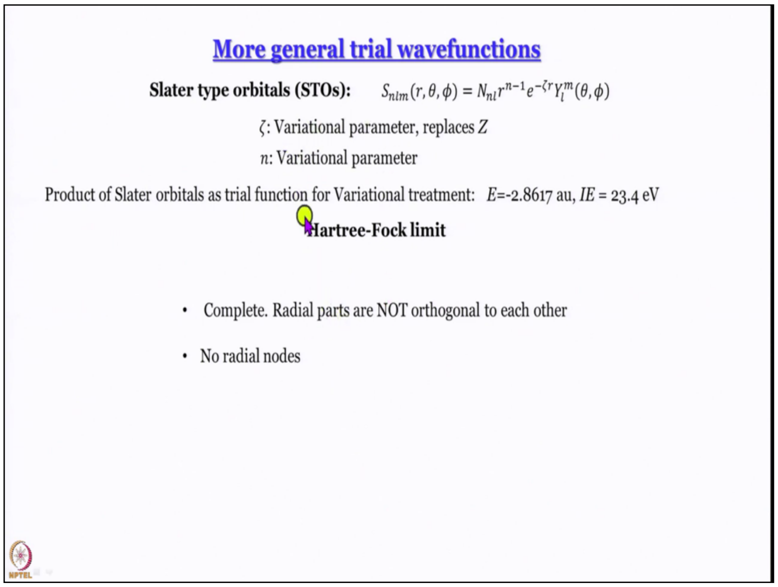

More general trial wavefunctions

Slater type orbitals (STOs): $S_{nlm}(r,\theta,\phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\phi)$

ζ: Variational parameter, replaces Z

n: Variational parameter

Product of Slater orbitals as trial function for Variational treatment: E=-2.8617 au, IE = 23.4 eV

Hartree-Fock limit

- Complete. Radial parts are NOT orthogonal to each other
- No radial nodes

And in trying to do better what one does first is that one can use more general trial wave functions. There is no need of sticking to hydrogen atom like wave functions. So, the first kind of wave functions that one can use are Slater type orbitals there are still one electron wave functions that is why you call them orbitals. So, stereotype orbitals are functions of r theta and phi as usual we could write them in terms of x y z but as we know it makes more sense to write them in terms of spherical polar coordinates it is easier to handle that way.

And that turns out to be a number normalization constant multiplied by r to the power n - 1 multiplied by E to the power minus zeta r instead of z we have written zeta where zeta is a variational parameter and that is multiplied by an angular part. So, we have something similar to the hydrogen atom wave functions once again we have a radial part multiplied by an angular part but something is missing here right.

What is missing? What is missing is that likewise polynomial remember likewise polynomial that polynomial is not even here right. We have an exponential decay in r we have this r to the power something and we have the angular part right. So, here not only is zeta the variational parameter but n is also a variational parameter and we discussed this in the previous module. When we talk about hydrogen atoms n can only take up integral values not so when you use these as starting points as trial functions.

You want to play around with n as well because you do not really care too much about whether they are integral or not. So, you are going to get values of n something like.9.8 whatever. Now so when we use this product of theta orbitals as trial wave function for variational treatment we get a value of E of -2.8617 atomic unit and ionization energy of 23.4 electron volt which is called the Hartree-Fock limit.

For leaving this discussion let me just reiterate that first of all these zeta type orbitals form a complete set however the radial parts are not orthogonal to each other precisely because that Laguerre polynomial whatever polynomial it is that is missing. Remember orthonormality in all these wave functions we talked about might be for your rigid rotor, harmonic oscillator, hydrogen atom. All the orthonormality well orthogonality came from the polynomials that were present there Laguerre polynomial, Legendre polynomial and so on and so forth hermite polynomial.

So, since the polynomial is not here they are not orthogonal to each other let us remember that we are not working with orthogonal functions. And as we said earlier there is no radial node again because there is no polynomial equate this to 0 where will it be equal to 0 at infinity nowhere else. But you can have angular nodes because the angular part is there and there is no guarantee that the angular part will be such that it would not be equal to 0 at some value of theta some value of phi right.

