Quantum Chemistry of Atoms and Molecules
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Lecture-49
Perturbation theory for many electron atoms

We are back to many election atoms at last but then the detour that we took was long perhaps meandering but fruitful because it has taught us 2 most important approximation techniques of quantum mechanics variation method and perturbation method. So, today what we will do is since we have talked about many electron atoms perhaps maybe 2 weeks ago or something we will just do a quick recap of what we have done.

Since we have done many perturbation theory calculations we are going to present the perturbation theory for helium but will not work out every step but we will just show you the results and hopefully that will convince you that perturbation theory is a good way to go for systems like helium. In the next module we are going to talk about variation method and perhaps will also mention certain things that we cannot avoid mentioning anymore we should do it now.

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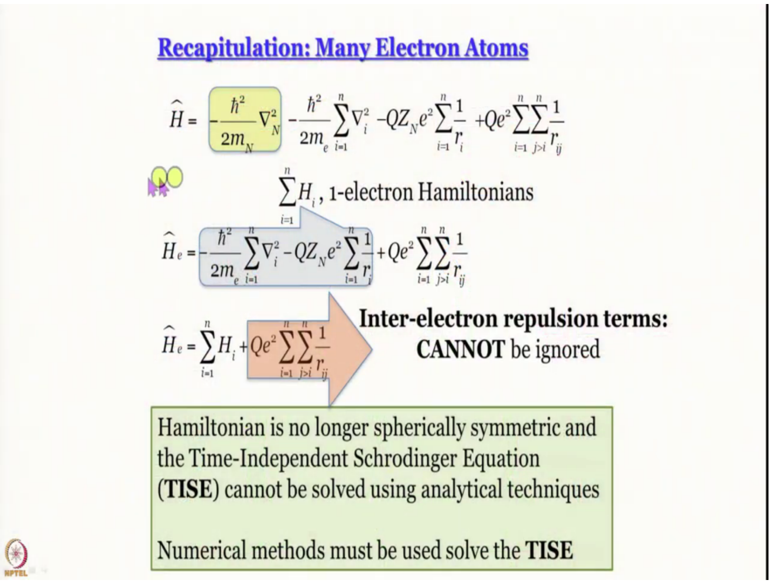

Recapitulation: Many Electron Atoms

$$\hat{H} = \boxed{-\frac{\hbar^2}{2m_N}\nabla_N^2} - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$\sum_{i=1}^{n} H_i$, 1-electron Hamiltonians

$$\hat{H}_e = \boxed{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i}} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$$\hat{H}_e = \sum_{i=1}^{n} H_i + \boxed{Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}}$$

Inter-electron repulsion terms:
CANNOT be ignored

Hamiltonian is no longer spherically symmetric and the Time-Independent Schrodinger Equation (**TISE**) cannot be solved using analytical techniques

Numerical methods must be used solve the **TISE**

But before that I hope we have not forgotten that for many electron atoms this is how we wrote the Hamiltonian in a concise form the Hamiltonian of many electron atom is essentially a sum of

N number of 1 electron Hamiltonians + a sum of 1 num of N number of not N number a sum of this N c 2 essentially number of electron-electron repulsions we are taking pair wise repulsions here. So, there are N number of electrons so each will repel the other so number of combinations of those electrons that we could take 2 in the combinations of 2 that we could take is Nc 2.

So basically that number of terms will be there for this electron-electron potential electron-electron repulsion and what we have learnt well 2 weeks ago is that this electron-electron repulsion cannot be ignored. Remember to start with we had tried to wish it away and learnt very soon that you cannot do that.

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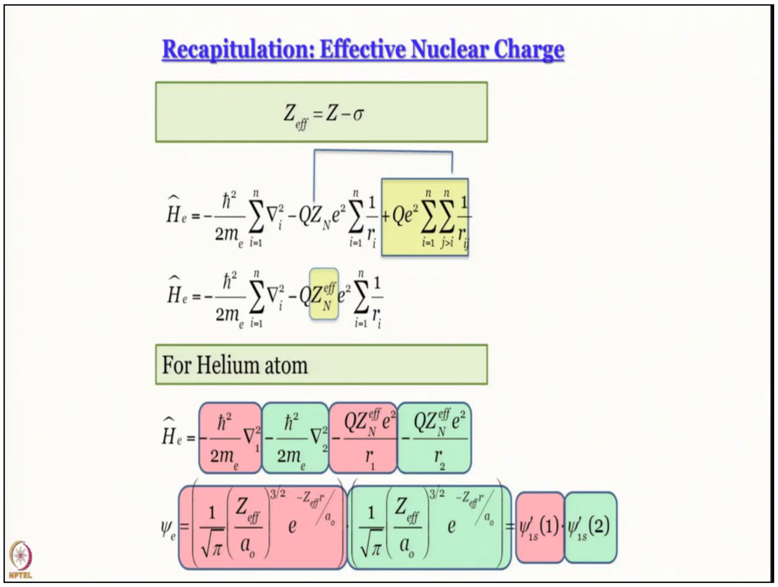

