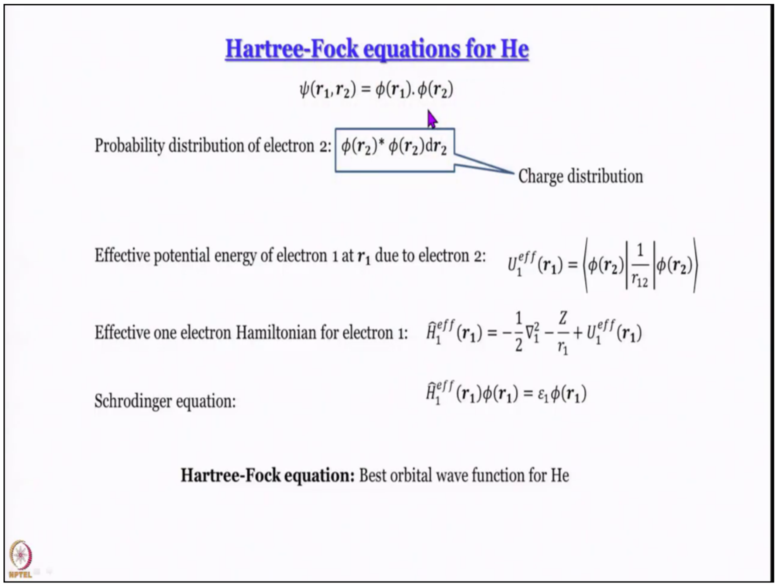
Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-53
Hartree-Fock Equations for He Part2

Today we conclude our discussion of many electron atoms and this is really a storytelling session because we are not really going to work out much I just tell you how things are done and we will let it be at that I have actually been contemplating whether we should be next not in the next semester but maybe in the semester after that have another course on advanced topics in quantum chemistry. If we float that then maybe we are going to talk a little more about Hartree-Fock calculations.

But today let us just finish up our discussion by showing you something and just by stating how the calculations are eventually done.

(Refer Slide Time: 01:09)



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: $U_1^{eff}(r_1) = \left\langle \phi(r_2) \middle| \frac{1}{r_{12}} \middle| \phi(r_2) \right\rangle$

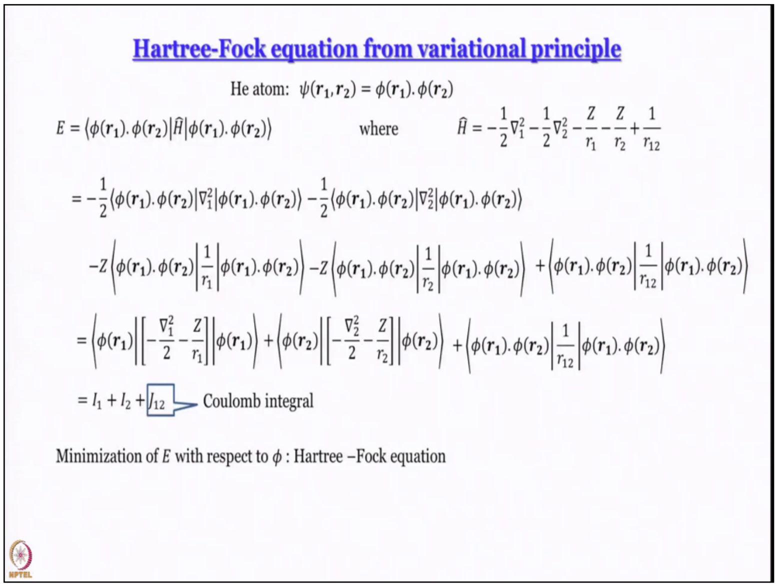
Effective one electron Hamiltonian for electron 1: $\hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1)$

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

You might remember that we have constructed the Hartree-Fock equations for helium atom using orbital approximation to start with. We have worked out we have said that this probability distribution of electron denotes the charge distribution and so from there we calculated or we worked out the expression for effective potential energy of electron 1 due to electron number 2 and hence we wrote the Schrodinger equation which is called Hartree-Frock equation and this epsilon that we get later on we learn from Kooupans theorem that this is not really energy but its ionization energy.