So these are close to hydrogen atom wave functions but not quite and they include variational parameters.

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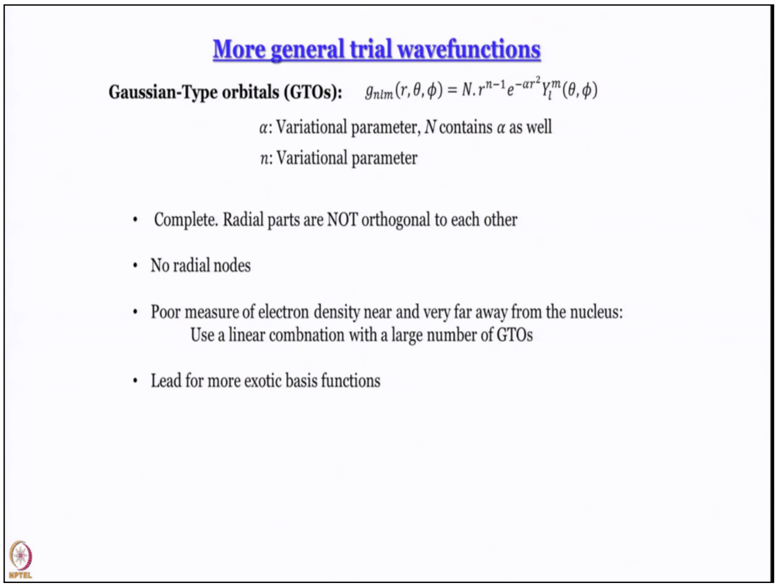

More general trial wavefunctions

Gaussian-Type orbitals (GTOs): $g_{nlm}(r,\theta,\phi) = N.r^{n-1}e^{-\alpha r^2}Y_l^m(\theta,\phi)$

α: Variational parameter, N contains α as well

n: Variational parameter

- Complete. Radial parts are NOT orthogonal to each other
- No radial nodes
- Poor measure of electron density near and very far away from the nucleus: Use a linear combnation with a large number of GTOs
- Lead for more exotic basis functions

The other kind of orbitals that I want to just mention here are Gaussian type orbitals these are very important then the starting point of well I said it 2, 3 times already but there are starting point of computational chemistry in big way. So, much so that the perhaps the most popular quantum chemistry computational quantum chemistry program that is used worldwide is called Gaussian this is where it derives the name from.

From Gaussian type orbitals so the difference between Slater type orbitals and Gaussian type orbitals is that in Gaussian type orbitals you do not use an exponential function rather you use a Gaussian function it is not E to the power minus zeta r rather it is E to the power minus alpha r square again alpha is a variational parameter and n is a variation parameter as well the advantage of using Gaussian type orbitals you might remember we had shown at one place when we used exponential function.

And no when you use the Gaussian function actually there was not a good match at the top but then you can use a lot of terms and take sums and make up for that. So, once again is a complete set and once again radial parts are not orthogonal to each other precisely because the polynomial is missing. For the same reason there is no radial node. Now when you use this Gaussian type orbitals what you get is if you use one orbital you get very poor measure of electron density near the nucleus and that we have discussed earlier, remember.

Because if you try to model 1s, 1s is like this and Gaussian has a some something like this. So, poor measure of electron density not only near but also very far away from the nucleus. So, to make up for that what do we do we do what we have discussed already we take linear combinations we take a large number of GTOs use linear combinations and that brings in an additional or not un additional, un additional type of variation and parameter in the form of the coefficients of these terms.

Coefficients also become variational parameter so that way more parameters we are happy in any case we have upper limit theorem we cannot do better than the best we cannot go below the actual energy. So, we happily add terms to the extent that our computational power allows us. And this opens up the field for more exotic basis functions. If you actually use Gaussian or Gammas or any other computational chemistry program you will see there are lot of basis functions that you choose from and different basis functions basic sets are good in different situations. This here is the beginning of all that the tip of the iceberg.