Recapitulation: Effective Nuclear Charge

$$Z_{eff} = Z - \sigma$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_N e^2 \sum_{i=1}^{n}\frac{1}{r_i} + \boxed{Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}}$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - Q\boxed{Z_N^{eff}}e^2 \sum_{i=1}^{n}\frac{1}{r_i}$$

For Helium atom

$$\hat{H}_e = \boxed{-\frac{\hbar^2}{2m_e}\nabla_1^2}\boxed{-\frac{\hbar^2}{2m_e}\nabla_2^2}\boxed{-\frac{QZ_N^{eff}e^2}{r_1}}\boxed{-\frac{QZ_N^{eff}e^2}{r_2}}$$

$$\psi_e = \boxed{\left(\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right)}\cdot\boxed{\left(\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right)} = \boxed{\psi'_{1s}(1)}\cdot\boxed{\psi'_{1s}(2)}$$

So, then what we said was let us build this electron-electron repulsion term into the nuclear charge itself. Let us talk about something called effective nuclear charge which is the actual nuclear charge well theoretical nuclear charge - a shielding constant. Because the effect of electrons repelling each other you can think is like 1 electron shielding the other 1 from the attractive potential of the nucleus.

So we said that instead of having three kinds well 2 kinds of terms here we might as well build this electronic electron repulsion into this z and then things become little easier to handle because this becomes Hamiltonian and the wave function also has to be changed and that becomes a wave function that involves not z but z effective.

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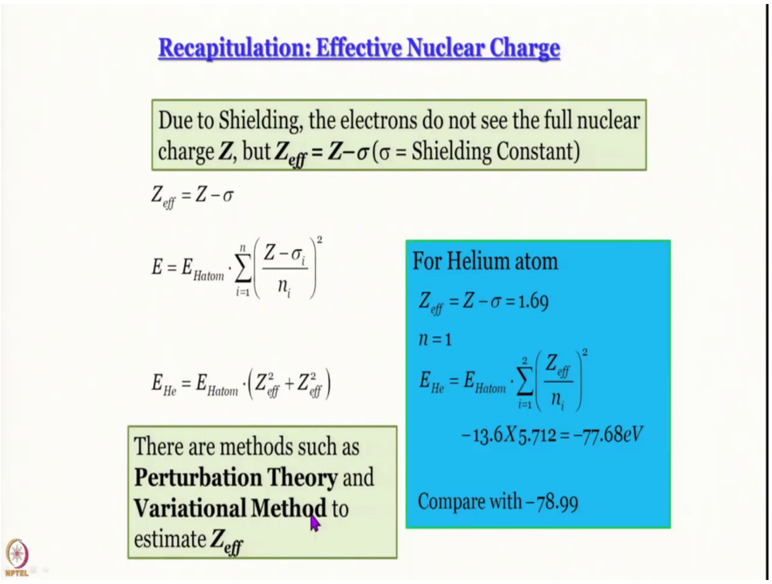

Recapitulation: Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge **Z**, but $Z_{eff} = Z-\sigma$ (σ = Shielding Constant)

$$Z_{eff} = Z - \sigma$$

$$E = E_{Hatom}\cdot\sum_{i=1}^{n}\left(\frac{Z-\sigma_i}{n_i}\right)^2$$

$$E_{He} = E_{Hatom}\cdot\left(Z_{eff}^2 + Z_{eff}^2\right)$$

There are methods such as **Perturbation Theory** and **Variational Method** to estimate Z_{eff}

For Helium atom

$$Z_{eff} = Z - \sigma = 1.69$$

$$n = 1$$

$$E_{He} = E_{Hatom}\cdot\sum_{i=1}^{2}\left(\frac{Z_{eff}}{n_i}\right)^2$$

$$-13.6X5.712 = -77.68eV$$

Compare with −78.99

With that we had shown you a calculation in which the shielding constant incorporating shielding constant we get the value of ionization potential or value of the energy of the potential of the of helium atom which is more or less close to the actual experimental value. So, that is what we had got and then at that time we had said there are methods like perturbation theory and variation method that help us estimate z effective.