(Refer Slide Time: 01:46)



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

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

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

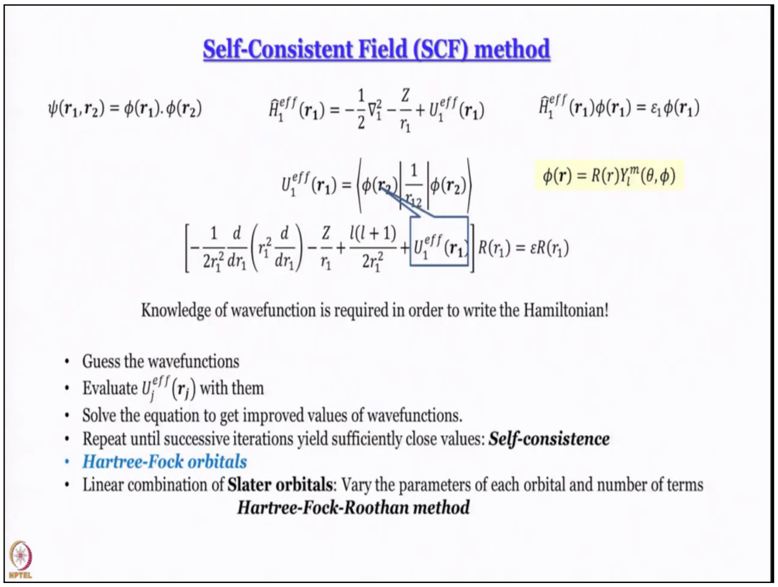
$$= \left\langle \phi(r_1) \middle| \left[-\frac{\nabla_1^2}{2} - \frac{Z}{r_1} \right] \middle| \phi(r_1) \right\rangle + \left\langle \phi(r_2) \middle| \left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2} \right] \middle| \phi(r_2) \right\rangle + \left\langle \phi(r_1).\phi(r_2) \middle| \frac{1}{r_{12}}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

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

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

So then we learnt how to do variational treatment of Hartree-Fock equation and while doing that we arrived at this very important integral called coulomb integral that we are going to use extensively when we discuss chemical bonding. Coulomb integral actually comes from many electron atoms itself. So, the idea is that if we minimize this expression for energy with respect to phi then we get Hartree-Fock equation and from there we are going to get the upper bound on the energy of the system.

(Refer Slide Time: 02:20)



Self-Consistent Field (SCF) method

$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi(\boldsymbol{r}_1).\phi(\boldsymbol{r}_2)$ $\hat{H}_1^{eff}(\boldsymbol{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(\boldsymbol{r}_1)$ $\hat{H}_1^{eff}(\boldsymbol{r}_1)\phi(\boldsymbol{r}_1) = \varepsilon_1\phi(\boldsymbol{r}_1)$

$U_1^{eff}(\boldsymbol{r}_1) = \left\langle \phi(\boldsymbol{r}_2) \left| \frac{1}{r_{12}} \right| \phi(\boldsymbol{r}_2) \right\rangle$ $\phi(\boldsymbol{r}) = R(r)Y_l^m(\theta, \phi)$

$$\left[-\frac{1}{2r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{d}{dr_1}\right) - \frac{Z}{r_1} + \frac{l(l+1)}{2r_1^2} + \boxed{U_1^{eff}(\boldsymbol{r}_1)} \right] R(r_1) = \varepsilon R(r_1)$$

Knowledge of wavefunction is required in order to write the Hamiltonian!