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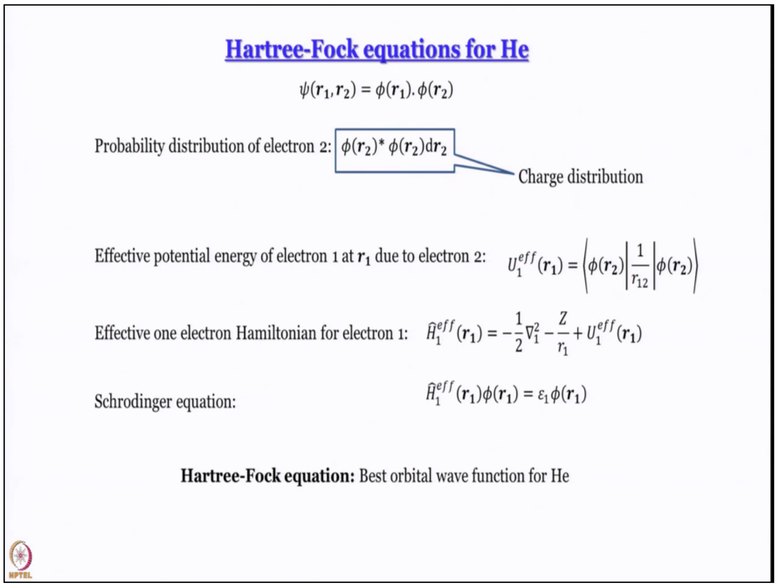

Hartree-Fock equations for He

$$\psi(r_1, r_2) = \phi(r_1).\phi(r_2)$$

Probability distribution of electron 2: $\boxed{\phi(r_2)^* \phi(r_2) dr_2}$

Charge distribution

Effective potential energy of electron 1 at r_1 due to electron 2: $U_1^{eff}(r_1) = \left\langle \phi(r_2) \middle| \frac{1}{r_{12}} \middle| \phi(r_2) \right\rangle$

Effective one electron Hamiltonian for electron 1: $\hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1)$

Schrodinger equation: $\hat{H}_1^{eff}(r_1)\phi(r_1) = \varepsilon_1 \phi(r_1)$

Hartree-Fock equation: Best orbital wave function for He

Great with that background let us now discuss how this Hartree-Fock equations for helium come and how they are handled once again we are not really going to try and write down every mathematical step because that would be too much and it makes no sense also. You have to remember a lot of things? No, what do you have to remember this, this what is written here the wave function used in Hartree Fock method is still within the ambit of orbital approximation please remember this.

It is a product of 2 1 electron wave functions. Hydrogen atom wave functions are not that will come to later but the orbitals 1 electron wave function. So, what we do is first of all we note something, we note that the probability distribution of electron number 2 is phi star phi dr 2 electron 2 right. So, this is phi the orbital written in terms of coordinates of 2 electron number 2 that is r 2 when I write r in bold letter what I mean is that that could mean r theta phi or x y z or something like that it just does not mean one coordinate.

It means coordinate system combination of all the coordinates for electron number 2. So, capital R would mean r 2 theta 2 phi 2 something like that or x 2 y 2 z 2 so phi star phi d r 2 as we know gives us the probability distribution of electron 2 phi star phi gives probability density. In case you are confused about this please go back and have a look at the discussion we are done while talking about hydrogen atom orbitals few weeks ago.

Now since this is the probability density what happens if I multiply it by electron charge yeah I should get charge density. So, this probability density is a measure of what is in classical mechanics called charge distribution that is a very important starting point of Hartree-Fock method. So what we do next is that we write down an expression for the effective potential energy of electron number 1 at point r 1, r 1 theta 1 phi 1 R well not capital sorry bolt r 1 bolt r 1 means a particular point characterized by say r 1 theta 1 phi 1.

So what is the effective potential energy of electron number 1 at its instantaneous position which we denote by bolt r 1 due to electron number 2 so what is the potential exerted by electron number 2 on electron number 1 at an instant at the position of electron number 1 denoted by bolt r 1 I have said it I have done as many permutations and combinations of the words in that sentence I hope you understood 1 of them.