So that time we had made a tricep destiny and now we must redeem our pledge you must see how perturbation theory and variation method can help us formulate the problem of any electron-electron many electron atoms in a suitable manner.

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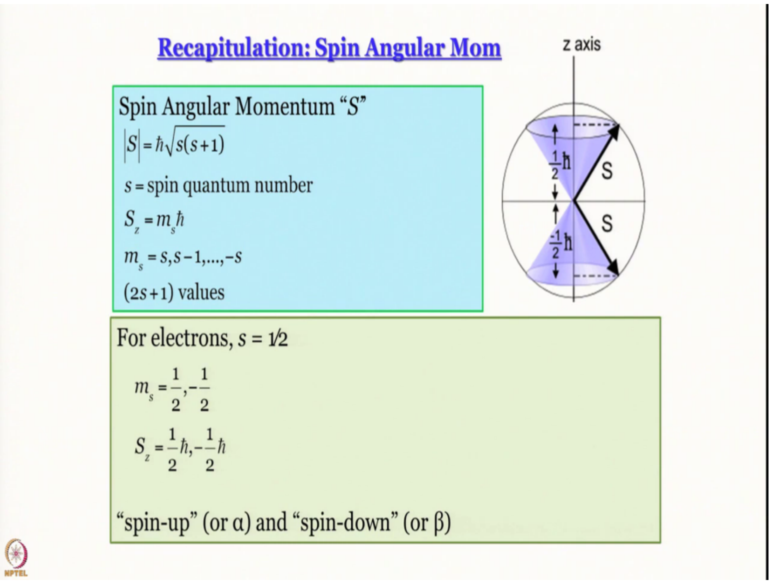

Recapitulation: Spin Angular Mom

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

For electrons, $s = 1/2$

$m_s = \frac{1}{2}, -\frac{1}{2}$

$S_z = \frac{1}{2}\hbar, -\frac{1}{2}\hbar$

"spin-up" (or α) and "spin-down" (or β)

And the other thing that we had discussed remember is spin angular momentum this I do not know why again I forgot to move this a little bit anyway we talked about spin angular momentum and the reason why I bring it up once again even though you are familiar with this term is that please do not forget that spin quantum number of electron is half m S is plus half and minus half, so spin angular momentum S is given by h cross into square root of S into S + 1 where S is the spin quantum number.

And z component of the triangular momentum is given by your S z which is m S multiplied by h cross when you say plus half minus half we are talking about m S and not about S.

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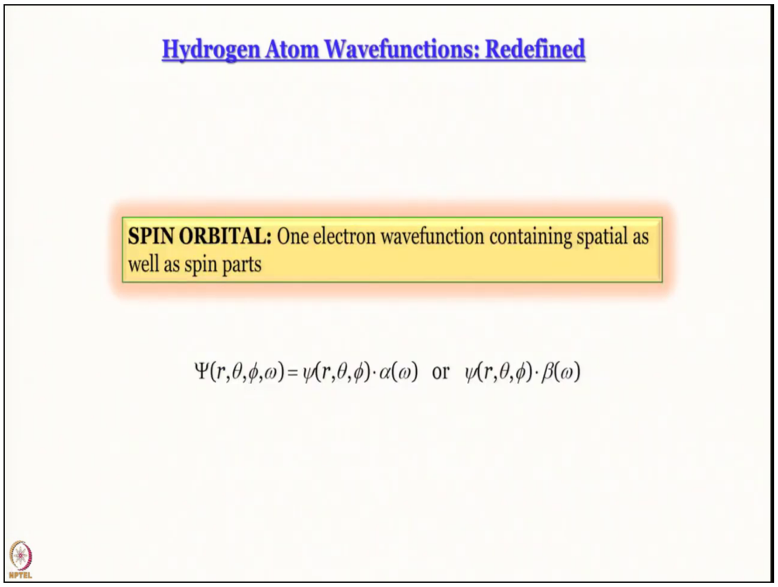

Hydrogen Atom Wavefunctions: Redefined

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

$$\Psi(r,\theta,\phi,\omega) = \psi(r,\theta,\phi)\cdot\alpha(\omega) \quad \text{or} \quad \psi(r,\theta,\phi)\cdot\beta(\omega)$$

And then we know that we have to talk about spin orbitals. We have to take this special part of the wave functions the orbitals and multiply them the by spin part whenever we talk about many electron systems because here spin is going to play a vital role.