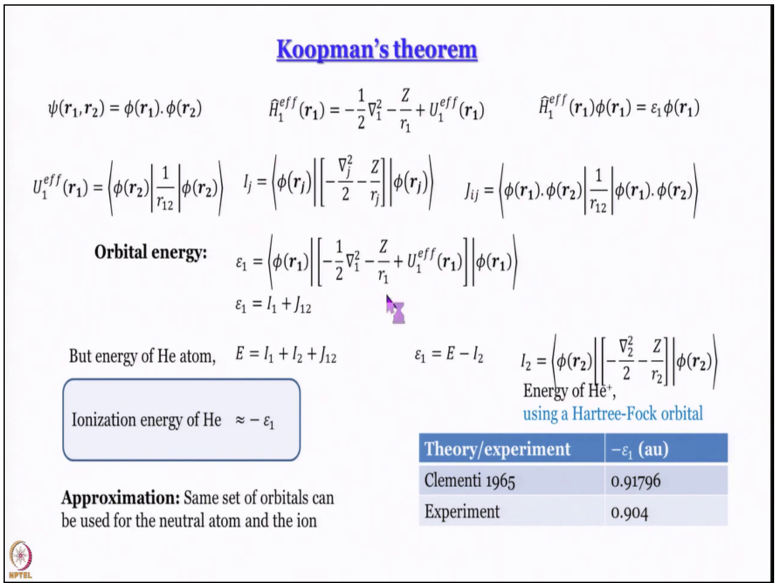
- Guess the wavefunctions
- Evaluate $U_j^{eff}(\boldsymbol{r}_j)$ with them
- Solve the equation to get improved values of wavefunctions.
- Repeat until successive iterations yield sufficiently close values: ***Self-consistence***
- ***Hartree-Fock orbitals***
- Linear combination of **Slater orbitals**: Vary the parameters of each orbital and number of terms
  Hartree-Fock-Roothan method

And how to go about doing this the problem is that it is not just any ordinary differential equation is a differential equation in which the operator consists of some term which contains these solutions. So, unless you know the solution you cannot set up the equation unless you set up the equation you cannot know the solutions it is a catch 22 situation. So, the self consistent field method helps us out of this strange problem what we do there is that we guess the wave function and today what we will do the only new thing that will do is we will show you like 1 kind of wave function that we actually can use.

So using this wave function we evaluate the effective potential solve the equation and then we solve the equation we do not get back the same wave function we get new set of wave functions which is slightly different from the initial guess value. So, keep on repeating until we get 2 successive calculations in which the values are close these are called self consistent results. And the orbitals we get at that time the self consistent orbitals they are called Hartree-Fock orbitals.

And generally what we do is we take linear combinations of Slater orbitals and we vary the parameters of each orbital and we also vary the number of terms to get what is to use what is called the Hartree-Frock Roothan method and today we will give you a very, very sketchy glimpse using helium for example or will also write it in terms of n electron atom how this is actually done.

(Refer Slide Time: 04:02)



Koopman's theorem

$\psi(r_1,r_2) = \phi(r_1).\phi(r_2)$ $\quad \hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1)$ $\quad \hat{H}_1^{eff}(r_1)\phi(r_1) = \varepsilon_1\phi(r_1)$

$U_1^{eff}(r_1) = \left\langle \phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_2) \right\rangle$ $\quad I_j = \left\langle \phi(r_j) \left| \left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j} \right] \right| \phi(r_j) \right\rangle$ $\quad J_{ij} = \left\langle \phi(r_1).\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1).\phi(r_2) \right\rangle$

Orbital energy: $\varepsilon_1 = \left\langle \phi(r_1) \left| \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1) \right] \right| \phi(r_1) \right\rangle$

$\varepsilon_1 = I_1 + J_{12}$

But energy of He atom, $E = I_1 + I_2 + J_{12}$ $\quad \varepsilon_1 = E - I_2$ $\quad I_2 = \left\langle \phi(r_2) \left| \left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2} \right] \right| \phi(r_2) \right\rangle$

Energy of He⁺,
using a Hartree-Fock orbital

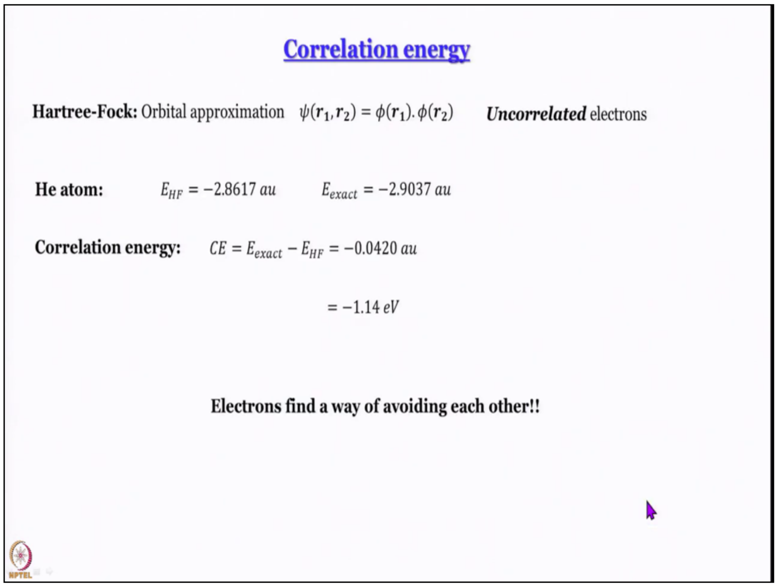
Ionization energy of He $\approx -\varepsilon_1$

