

Quantum Chemistry of Atoms and Molecules
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Lecture-52
Hartree - Fock Equations for He

We are in a very interesting juncture of discussing Hartree-Fock equations and how they are solved using self-consistent fields. We have learned what Hartree-Fock equations are we have written the Hartree-Fock equation for helium atom and while doing that we have invoked this effective potential energy of electron 1 at its position r_1 due to the presence of electron 2.

(Refer Slide Time: 00:51)

Hartree-Fock equations for He

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

Probability distribution of electron 2: $\phi(r_2)^* \phi(r_2) dr_2$ Charge distribution

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

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: $\hat{H}_1^{eff}(r_1) \phi(r_1) = \epsilon_1 \phi(r_1)$

Hartree-Fock equation: Best orbital wave function for He



And we have written it as integral phi of r_2 star multiplied by phi of r_2 divided by r_{12} well I should say dr_2 not theta, what does this mean it means that phi star phi that is essentially charge density what is the charge density that is given by phi star phi and the distance is r_{12} so that is the interaction between a charge cloud and a point charge that is the electro-electron repulsion. Electron number 1 is taken as a point at r_1 electron number 2 is taken as a cloud.

You get similar expressions if you think of say ionic atmosphere in solutions of electrolytes very similar kind of thing. And then using it we wrote this effective 1 electron Hamiltonian for electron number 1. The change that we see in this 1 electron Hamiltonian is the incorporation of

this effective potential energy due to electron-electron repulsion that we have discussed just now and with that we wrote down Schrodinger equation as usual we said this Schrodinger equation is called Hartree-Fock equation.

(Refer Slide Time: 02:04)

Hartree-Fock equation from variational principle

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

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

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

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

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

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

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

We also said that Hartree-Fock equation is obtained from variation principle by defining energy like this take the wave function as a product of 2 orbitals work out the expectation value of energy using the Hamiltonian for helium atom. So, we have not explicitly used that effective potential here eventually we will reach the same place but this is just what we know for a long, long time. Then we expand it and some of the double integrals become a single integral 1 remains a double integral that is called J_{12} the coulomb integral the other ones which essentially give your 1 electron energies for electron number 1 and electron number 2 they are called I_1 and I_2 .

So what does I_1 stand for if I write a general index I for 1 or 2 that would give me a energy of a 1 electron system and J_{12} is the electron-electron repulsion term that is what we have that is how far we got in the last class.

(Refer Slide Time: 03:12)

Self-Consistent Field (SCF) method

$$\psi(r_1, r_2) = \phi(r_1) \cdot \phi(r_2) \quad \hat{H}_1^{eff}(r_1) = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1) \quad \hat{H}_1^{eff}(r_1) \phi(r_1) = \epsilon_1 \phi(r_1)$$

$$U_1^{eff}(r_1) = \left(\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_2) \right) \quad \phi(r) = R(r) Y_l^m(\theta, \phi)$$

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

Differential equation. Waiting to be solved!!

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

- Guess the wavefunctions
 - Evaluate $U_j^{eff}(r_j)$ 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**



Now we learn how to invoke what is called self consistent fields and try to solve these equations this is the beginning of a very what should I say ubiquitous technique that keeps on coming back in the field of computational chemistry. But we will talk about that in a more appropriate time for now what we have is we have this orbital well product of orbitals that is a wave function that we have said. So, we are working under orbital approximation.

And so if I remember you the way Atkins puts it is very nice. Atkins says that the meaning of this is that each electron is in its own orbital. So, electron number 1 its coordinates are defined by its coordinates only electron number 2 well sorry what am I saying its wave function is defined by its own coordinates only phi is only a function of r 1 nothing to do with r 2, phi of r 2 is only a function of r 2 nothing to do with r 1.

So we are pretending as if the electrons move around in whatever way they move around that we cannot really talk about trajectories but their movement of course there is a repulsion and the wave function gets corrected and all that but then they move around as if the other 1 is not even there. When they come close together they repel each other when they go far away they repel each other to a lesser extent. But there is no correlation in the movements of the 2 electrons that is what orbital approximation essentially suggests.

Whether that model holds or not let us hope will get there by the end of this class and we have talked about the Hamiltonian already make this Hamiltonian operate on this wave function and we get this equation and the first question that will answer actually is what is ϵ_1 and this is the effective potential that we talked about earlier great. Now let us think a little bit about what the functional form of this r dependent wave function should be well not r dependent capital R remember is combination of r θ and ϕ .