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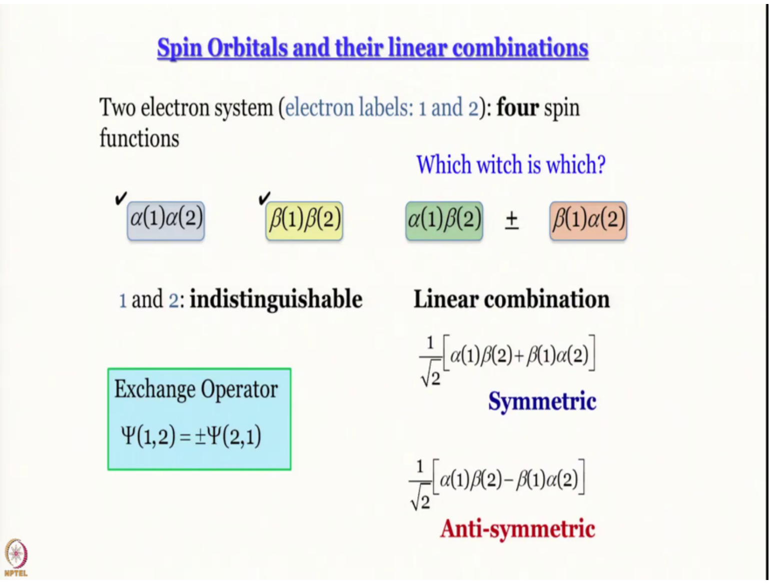

Spin Orbitals and their linear combinations

Two electron system (electron labels: 1 and 2): **four** spin functions

Which witch is which?

✓ $\alpha(1)\alpha(2)$ ✓ $\beta(1)\beta(2)$ $\alpha(1)\beta(2)$ ± $\beta(1)\alpha(2)$

1 and 2: **indistinguishable**

Linear combination

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

Symmetric

Exchange Operator

$\Psi(1,2)=\pm\Psi(2,1)$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

Anti-symmetric

And how it plays a vital role was manifested when we try to think what how many different spin orbitals we can write for simple 2 electron system you can write alpha 1 alpha 2 beta 1 beta 2 both the electrons have offspring both the electrons have downswing no problem you can even see it experimentally but we cannot write alpha 1 beta 2 or beta 1 alpha 2 because you do not know whether it is 1 or 2 that has alpha spin you do not know whether it is 2 or 1 that has beta spin so you must take linear combinations.

And linear combinations can be taken in 2 ways symmetric with respect to exchange and anti-symmetric with respect to exchange symmetric or anti-symmetric with respect to the exchange operator. So, we see that we can when we talk about spin orbitals we can have symmetric and anti symmetric spin orbitals with respect to exchange.

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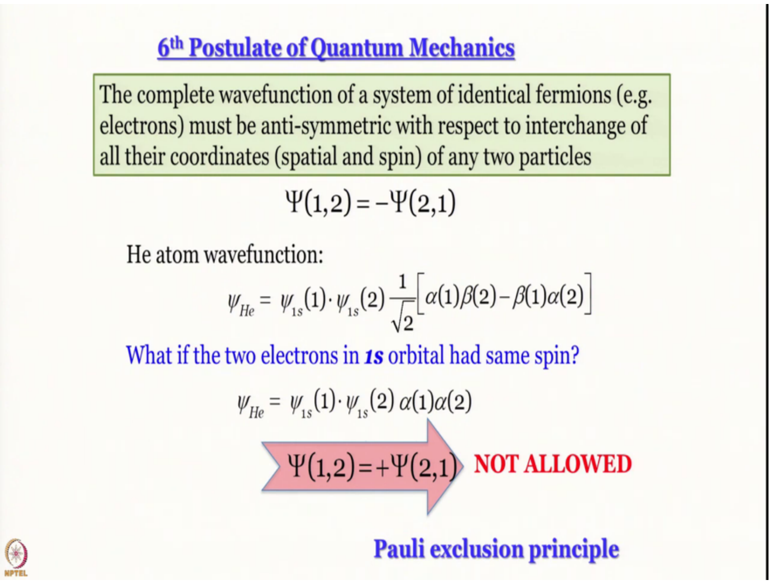

6th Postulate of Quantum Mechanics

The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles

$$\Psi(1,2) = -\Psi(2,1)$$

He atom wavefunction:

$$\psi_{He} = \psi_{1s}(1)\cdot\psi_{1s}(2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

What if the two electrons in *1s* orbital had same spin?

$$\psi_{He} = \psi_{1s}(1)\cdot\psi_{1s}(2)\,\alpha(1)\alpha(2)$$

$\Psi(1,2) = +\Psi(2,1)$ **NOT ALLOWED**

Pauli exclusion principle

And that takes us to the sixth postulate of quantum mechanics which says that for identical fermions like electrons the total wave function must be anti symmetric with respect to interchange of all the coordinates and that essentially as we learned led to poly exclusion principle.