Theory/experiment	$-\varepsilon_1$ (au)
Clementi 1965	0.91796
Experiment	0.904

Approximation: Same set of orbitals can be used for the neutral atom and the ion

Next we talked about Koopman's theorem which essentially tells us that this epsilon that we had got gives us an estimate of ionization energy and ionization energy calculated using Koopman's theorem is usually in good agreement with the experimental values.

(Refer Slide Time: 04:19)



Correlation energy

Hartree-Fock: Orbital approximation $\psi(r_1,r_2) = \phi(r_1).\phi(r_2)$ ***Uncorrelated*** electrons

He atom: $E_{HF} = -2.8617\ au$ $\quad E_{exact} = -2.9037\ au$

Correlation energy: $CE = E_{exact} - E_{HF} = -0.0420\ au$

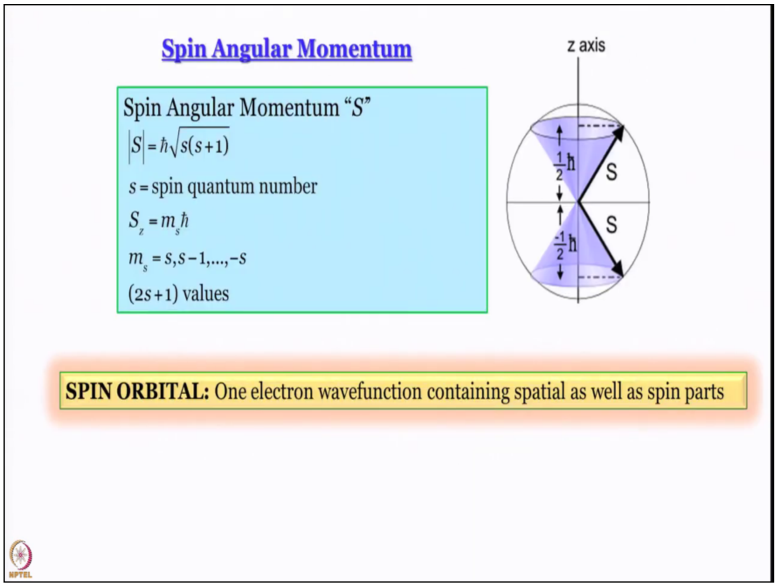
$= -1.14\ eV$

Electrons find a way of avoiding each other!!

And finally we had discuss this very interesting concept of correlation energy where we said that see we start with orbital approximation so we essentially behave as if the electrons move irrespective of each other I mean if they come close together they repel. What we learn is that it is not like that movement of electrons is actually correlated and they move in some devious way in which that can avoid each other to some extent and that is manifested in the correlation energy.

Correlation energy is the difference in energy is calculated by the SCF method Hartree-Fock method and some exact method that we had discussed earlier. The difference in energy there is equal to the amount of energy that can be attributed to correlation electron correlation that is a very, very important concept that has led to many important avenues later on.

(Refer Slide Time: 04:19)



Spin Angular Momentum

Spin Angular Momentum "S"

$|S| = \hbar\sqrt{s(s+1)}$

s = spin quantum number

$S_z = m_s\hbar$

$m_s = s, s-1, \ldots, -s$

$(2s+1)$ values

SPIN ORBITAL: One electron wavefunction containing spatial as well as spin parts

Now 1 thing in all this discussion that we did not consider but we have talked about it earlier is spin. Remember electrons are associated with this strange quantity called spin and spin is essentially associated with an angular momentum. The spin angular momentum is given by h cross multiplied by root over s into s + 1 where s is a spin quantum number which is characteristic of the particle. So, for electron spin quantum number is a half I said this earlier but since this misconception is ubiquitous I will say it again.