So this effective potential what will it be we all know the formula for potential energy from electrostatics. If we relate it to our knowledge of quantum mechanics this is what it will be, we call it U 1 effective at r 1 that would be equal to integral phi star r 2 1 by r 1 to phi r 2 what is r 1 2 r 1 2 is a separation between electron number 1 and electron number 2. So, this is the average value of the potential energy that we get and we call it the effective potential.

Of course if you could measure at different times of course you would get different values that is why as we know we in quantum mechanics we only handle we only work with average values. This is the effective or average value of potential of electron number 1 in its own position due to the presence of electron number 2 because they are going to repel each other right. So, this is how we define U 1 effective great knowing that can we write down an effective 1 electron Hamiltonian for electron number 1.

What is Hamiltonian? Total energy operator right, so total energy operator would involve kinetic energy as well as potential energy. If we talk about a 1 electron system kinetic energy is given by that minus del square by 2 in atomic unit right minus h cross square by 2 m into del square so if you write in atomic units it is just minus half into del square that is kinetic energy. For 1 electron system what is the potential energy just 1 by r or 1 by r 1 in this case.

What is the additional term I get in this effective 1 electron Hamiltonian for electron number 1 for helium this U 1 effective also has to be included right. So, the effective Hamiltonian for electron number 1 one would be minus half del 1 square minus z by r 1 this is for the attraction of the electron with the nucleus plus U 1 effective at r 1 this is our effective 1 electron Hamiltonian remember 1 electron.

So we are going step by step we are building the problem. So, now that we know the Hamiltonian it is very easy for us to write Schrodinger equation whether we can solve it for now or not that is a different question altogether we will cross that bridge when we come to it but we can write right. So, the Schrodinger equation that we can write is going to be well H psi equal to E psi we know what psi is is a product of the 2 1 electron wave functions.

We know what the Hamiltonian is effective 1 electron Hamiltonian so we just write the Schrodinger equation like this. Remember this Schrodinger equation for 1 electron so I am not using the product here so I had gone and I got a little distracted 1 minute ago sorry so I am just working with the 1 electron wave function here. So, this here is your Hartree Fock equation and this Hartree-Fock equation yields the best orbital 1 wave function that you can get for helium orbital wave function.

When we talk about 1 electron wave functions when you want to retain the memory of hydrogen atom then Hartree-Fock equation works best. In more advanced theories we first check the concept of orbitals and we go ahead and so I have heard practitioners of quantum chemistry of now saying something that would seem to be perhaps very cheeky to you I have heard them saying there is no such thing as orbitals. Let us not get so advanced right now, for now we will use orbitals it works fine for us, great.

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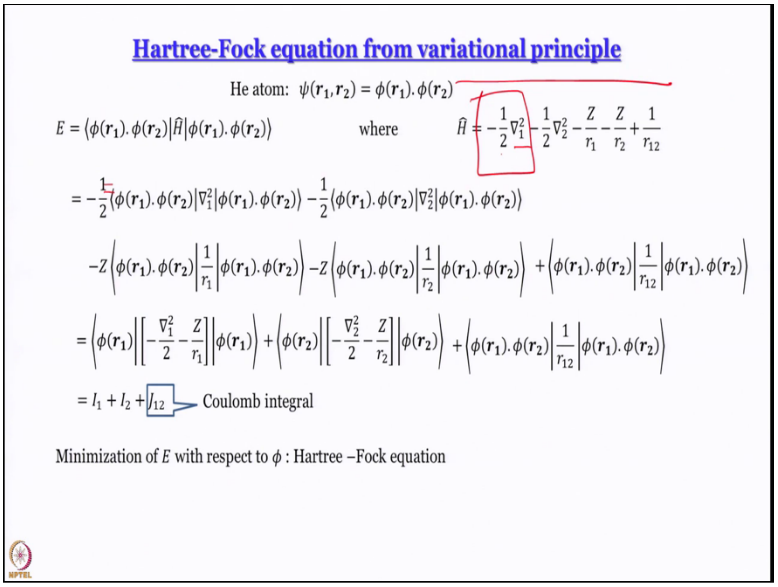

