Quantum Chemistry of Atoms and Molecules
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Lecture-50
Variational method for many electron atoms

Over the last few classes we have written a lot of mathematical expression done some algebra done some calculus and we have not done most of it have said that it can be done this problem in this book that problem in that book you can do it yourself, too tedious and we have not done it. Now we have not done it for a reason if you try to do it then it is impossible to stick to the limits of NPTEL and also it will be very boring to go through all that mathematics and then we will lose the sight of chemistry.

As I said many times what we really need to understand is the philosophy and the logic that goes into this mathematical detail and we do not really need so much we do but we do not have to work out everything at least for now. But today it is more or less a storytelling session well the story also involves a lot of mathematical expressions but we will just do some very, very simple algebra by and large I will just tell you what happens when something is done.

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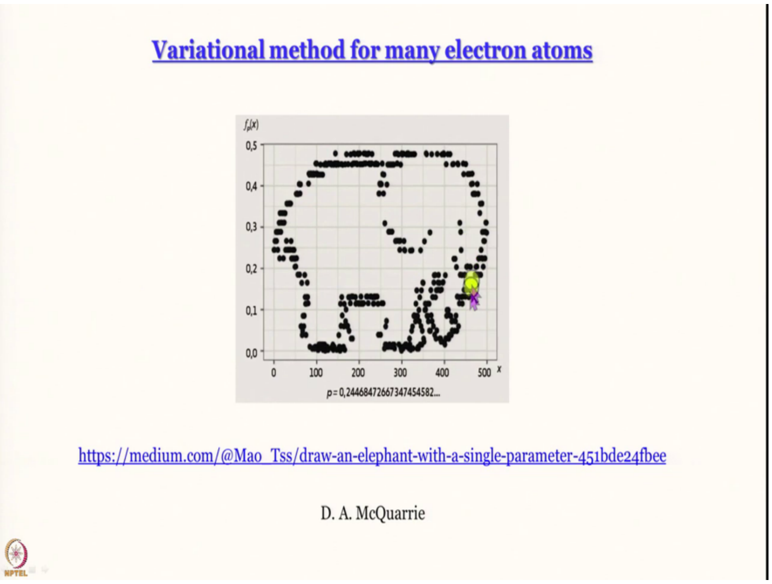

Variational method for many electron atoms

https://medium.com/@Mao_Tss/draw-an-elephant-with-a-single-parameter-451bde24fbee

D. A. McQuarrie

And to start with I show you a picture a picture of an elephant and you might be wondering what is going on here, do we have an elephant in the room? No actually look at this picture carefully it is really a plot is not, x axis is something independent variable y axis is a function of x and to know more about the functional form you can visit this website. But the point that we wanted to stress here is that by using proper combination of mathematical functions 1 can actually generate whatever shape 1 wants.

What you need is sufficient number of terms this if you go into this website you see this is the picture of an elephant generated using a single parameter what that is what is the detail that will not get into I was actually looking for this picture of an elephant that is drawn using 30 exp1ntial functions I did not find it on the net I found this. And the reason why we show this is that this is the way we are headed now.

Until now we have been talking about exact solutions approximate solutions worrying about analytical form and trying to make sense of it out of it. Slowly we are entering a regime where we cannot do that any longer it will all boil down to drawing the shape we require like an elephant using a suitable combination of functions. And while doing that the saving grace of course is variation theorem or upper limit theorem which tells you that you can never get an energy that is less than the actual energy.

So let us see how far we can get today. Last day we had talked about the perturbation theoretical treatment of atoms. Today we will talk about variational methods and we will need maybe 1 or 2 more lectures before we can complete our discussion of atoms.