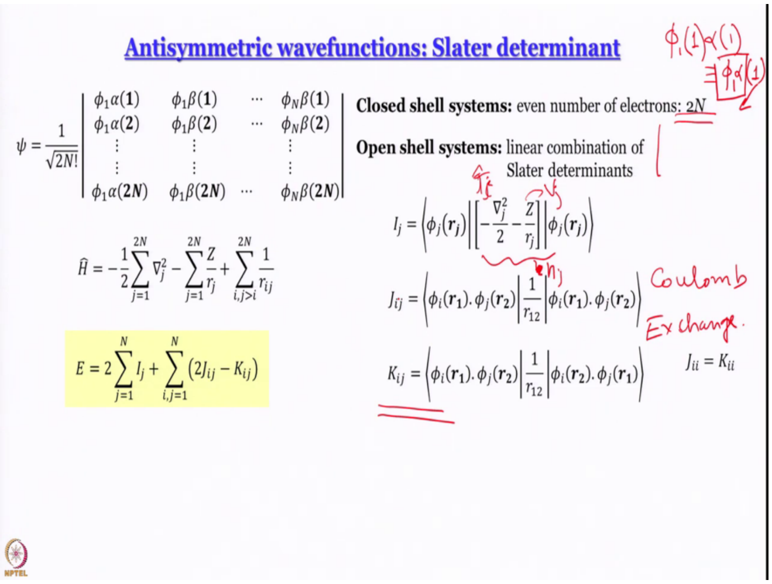
Please remember spin quantum number for electron is not plus half and minus half spin quantum number of electron is half and of course using atomic units we do not even have to write h cross we can just write spin angular momentum is square root of s into s + 1 in terms of h cross setting h cross to be 1. So, what is that plus half and minus half that we always talk about that is m s analogous to the magnetic quantum number that we got for electrons in hydrogen atom.

This m s tells you what is the z component of the angular momentum and as we have discussed I think earlier for m and m l and l knowing the value of m s you know this length this is basically h cross by 2 and what is the length of the arrow root over half into half plus 1. So, that is root 3 by 2 so if this is root 3 by 2 and this is half what is this angle root 3 by 2 divided by half so sorry what am I saying it is half divided by root 3 by 2 that is 1 by root 3 I believe we have encountered this angle already.

So please refresh your memories and tell me well how will you; tell me tell yourself that what the value of this angle is. So, this theta is actually defined for the particle. So, m s can take up 2 s plus 1 values for electrons it can be only 2 values plus half and minus half and then if you remember once again couple of weeks ago we talked about spin orbitals where spin orbitals are 1 electron wave function containing spatial as well as spin part.

So today the only new thing that we are going to learn is when we write this spin orbital how during energy calculation we separate out the contribution of spin and we will restrict our discussion to ground state.

(Refer Slide Time: 07:57)



Antisymmetric wavefunctions: Slater determinant

$\phi_1(1)\alpha(1)$

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

$$\psi = \frac{1}{\sqrt{2N!}}\begin{vmatrix} \phi_1\alpha(1) & \phi_1\beta(1) & \cdots & \phi_N\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) & \cdots & \phi_N\beta(2) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ \phi_1\alpha(2N) & \phi_1\beta(2N) & \cdots & \phi_N\beta(2N) \end{vmatrix}$$

Closed shell systems: even number of electrons: $\underline{\underline{2N}}$

Open shell systems: linear combination of Slater determinants

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

$$I_j = \left\langle \phi_j(\mathbf{r}_j) \middle| \underbrace{\left[\overset{\hat{T}_j}{-\frac{\nabla_j^2}{2}} \overset{V_j}{-\frac{Z}{r_j}} \right]}_{h_j} \middle| \phi_j(\mathbf{r}_j) \right\rangle$$

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

Coulomb

Exchange.

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

$J_{ii} = K_{ii}$

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

I will give you a pointer for excited state and this is something that we have learnt also that since the wave functions have to be asymmetric by Pauli principle remember if you do not remember please go back and see that lecture for fermions the wave function has to be estimate antisymmetric. So, a good way of writing the wave functions is Slater determinant. In Slator determinant when you go from left to the electron index remains the same the spin orbital changes when you go from top to bottom the spin orbital remains the same electron index changes.