Hartree-Fock equation from variational principle

He atom: $\psi(r_1,r_2) = \phi(r_1).\phi(r_2)$

$E = \langle \phi(r_1).\phi(r_2)|\hat{H}|\phi(r_1).\phi(r_2)\rangle$ where $\hat{H} = \boxed{-\frac{1}{2}\nabla_1^2} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$

$$= -\frac{1}{2}\langle \phi(r_1).\phi(r_2)|\nabla_1^2|\phi(r_1).\phi(r_2)\rangle - \frac{1}{2}\langle \phi(r_1).\phi(r_2)|\nabla_2^2|\phi(r_1).\phi(r_2)\rangle$$

$$-Z\left\langle \phi(r_1).\phi(r_2)\left|\frac{1}{r_1}\right|\phi(r_1).\phi(r_2)\right\rangle - Z\left\langle \phi(r_1).\phi(r_2)\left|\frac{1}{r_2}\right|\phi(r_1).\phi(r_2)\right\rangle + \left\langle \phi(r_1).\phi(r_2)\left|\frac{1}{r_{12}}\right|\phi(r_1).\phi(r_2)\right\rangle$$

$$= \left\langle \phi(r_1)\left|\left[-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}\right]\right|\phi(r_1)\right\rangle + \left\langle \phi(r_2)\left|\left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}\right]\right|\phi(r_2)\right\rangle + \left\langle \phi(r_1).\phi(r_2)\left|\frac{1}{r_{12}}\right|\phi(r_1).\phi(r_2)\right\rangle$$

$= I_1 + I_2 + \boxed{J_{12}}$ Coulomb integral

Minimization of E with respect to ϕ : Hartree –Fock equation

So, now that is the equation that we wrote from sort of common sense you can arrive at the same equation we are not going to go all the way in this discussion but will still go through this because it introduces to us very important quantity. You could arrive at Hartree-Fock equation from variational principle also, how? You start with this trial wave function then you define energy what is energy expectation value integral phi r 1 star phi r 2 star left multiplying Hamiltonian operating on phi r 1 phi r 2 over all function space.

What is the Hamiltonian we know what the Hamiltonian is in atomic unit all right. So, let us just plug in this expression for Hamiltonian in the expression for energy and see what we get how many terms will we get 1 2 3 4 5 what is the first term integral phi r 1 phi r 2 left multiplying minus half del 1 square operating on phi r 1 phi r 2 what happens when this minus half del 1 square operates on the product of phi r 1 phi r 2 phi r phi of r 1 phi of r 2.

Phi of r 2 is not a function of r 1 right so as far as this del 1 square is concerned it is just a constant so it would come out. And del 1 star square minus half del 1 square would operate on phi r 1 to yield the kinetic energy which would would be a constant and it is important to understand that this what we have written in bracket notation is really a double integral yeah so just write it. So, this thing is I will write it then erase it also because otherwise it will overlap with something else.

This is really equal to integral I will write 2 integral signs 1 for r 1 one for r 2 phi of r 1 star phi of r2 star then we have the Hamiltonian operating on why did I put a bracket there phi of r 1 phi of r 2 d r 1 d r 2 right and this Hamiltonian that we have is entirely well we have something the first term in Hamiltonian is entirely in terms of 1. So, if I just take the first term I do not take all of h but I just take the first term then it is going to be something like this minus half del 1 square and you understand that del 1 square is going to operate on phi of r 1 but not on phi of r 2 right.

So this double integral conveniently becomes a product of 2 integrals integral of phi of r 1 star multiplied by minus half del 1 square operating on phi of r 1 d r 1 the first integral multiplied by the second integral is phi of r 2 star multiplied by phi of r 2 d r 2 all right and the good thing is that if this 1 is either normalized or we can normalize it so this is going to become 1. So, in the first term when we expand this when we expand this Hamiltonian and put in all these 5 terms I am actually going to get single integrals instead of double integrals because 1 of them is going to get normalized and therefore will be equal to 1 right.