So remembering what we had done for hydrogen atom wave functions we can write it as a product of an r dependent part and a θ ϕ dependent part capital R multiplied by y . So, capital R would lead to a quantum number n the only thing is that eventually n becomes a variational parameter and the θ ϕ dependent part is associated with the quantum numbers l and m . So, the moment I write it like this I have to do something to the Hamiltonian.

I should actually write the Hamiltonian in terms of spherical polar coordinates also and if you remember what we did in case of hydrogen atom we wrote we had showed you 13; well we rush through 13 slides which we did not discuss and that tells us how to generate the Hamiltonian in terms of r θ and ϕ and then we did separation of variables. So, when you do all that I am not going through the steps again they are quite mundane and you do not have to remember the steps you do not even have to remember the final answer.

But I hope you will not have problems in believe me if I write that the equation that we end up with for the r dependent part and we do not bother about the θ ϕ dependent part because we are discussing helium in case of helium ground state only $1s$ orbitals are involved they are θ ϕ independent so who cares about θ ϕ now. So, we get this equation in r dependent part the first term and the second term.

In the second term remember what this l into $l + 1$ is that is β . If you remember the separation of variables in case of hydrogen atom that we had performed this β turned out to be that l into $l + 1$. So, exactly similar treatment but for helium not for hydrogen this is what we have got. Then what have we got here this r of r^{-1} is a wave function in terms of one coordinate that is r^{-1} then we have something like energy ϵ_1 or ϵ_1 that we have written here.

Here I have forgotten write that subscript 1 and we are an operator that operator essentially what is the operator? Some differential ddr kind of thing is there so it is a differential equation so this is a time when we should be really happy and say hey we got a differential equation we have solved so many or well at least we know the solutions of so many this can be solved as well look up a book it can be solved.

There is a problem, the problem is that in this differential equation in the operator part itself your contribution from the wave function and that sort of lands us in a little bit of a fix because how are we supposed to get the wave function by solving the equation. But then how do you solve the equation if the wave function is sitting in the form of the operator itself. So, this is sort of a egg and chicken problem which came first egg or chicken or is the egg inside the chicken or what?

So we got a problem we cannot really solve it as easily as we solve the differential equation for the hydrogen atom problem but we have come a long way from hydrogen atom problem already and we know many ways in which we can at least have an intelligent guess of wave functions. So, since we do not know what the wave function would be and that knowledge is required in order to write the Hamiltonian itself we can make an intelligent guess.

And we have already discussed at length how many different kinds of trial functions are used and these what we discussed are actually very classical kind of trial functions there are many more that came later. So, we make an intelligent guess of an appropriate wave function and then we evaluate this U effective with it that now becomes a number. Now you can solve this this particular differential equation for the trial wave function what do you get? Now you get a new set of wave functions will they be exactly the same as the trial wave function?

Not necessarily this is the beauty of this technique, so you guess some function. So, what you are doing essentially is that you kind of come up with a rough model of the potential energy with that solve this Schrodinger equation kind of thing and get what the wave function is that wave function will be for the system that you model using that rough potential energy and mostly that

wave function that you generate is going to be slightly different usually not very different but slightly different from the trial wave function.

So solve the equation and to get what I call improved values of wave functions with functions that are closer to reality. What you do then? Well do it again. Now using those wave functions newly generated wave functions plug them into the expression for the effective potential write the equation once again the Hamiltonian will change solve it the solution will also change a little bit most likely and you are going to go towards better and better and better match to the reality of wave function.

Remember building that elephant perhaps you start with a mouse the wave function that you choose and slowly as you add terms and all that mouse becomes fatter and fatter and fatter starts looking like a pig and then like a tapir or an anteater which has a small snout and finally it looks something that is close to the elephant may be a little thin elephant since you started from a mouse. So, that is the idea, so when there is not much of change in successive iteration then you have what is called self consistent field.

The field that you have generated is now self consistent and that is as good as you can get using the wave functions that you have chosen to work with. So, the orbitals that you thus generate are called Hartree-Fock orbitals and usually the guess functions that you use are linear combinations of stator orbitals remember construction drawing of elephant problem. There is no restriction on how many functions we want to use, how many coefficients we want to use we just play around with them until we get a suitable match.