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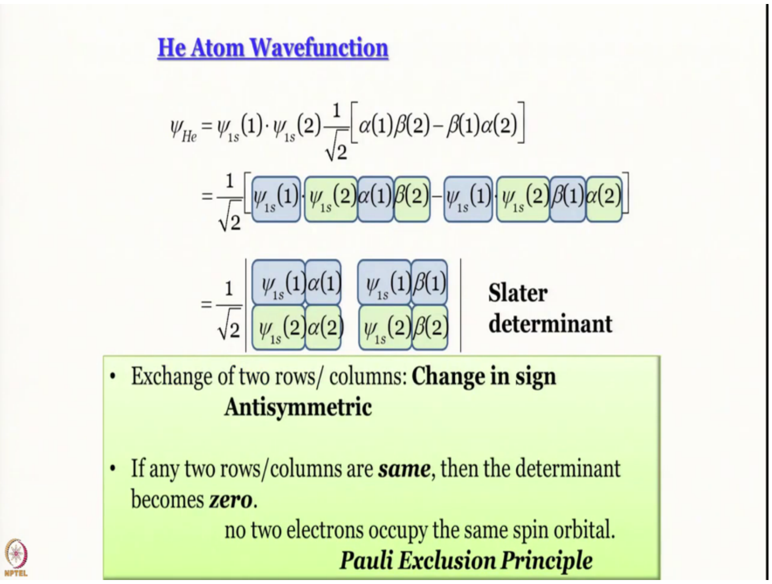

He Atom Wavefunction

$$\psi_{He} = \psi_{1s}(1)\cdot\psi_{1s}(2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

$$= \frac{1}{\sqrt{2}}\left[\boxed{\psi_{1s}(1)}\cdot\boxed{\psi_{1s}(2)}\boxed{\alpha(1)}\boxed{\beta(2)} - \boxed{\psi_{1s}(1)}\cdot\boxed{\psi_{1s}(2)}\boxed{\beta(1)}\boxed{\alpha(2)}\right]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \boxed{\psi_{1s}(1)}\boxed{\alpha(1)} & \boxed{\psi_{1s}(1)}\boxed{\beta(1)} \\ \boxed{\psi_{1s}(2)}\boxed{\alpha(2)} & \boxed{\psi_{1s}(2)}\boxed{\beta(2)} \end{vmatrix}$$

Slater determinant

- Exchange of two rows/ columns: **Change in sign**
  Antisymmetric
- If any two rows/columns are ***same***, then the determinant becomes ***zero***.
  no two electrons occupy the same spin orbital.
  Pauli Exclusion Principle

Which said that the ms value must be different and incorporating that we learnt how to write this many electron atom wave function very conveniently in the form of Slater determinant. The good thing about Slater determinant is that we just exchange the 2 rows or columns there is a change in sign which implies that it is anti symmetric and also if any 2 rows and columns are same then the determinant is 0 which ensures that no 2 electrons can occupy the same spin orbital it is as simple as that.

So this is the point where we stopped talking about many electron atom and started talking about your approximation methods.

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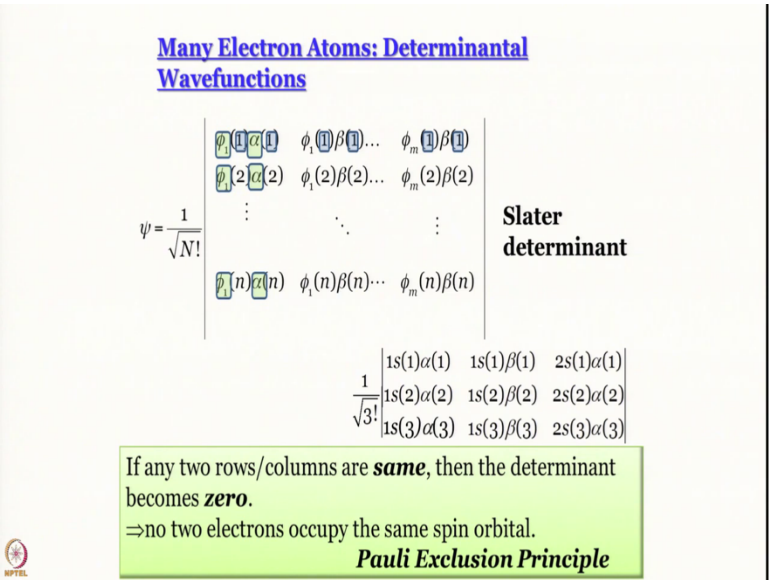