So this is something that I wanted to bring your attention to in case somebody missed it if I skipped it and just went on. This one is not really written explicitly in the books that we are following by the way today we are following Macquarie’s book I will at the end of the discussion I will have a word to say about something that is there in your Pillars book but will not do it explicitly. So, I have reduced that equal to sign also forget it all right.

So this is what we have this is the first 1 I have not got rid of phi of r 2 yet. So, integral minus half minus half integral phi of r 1 multiplied by phi of r 2 del 1 square phi of r 1 phi of r 2 minus a similar term but this time in terms of electron number 2 and not electron number one the third term will be minus z so this 1 right. Again the same thing will happen once again is a double integral and we can make it a product of 2 integrals 1 in terms of 1 one in terms of 2 and the 1 in terms of 1 sorry the 1 in terms of 2 is going to become 1.

Similar thing here the only difference is that this time it is the turn of the integral in r 1 to become one so the triple product in electron number 2 terms is going to survive well is going to remain like that and what is the last one? In the last one we cannot separate like that no matter how much we like separating this 1 and 2 well I have not shown you the separation yet I will show you in a minute no matter how much you might have liked it we cannot do it here because here we have 1 by r 1 2 separation between electron number 1 and electron number 2.

There is nothing we can do about it so this has to contain terms in 1 as well as 2 it has to remain like that. So, the first one what we will do is we will collect the terms in 1 and here you see we have got rid of terms the factor of two because that integral has become equal to 1 by normalization. So, this integral becomes integral phi of in r 1 star left multiplying minus del 1 square by 2 minus z by r 1 operating on phi r 1, what is it? Do you recognize it? Do you recognize it? It is actually your it is a it is like expectation value of energy for a 1 electron system is not it yeah this is the kinetic energy term of Hamiltonian is a potential energy term when the the only thing that is there is attraction of nucleus and electron.

So if the second electron is not there then this is going to be the actually the expression for the energy of electron number 1. Similarly the second term in electron number 2 is going to be the expression for energy of electron number 2 in absence of electron number one suppose its helium ion H plus then this will be the average value of energy. How did I get this remember there are 5 terms I have already written 4 of them condensed in these 2 terms.

There is a minus sign here there is a minus sign here so this is a combination of 2 terms potential kinetic energy potential energy of one this is also combination of 2 terms kinetic energy potential energy of 2 right. So, 4 terms are actually written after simplifying after converting the double integrals to a product of 2 integrals and finally only 1 integral last 1 remains intact. So, what we do is we call this first integral I 1 we had encountered this earlier also remember when we could not work out an integral or even when there was some hope of working out an integral later on we gave it a name and we worked with it remember s ij yeah or H 11 all those things we are not familiar with.

So similarly we will call this one I 1 will call this to I 2 collectively they belong to the family ii and this one will call j so I will get I 1 + I 2 + j 12 the subscript means which electron coordinates this integral has contributions from the last integral j 12 has is made up of coordinates of electron number 1 as well as electron number 2 so it is called j 12 and it has a name also the name is coulomb integral.

Now why coulomb integral just think what is it that you know about in which context you have heard the name of coulomb coulomb attraction remember coulomb attraction. So, the same thing right so electrostatics so coulomb integral essentially stands for an electrostatic interaction well repulsion between electron number 1 and electron number 2 not very difficult to see from here. So, later on we are going to encounter when we talk about bonding we will encounter coulomb integral once again.

Additionally we will encounter something called an exchange integral and as we will see it is not possible for us to have a classical mechanical analog of exchange integral coulomb integral we can sort of make sense of it by classical mechanics not so for exchange integral which will come when we introduce 1 more nucleus right. Now we do not have to worry about it so the way you get Hartree-Fock equation from here is that you minimize E with respect to phi and that leads you to the Hartree-Fock equation that we have discussed earlier.

So that in a nutshell is Hartree-Fock equation for you will be able to solve it. Do we need some trick to solve it will take that in the next module.