So you see you may not end up getting a proper basis set to start with. Suppose you start with 1 Slater orbital and you might get what looks like convergence but that may be far away from reality. So you want to increase the number of terms. So, it is not just iteration with one trial function you want to play around with trial functions as well that is what makes it a numerical computational problem.

Analytically if you want to do it by hand it will take ages and you will get frustrated and not do it that is why you want computers to do it for you and that is what leads to this very sophisticated software like that is written and is now available some for a charge some in free domain in which with which you can do this computational chemistry calculations and their choice of basis is of utmost important importance not all bases work equally well for all problems.

So here at our level for now we talk about linear combinations of Slater orbitals as the initial guess and then we keep on using this self consistent field method until we get convergence this is called the Hartree-Fock Roothon method which we might mention in the next class I am actually in 2 minds because we are running out of time we want to talk about molecules not much time is left but we have to finish what is started let us see.

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Koopman's theorem

$$\psi(r_1, r_2) = \phi(r_1) \cdot \phi(r_2) \quad \hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1) \quad \hat{H}_1^{eff}(r_1)\phi(r_1) = \epsilon_1\phi(r_1)$$

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

Orbital energy: $\epsilon_1 = \left\langle \phi(r_1) \left| \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(r_1) \right] \phi(r_1) \right\rangle = \left\langle \phi(r_1) \left| \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \right] \phi(r_1) \right\rangle + \left\langle \phi(r_1) \left| U_1^{eff}(r_1) \right| \phi(r_1) \right\rangle$

$\epsilon_1 = I_1 + J_{12}$

But energy of He atom, $E = I_1 + I_2 + J_{12}$ $\epsilon_1 = E - I_2$ $I_2 = \left\langle \phi(r_2) \left| \left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2} \right] \phi(r_2) \right\rangle$

Energy of He⁺,
using a Hartree-Fock orbital

Theory/experiment	$-\epsilon_1$ (au)
Clementi 1965	0.91796
Experiment	0.904

Ionization energy of He $\approx -\epsilon_1$

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

That being established we want to now focus on this chap epsilon 1. Epsilon 1 looks like energy and we get it by as an eigen function of an equation that looks like Schrodinger equation, 1 electron Schrodinger equation is it energy? Is it energy of the atom? Is it energy of the orbital or is it something else what is it? To know that well it is called orbital energy its expectation value is called the orbital energy and this is how you define it.

Of course now how do you evaluate this again you can expand it so this will be integral phi of r 1 star multiplying minus half del 1 square operating on phi of r 1 plus integral phi of r 1

multiplying this U_1 effective r_1 and so on and so forth. So, what you get is sorry I forgot to say that in the first integral you include this minus z by r_1 as well since I forgot I will write. So, this becomes $\int \phi^*(r_1) U_1 \phi(r_1) dr_1$ please do not forget that when you write a wave function in the bra vector your writing is complex conjugate.

Write this minus half Δ^2 minus z/r_1 so this is Hamiltonian that you get for 1 electron system pretending as if there is no other electron that operates on $\phi(r_1)$ that is my first integral. The second integral is $\int \phi^*(r_1) U_1 \phi(r_1) dr_1$ there is no need to write that bracket $\phi^*(r_1)$ something like that. So, essentially you get $J_{11} + J_{12}$ I hope it is not very difficult for you to see that this U_1 effective actually contains this $\phi^*(r_2)$ by r_2 you might be wondering the way I have written it here in my bad handwriting how am I equating this to J_{12} .

That is because you have to plug this in there as well U_1 effective of r_1 so all this will go in there that is how you will get it great. Now this is the energy of the helium atom actually it is it not because if you remember what we discussed earlier energy of helium atom turned out to be $I_1 + I_2 + J_{12}$. Remember that variational treatment that we did before this, that is what we get. So, it is not the same as ϵ_1 . So, ϵ_1 is not really the energy of helium atom what is it subtract 1 from the other ϵ_1 turns out to be $E - I_2$.

Or I can write E equal to $\epsilon_1 + I_2$ something like that whatever way you want to write what is I_2 ? Remember I_2 is the expectation value of energy for helium? No expectation value of a 1 electron system with the same atomic number as helium what would that be? Helium has 2 electrons so if I remove 1 of those electrons I get a 1 electron system with the same atomic number as helium what is that? It is helium plus iron.