So here I have written this letter determinant in a slightly different way compared to what we had written earlier. I have written it exactly in the way in which it is written in Macquarie’s quantum chemistry book and just to differentiate between this one and that one I have written the electron indices by bold letters bold numerals. So, what I mean by phi 1 alpha and 1 bold 1 inside bracket is that well in the earlier notation that we use I essentially mean electron number 1 is in phi 1 orbital and it has alpha spin.

So this is what I mean when I write phi 1 alpha 1 I have forgotten write this one there it is phi 1 alpha 1. So, I hope you understand what I am talking about this here is your spin orbital phi 1 is a special part alpha is the spin part and this one is the electron number roll number of electron. Now so this expression that I have written is strictly valid for closed shell systems. Close shell systems would always have even number of electrons and also all the orbitals that are there would be fully occupied.

If you have open shell systems then you can have unpaired electrons as well in that case how do you handle the situation we had left this question open as well when we discuss it last now I am telling you, you have to take linear combinations of Slator determinants to define the wave function there. So, you can use set of determinants to write wave functions for closed as well as open systems. Now what we do is we can use this slater determinants as the initial trial functions in our SCF method for Hartree-Fock calculations.

So when we do that of course we need to know what the Hamiltonian is this is the Hamiltonian for a 2 n electron system. I am writing 2 n because it is convenient otherwise I have to write n by 2 somewhere see if I use 2 n number of electrons I will need half the number of orbitals is not it I am talking about spatial orbitals they are not spin orbitals. Because each spatial orbital is associated with gives rise to each special orbital gives rise to 2 spin orbitals.

Because the phi 1 can be associated with alpha or beta so if I take n number of spatial orbitals I will end up getting 2 n number of spin orbitals and since I am talking about close shell systems we will have 2 n number of electrons so we just assign 1 electron to each spin orbital remember Poly principle essentially means that an electron that a spin orbital can only contain one electron that is why an orbital can contain at most 2 electrons because an orbital is associated with 2 spin orbitals.

So this Hamiltonian then is given by minus half del j square summed over j equal to 2 n for 2 n number of electrons second term is minus z by r j summed over j equal to 1 by 2 n I have written the third term in a little different manner compared to Macquarie's book they have written 2 summations I have written 1 I hope it is not a problem its basically 1 by r j so its electron-electron repulsion term and I and j well j has to be greater than i something like that.

So, this is our Hamiltonian using the Hamiltonian if you start; if you try to work out the expectation value of energy what will I get? So, I will get something like integral psi star h psi over all space. So, when we do that and when we simplify so this is why I was saying it is a storytelling session I am not working out anything today you do not need to work out either but just understand the flow of logic.

So E turns out to be integral j equal to 1 to capital N ij and what is ij this is ij, ij is this integral so you can see what we have done we have defined 3 integrals and we have defined it that way because they arise automatically when you write Schrodinger equation then left multiply by an orbital integrate over all space you will end up getting these integrals. So, the first integral contains the operator in kinetic energy and potential energy for a single electron.

So phi j of r j left multiplying essentially it is a kinetic energy term you can say t n operator remember t j operator so I can call this essentially the t j operator I miss that half, half should also actually go in this is t j operator and this is basically v j operator kinetic energy and potential energy so the whole thing I can perhaps write as now I will use the convention of your Pillars book they have written it very bad handwriting they have written it as small h j, h for Hamiltonian 1 electron Hamiltonian.

It is just that they have written a small you can read pillars book as well for this part because they have been able to simplify the notation a little bit and they have written it very nicely. So, you can write it like that. The second integral what is it? It is called j I j we have encountered it already coulomb integral remember phi i of r i phi j of r r 2 r 1 phi j of r 2 of course these 2 are complex conjugates of this called orbitals.

1 by r 1 2 the electron-electron separation and that operates on phi i r 1 dot phi j r 2 we have encountered this this is called the coulomb integral and it talks about the basically effect of 1 electron cloud on the other last we get another integral that we are encountering for the first time it is phi i of r 1 multiplied by phi j of r 2 so far so good 1 by r 1 2 then we get phi i of r 2 phi j of r 1 the labels have been interchanged there has been exchange so this is called an exchange integral I think I mentioned it briefly earlier now for coulomb integral you know that you can actually make physical sense out of it I just did that.