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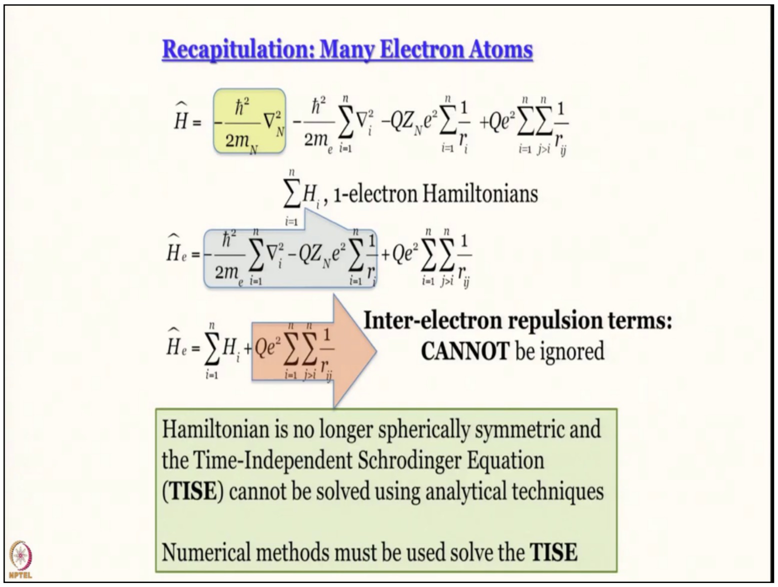

Recapitulation: Many Electron Atoms

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

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

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

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

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**

So, to recapitulate we now are sufficiently familiar with the Hamiltonian of many electron atoms we know that it is a sum of 1 N number of 1 electron Hamiltonians and there are these N c 2 combination of electron-electron repulsions these you cannot ignore you have to account for them somehow.

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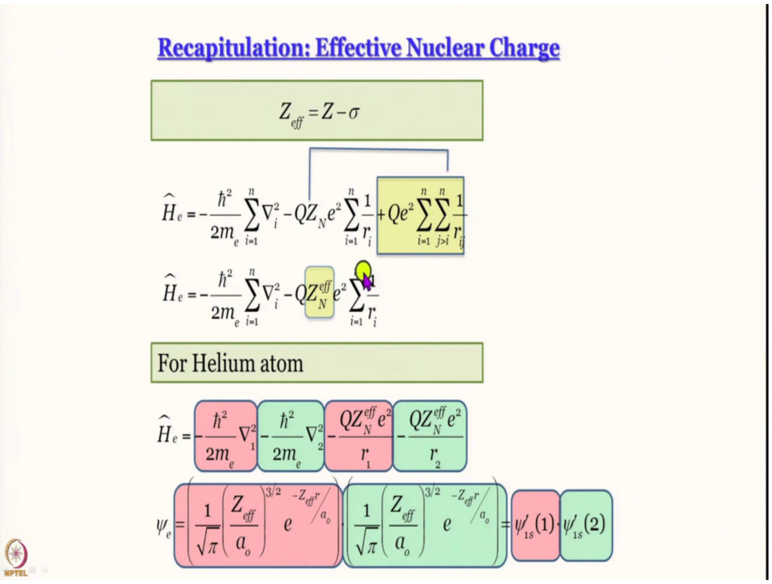

Recapitulation: Effective Nuclear Charge

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

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

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

For Helium atom

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

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

And the way we are accounting for this so far is considering something called your shielding constant and considering that the effective nuclear charge is what an electron sees an effective nuclear charge is the actual nuclear charge - the repulsion that an electron experiences from the other electrons and doing that what we have done is we have modified the wave function instead of z we will write z effective.

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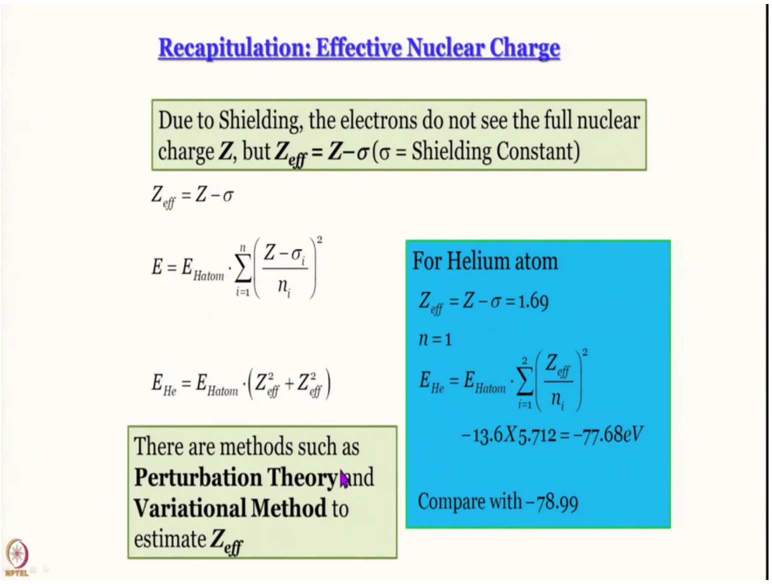