Many Electron Atoms: Determinantal Wavefunctions

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

Slater determinant

$$\frac{1}{\sqrt{3!}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

If any two rows/columns are ***same***, then the determinant becomes ***zero***.
⇒no two electrons occupy the same spin orbital.
Pauli Exclusion Principle

Well this is the point after showing the Slater determinant for an N electron atom we did not stop at 2 or 3.

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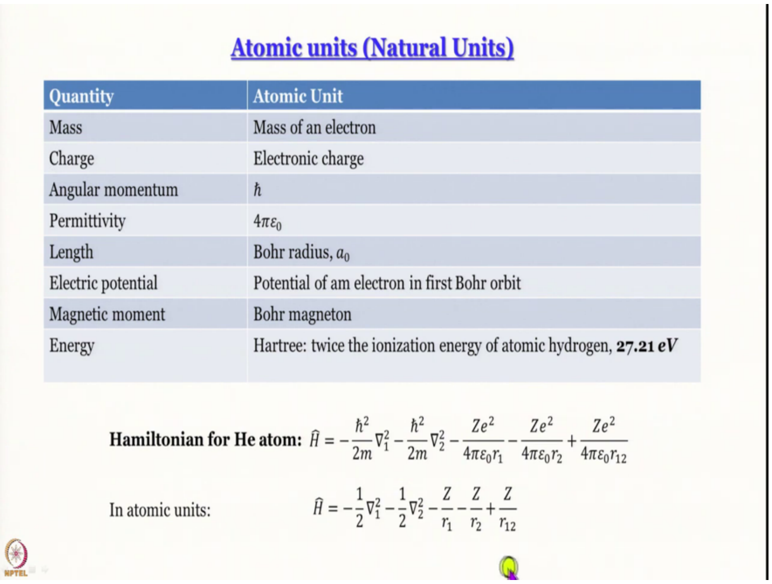

Atomic units (Natural Units)

Quantity	Atomic Unit
Mass	Mass of an electron
Charge	Electronic charge
Angular momentum	$\hbar$
Permittivity	$4\pi\varepsilon_0$
Length	Bohr radius, a_0
Electric potential	Potential of am electron in first Bohr orbit
Magnetic moment	Bohr magneton
Energy	Hartree: twice the ionization energy of atomic hydrogen, **27.21 *eV***

Hamiltonian for He atom: $\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{Ze^2}{4\pi\varepsilon_0 r_{12}}$

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

Now before going forward and presenting the; perturbation theoretical treatment of helium ground state let me just introduce atomic units which I am sure many of you must be familiar with. In the subsequent discussion most of the time we are going to use atomic units or natural units so that helps us a little bit because we do not have to write complicated expressions. Our expressions all become smaller.

But the danger of that is that you must not forget that there are lots of ones in there and you should not forget which one is one. What am I talking about here this is what I am talking about for mass the unit I use is not kg or gram or pound or anything I use the unit I use mass of an electron as unit right. What is the mass of an electron? I do not even remember very, very small quantity in gram so that much of gram I say is 1 unit of mass 1 atomic unit of mass.

So, wherever mass is there in any expression I will get one. So, expression will become simple but I must not forget that mass is actually there. This actually reminds me of this question that we often ask activity and activity coefficient. Activity has no unit activity coefficient has no unit but concentration is unit. So, what is the fallacy here? How can you have something with a unit multiplied by something that does not have any unit giving you something that does not have any unit.

Actually that also is a ratio this is essentially a ratio when I say when I use atomic units what I am doing essentially is that I am dividing the mass of any object that I am handling by the mass of an electron and representing it in units of electronic mass. Similarly charge is represented as units of electronic charge. Charge of an electron is said to be 1 in atomic unit. Angular momentum is written in terms of h cross most important we do not stop writing all those h crosses that we have been writing.

So if you ask what is the spin angular momentum we simply say root over S into S + 1 and similarly z component of angular momentum we similar simply say m S we do not even write that h cross because we are setting h cross to be 1 atomic unit. Permittivity we stop writing that annoying 4 pi epsilon 0 we said that to be 1 pi. Now length is represented in terms of Bohr radius I have not written the expression but we know what Bohr radius is.