This is called exchange integral and this is a purely quantum mechanical quantity we will encounter it again when we talk about chemical bonding. There is no classical analog there is no classical sense that we can make out of the exchange integral. There are many text books in which they try to make sense by saying that the electron can does not have to be confined in its own orbital it can go there.

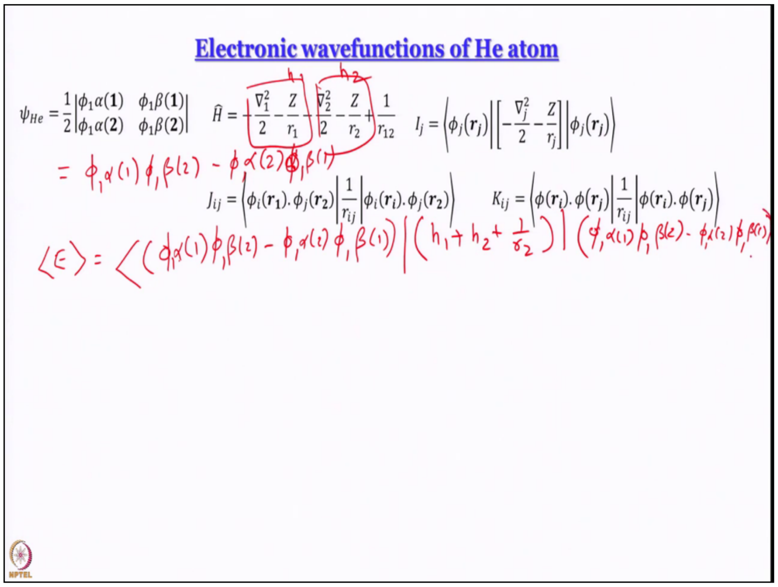
So it has more space I do not like doing that because the honest truth is that there is no classical analogue, so why should I unnecessarily make up a story and not to do that let us recognize that. Even though we have started from classical mechanics we have started from a classical mechanical equation that is Schrodinger equation for these de Broglie waves we have arrived at quantum mechanics whose scope is different.

We need quantum mechanics because in the quantum world behaviors are all different so why should we be daunted or surprised if we get quantities that have no classical analog. So, let us not give any hand waving argument. Let us be upfront in saying that this exchange integral is a purely quantum mechanical phenomenon no classical analog at all. So, I am not working this out because you understand that is going to be quite tedious.

In fact it is not worked out in these 2 text books that we are discussing either I think it is there in Sabo's book but let us not go there this is a long has been a long course we have learnt a lot of things let us not unnecessarily burden us with detail and just give you the final result the result is when you work this out you get an expression for energy in terms of this integrals equal to 2 sum over j equal to 1 to n i of j plus sum over ij equal to 1 to n 2 j ij minus k ij.

Now we have something interesting what do we have here we have spin orbitals what do we have here in this integrals we have spatial orbitals only no mention of spin. So, where did the spin part go? So what will do is that is that is one question will answer at least we will demonstrate using helium we are going to come back to this slide we are going to come back to this expression we are not done telling you what we actually do with this expression and again that is going to be only story telling in this course.

(Refer Slide Time: 18:00)



Electronic wavefunctions of He atom

$$\psi_{He} = \frac{1}{2}\begin{vmatrix} \phi_1\alpha(\mathbf{1}) & \phi_1\beta(\mathbf{1}) \\ \phi_1\alpha(\mathbf{2}) & \phi_1\beta(\mathbf{2}) \end{vmatrix} \quad \hat{H} = \boxed{\overset{h_1}{-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}}} \boxed{\overset{h_2}{-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}}} + \frac{1}{r_{12}} \quad I_j = \left\langle \phi_j(\mathbf{r}_j) \middle| \left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j}\right] \middle| \phi_j(\mathbf{r}_j) \right\rangle$$

$$= \phi_1\alpha(1)\phi_1\beta(2) - \phi_1\alpha(2)\phi_1\beta(1)$$

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

$$\langle E \rangle = \langle (\phi_1\alpha(1)\phi_1\beta(2) - \phi_1\alpha(2)\phi_1\beta(1)) \,|\, (h_1 + h_2 + \frac{1}{r_2}) \,|\, (\phi_1\alpha(1)\phi_1\beta(2) - \phi_1\alpha(2)\phi_1\beta(1))$$

But before that let me at least try to convince you that what I am saying is not all story it is reality if you are patient enough you will be able to work this out, it is just that we do not have time and will not do it here. So, let us go back to helium and write the expression for this helium wave function. Helium wave function is this Slator determinant phi 1 alpha of 1 phi 1 beta 1 phi 1 alpha containing 2 phi 1 beta containing 2.