So this I_2 essentially is the energy of helium plus same way you can define I_1 also so but there is a catch here. It is energy of helium plus but using a Hartree-Fock orbital not using your hydrogen atom orbital using a Hartree-Fock orbital that we have discussed so if we just plug that value what does it turn out to be. So, ionization energy this minus ϵ_1 turns out to be the ionization energy of helium what is ionization energy?

Energy of He plus minus energy of your helium atom. So, essentially it is going to be minus of hand side so minus epsilon 1. So, we see that this epsilon 1 that we got well the negative of that gives us a good measure of the ionization energy of helium and that is the celebrated Koopman's theorem do not forget that the approximation that we use here is that the same set of orbitals can be used for neutral atom and the ion which may or may not be correct or necessary.

But then when you do a calculation this is from Clementi's work of 1965. The value of ionization energy that we get is 0.919796 atomic unit and from experiment it is 0.904 atomic unit so not very bad actually. So, Koopman's theorem is something that forms a cornerstone in discussion of quantum mechanics of many electron systems.

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[Correlation energy](#)

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

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

Correlation energy: $CE = E_{exact} - E_{HF} = -0.0420 \text{ au}$
 $= -1.14 \text{ eV}$

Electrons find a way of avoiding each other!!



We end the discussion today with another very, very interesting perhaps intriguing concept and that is of correlation energy. Remember we had touched upon this a little while ago we said that the moment we use orbital approximation we essentially are saying that the electrons are uncorrelated the motion is uncorrelated. Their expressions might get modified a little bit of course they repel each other but they move in the same way as they were moving when the other 1 was not present.

So all this Hartree-Fock calculation that we do is for uncorrelated electrons so the energy that we get doing the calculation is minus 2.8617 atomic unit. When we do a more exact calculation when I say exact calculation of course you cannot solve it like that but when you go back to what we had discussed a couple of classes ago that perturbation theory using 13th order perturbation or that variation method using a large number of terms like 1000 something terms.

Remember then the value that we had reported or not reported the value that we had seen at that time was minus 2.9037 atomic unit so this is as good as it gets. So, using Hartree-Fock method the energy that we get is more than that minus 2.8617 atomic unit but then see it is more not because we have not tried to account for these repulsions at all, we actually work very hard we have tried to modify the wave function. We are try to play around with the field we have done SCF calculation.

So the only thing that we have not done is that we have not considered the correlation between electrons. We are not considered that motion of 1 electron can affect the motion of the other what does it mean you know sometimes celebrities do not like each other. So, in a party if the moment 1 celebrity enters another celebrity leaves by the other door that is correlation. 2 electrons behave like that in an atom.

So otherwise they would move in whatever way but now if they happen to come close together if they see that they are going to come close together maybe they avoid each other that would be correlation. And what we are saying is that this difference in energy what is the difference in energy? Correlation energy turns out to be minus 0.0420 atomic unit you think that is a small number, it is not. It is like 1.14 when -1.14 electron volt significant for the systems that we are talking about.

So what we learnt from here is very interesting electrons are the celebrities of atomic world they find a way of avoiding each other when they are in the same atom and the energy that they save by avoiding each other is about 1.14 electron volt get what I am saying if you do not account for correlation then the value that I get is -2.8617 when we account for correlation unknowingly

when we do those exact calculations we are not really explicitly saying that electrons are correlated.

All we are doing is that we are trying to minimize the energy and your upper limit theorem tells us that you can get as close to the actual energy as possible. And actual energy would involve correlation even though we cannot calculate it. So, the difference gives us the correlation energy so electrons 2 these 2 electrons of helium end up saving 1.14 electron volt energy for the atom by moving in an intelligent manner and avoiding each other.

I strongly suggest that you also read this we have followed Macquarie's approach but please also read this from Pillars book their notation is a little different so you have to go back and read a little more and in fact they have used something that we thought we will discuss but then for the want of time we are not getting into. They use something called viral theorem. Using viral theorem they have reached the same conclusion they view some very nice language which are now forgotten.

But it essentially says electrons in that atom find a way of avoiding each other smart particles that is the in my opinion most interesting thing that we have learned in our discussion today.