Electric potential is written in terms of potential of an electron sorry for the typo and electron in first 4 orbit magnetic moment is in written in terms of Bohr magneton we are not really using it right now and energy very important is written in terms of hartree. So, hartree is twice the ionization energy of atomic hydrogen and if you remember the atomic the ionization energy of atomic hydrogen is 13.6 right actually 13.605.

So twice that is 27.21 electron volt so 1 hartree is 27.21 electron volt so that is a large number for atomic systems a significant number. So, when we talk about atomic union energy in atomic unit you see that we often go into many decimal places and you might wonder what is going on why are we writing 5, 6, 7 decimal places because when we convert that to electron volt we get a number that would perhaps differ in so many decimal places of atomic unit.

With that background and knowing the Hamiltonian for helium atom what is Hamiltonian for helium atom it is - h cross square by 2 m del 1 square - z d square by 4 pi epsilon 0 r 1 that is the Hamiltonian for electron number 1. For number 2 it is - h cross square by 2 m del square - z square by 4 pi epsilon 0 r 2 and what is this sore finger sticking out z square by 4 pi epsilon 0 r 1 2 that is your electron-electron repulsion term because of which we have had to study all these new things over the last couple of weeks.

So what I will do is I take this start from this Hamiltonian for helium atom and I will write it in atomic units what will happen? All the h cross square will become 1 all the m's will become 1 because here m is mass of an electron so the first term and the second term what will they become - del 1 square - del 2 square what will the third term become e is said to be 1 4 pi epsilon 0 1 so you are left with - z by r 1.

Similarly in the 4th term you are left with - z by r 2 but do not forget that if c square is there 4 pi epsilon 0 is there is just that we write in atomic units. So, we do not put those in but if you want to calculate actual energy we have to incorporate all those once again last term what does it become numerator becomes z denominator becomes r 12. So, this is your Hamiltonian for helium atom in atomic units.

Hamiltonian is half del 1 square - half del 2 square - z by r 1 - z by r 2 + z by r 12 remember atomic units.

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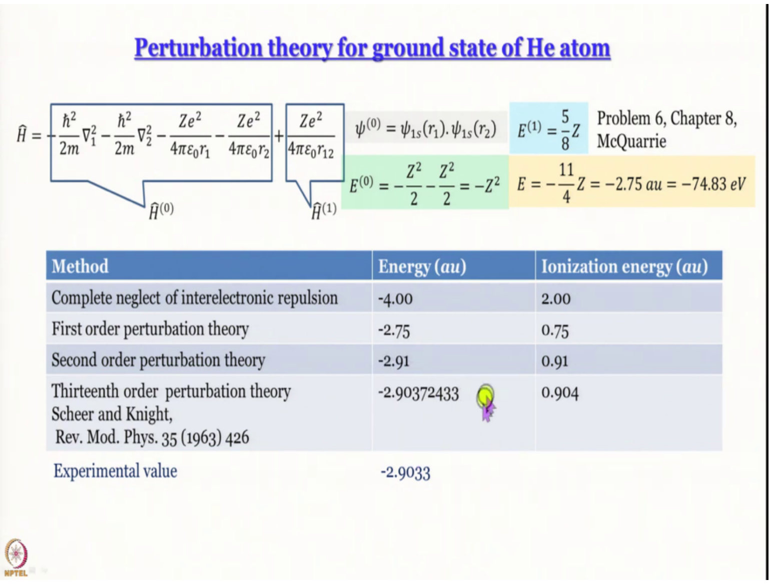

Perturbation theory for ground state of He atom

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{H}^{(0)}} + \underbrace{\frac{Ze^2}{4\pi\varepsilon_0 r_{12}}}_{\hat{H}^{(1)}}$$

$$\psi^{(0)} = \psi_{1s}(r_1).\psi_{1s}(r_2)$$

$$E^{(0)} = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2$$

$$E^{(1)} = \frac{5}{8}Z$$

Problem 6, Chapter 8, McQuarrie

$$E = -\frac{11}{4}Z = -2.75\ au = -74.83\ eV$$

Method	Energy (au)	Ionization energy (au)
Complete neglect of interelectronic repulsion	-4.00	2.00
First order perturbation theory	-2.75	0.75
Second order perturbation theory	-2.91	0.91
Thirteenth order perturbation theory Scheer and Knight, Rev. Mod. Phys. 35 (1963) 426	-2.90372433	0.904
Experimental value	-2.9033	

So, now I will start from this Hamiltonian and will try to develop a perturbation theoretical treatment for the ground state of helium atom. If you want to do perturbation theoretical treatment what is the first thing we need we need the 0th order or unperturbed Hamiltonian what would that be that would be the sum of the 1 electron Hamiltonian right I do not understand this why have I not written it in atomic units do not believe I read that after saying all that anyway let us go ahead.