Now this is a special case what is the special case what is i here for helium i is equal to 1 j also equal to 1 because in the ground state the only orbital that is involved is 1 s so see I am not writing 1 s because now by now we know that 1 s is not going to remain 1 s when we do a safe calculations we are going to get something that we arrive at starting from 1 s perhaps it will have similar features like 1 s but its not going to be exactly 1 s there will be some strange big expression for the orbital.

So what we do is to keep things general and to remember that these are actually Hartree- Fock orbitals not the orbiters that we got from hydrogen we will just write phi 1 phi 2 so on and so forth. So here the only special orbital involved is phi i phi 1 so i equal to 1 j is also equal to 1, i equal to j now this was written in the earlier slide but I just show you here think of what happens to j i j and k iI j if i is equal to j so all I have to do here is that instead of this j I will write Ii instead of this I will write i actually this is not r ij this is r 11 12 sorry sorry for the mistake here this is r 12.

If you write r ij then you got a problem that is why we write r 12 here so that we are no doubt that this is the separation between 2 electrons. So, here this 1 and 2 denote electrons I and z they denote the orbital numbers so phi i of r 1 phi I of r 2 phi i f r r 1 r 1 sorry sorry and this j becomes i once again what about here I this becomes I this is why did I write this is okay this is fine phi I mean lots of mistakes here this is r 1.

This is phi i sorry I forgot to make my corrections there but now I have done it so now do you see that when i is equal to j your j ii is going to be k ii because there is no question of exchange now you are using only 1 orbital. So, exchange essentially means that or electron of this orbital is there an electron that orbital is here that is the basis of that hand waving argument that we talked about a little while ago but now we cannot do that yeah so there is no question of exchange because it is only 1 orbital .

So, what will happen is that this k will not even feature we will get whatever expression we get in terms of j ii itself j 11 in this case. So, let us just try and expand this wave function this psi h E will be equal to um I will not even write this half for now; let me just write phi 1 alpha 1 phi 1 beta 2 minus phi 1 alpha 2 phi 1 beta 1 I am not about to do this calculation all the way I just show you a little bit. So, now see if you want to know what the value of say ij is we will get everything in terms of this anyway you just believe me on that.

But let us say I want to work out this I 1 in this case so I 1 will be integral phi 1 alpha 2 phi 1 beta i sorry sorry I made a mistake no phi 1 phi 1 alpha 1 phi 1 beta 2 is phi 1 alpha 1 let me just start instead of this phi I am going to write this expression or rather let me try to work with this I am I think I am confusing you by saying this let us not write that let us do this. So, I will just write the whole thing now phi 1 alpha 1 phi 1 beta 2 minus phi 1 alpha 2 phi 1 beta 1 this.

And in Hamiltonian what I can do is I can just write this as say h 1 plus h 2 this here is h 1 for electron number 1 one electron Hamiltonian this is h 2 one electron Hamiltonian for electron number 2. So, I can write h 1 + h 2 plus+ 1 by r 1 2 and now this is not i 1 sorry oh man okay sorry about that so I am writing an expression for wave function phi 1 alpha 1 phi 1 beta 2 minus phi 1 alpha 2 phi 1 beta 1 remember subscript 1 and then bracket 1 they are different.

Subscript 1 means orbital 1 in bracket means electron number. ,So, the energy is given by we also said that this is h 1 this is h 2 the 2 1 electron Hamiltonians 1 in terms of 1 electron 1 one in terms of electron 2 this gives us phi 1 alpha 1 phi 1 beta 2 minus phi 1 alpha 2 phi 1 beta 1 next I will write h 1 plus h 2 plus 1 by r 2 then I will write the expression for the wave function once again phi 1 alpha 1 phi 1 beta 2 minus I hope the space phi 1 alpha 2 phi 1 beta 1.

So this is our integral so I may not have time to complete this in this module. So, let me take a break now will come back and in a short module we will complete this discussion.