So this here is the 0th order Hamiltonian and what is z square by four pi epsilon 0 r 1 2 or in atomic units z by r 1 2 that is the first order correction to Hamiltonian. What would the unperturbed wave function be? Unperturbed wave function would be the product of psi 1 S of r 1 and psi 1 S of r 2 that means see we are still using orbital approximation sort of right we are keeping the or the electrons in their own orbitals.

So electron number 1 is in 1 S orbital electron number 2 is in the other 2 S orbital other 1 is orbital these 2 are written in terms of r 1 and r 2 the 2 position vectors of the 2 electrons this is my 0th order wave function. What do I need to do I need to know also the 0th order energy what would that be this 1 is written in atomic units sorry for not writing the Hamiltonian atomic units here but I hope this is not very difficult for you to understand the 0th uncorrected energy will be simply the sums of the 2 unperturbed energies of the 2 electrons.

So - z square by 2, - z square by 2 in atomic units gives me - z square atomic units. I will just give you the result for the first order correction to energy and just believe me when I say it is 58z it is not really worked out in any of these books that we are consulting but pointers are provided on how to work this out in problem number 6 of chapter 8 of Macquarie's quantum chemistry book right.

If you work out that problem you will arrive at this expression for the first order correction to energy to be 5z by 8 what is total energy then total energy is - z square + 58 z thats that turns out to be – 11 by 4 z there is a minus sign here that I missed I am sorry. So, or I have to write E 0 - E first, so that turns out to be – 2.75 atomic units which is 74.83 electron volt is that good or is that bad? Actually it is not all that good. So, let me now show you another compendium of results.

Remember when we had completely neglected inter electron repulsion the energy that we got in atomic units was -4 here we at least we get -2.75. First order perturbation theory calculation gives us – 2.75 atomic units. If you increase if you do second order perturbation theory treatment then the energy we get is - 2.91 atomic unit. If you keep on going then I just show you the 13 order perturbation theory result this is by Sheer and knight published in 1963.

Here we get and now you see what I was talking about you have to go to a lot of decimal places if you want to work with atomic units you get – 2.90372433 what is the experimental value – 2.9033 so the difference between the experimental value and the calculation involving a 13th order perturbation is in the fourth decimal place. Not bad so using perturbation theory you can actually get pretty close to the experimentally observed value.

And see your variation the upper limit theorem applies here as well right we are not crossing it - 2.90372 whatever is still more than – 2.9033 so that is what we get by using perturbation theory for our helium atom ground state. Next what we want to do is we want to use variational method and see what we get and as we said we have to discuss some more topics before we can get there. But one thing that I want to say here is that this is actually the beginning and not the end.

Once we are done with this discussion of variation method we will embark upon what is called the hartree fock method using self consistent fields to achieve a better value of the energy and we will see what that means but what it will involve is where we had stopped the last module at. Remember we have said that we should use a wave function that is a linear combination of orthonormal eigen functions of the Hamiltonian.

Hamiltonian means Hamiltonian of the exactly solvable system if there is one and then we do not work with those functions as such but we build in some variation and parameter in the functions themselves not only coefficients. So, the coefficients are variational parameters functions themselves also contain variation parameter that gives us greater flexibility. So, it becomes again a numerical problem right and that would require algorithms that will require quantum chemistry.

And essentially what you want to do there is you would want to minimize the energy with respect to each of the parameters. If you remember a few modules ago I had very, very sketchily talked about this and we will talk about that once again later on. But Hartree Fock actually enables us to handle larger systems. You do not want to stop at helium and even for helium we need a 13th order perturbation theoretical calculation.

So what is going to happen for benzene right we want to talk about benzene right and nowadays people talk about much larger aromatic molecules bigger molecules so on and so forth. How do we handle those in fact I remember a very senior quantum chemist once told me that for him quantum mechanics begins after hartree fock. So, for us in this course let us at least go up to hartree fock and then later on when we talk maybe in some other more advanced quantum chemistry course we can learn about more contemporary methods.

Here will at least provide the state of the art a glimpse of state of the art later on. But we have made a good beginning today we have discussed what kind of results we get and what kind of improvement we get in the perturbation theoretical treatment of ground state of helium as we increase the order of perturbation. Coming up next is the variation method for helium atom.