Recapitulation: Effective Nuclear Charge

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

And then we showed you some result remember this value - 78.99 this is the energy of your helium atom. So, we are trying to get close to this 78.99 electron volt that is where we want to get. In this simple shielding constant kind of calculation we are showing you -77.68 and today finally we will see how we can get to the shielding constant using variational method.

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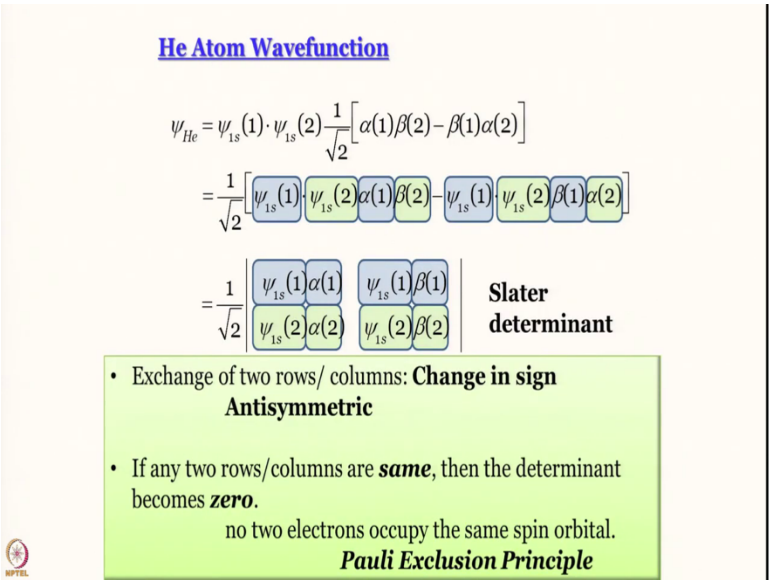

He Atom Wavefunction

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

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

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

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

And also this is something that will not use today but in the next class we are going to get back to the Slater determinant determinantal way of representing wave functions after today's lecture.

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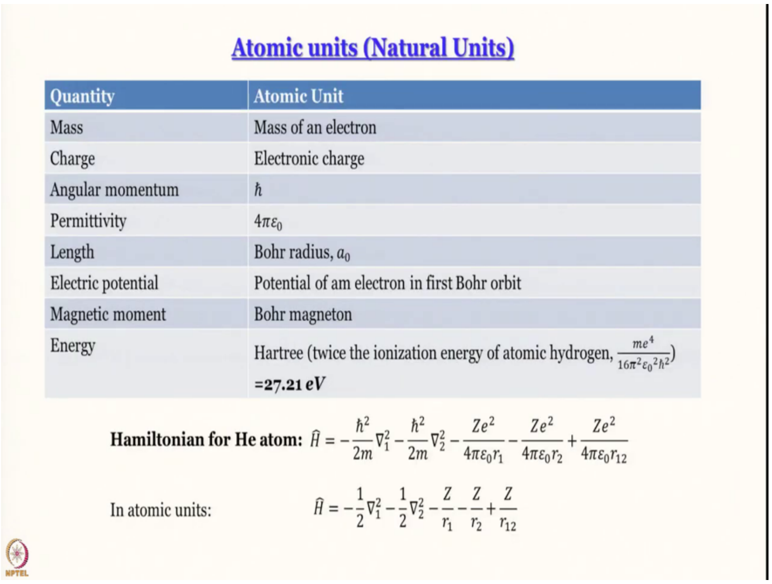

Atomic units (Natural Units)

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, $\frac{me^4}{16\pi^2\varepsilon_0{}^2\hbar^2}$) $=27.21\,eV$

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

And 1 thing that we talked about yesterday is that from now on to just make things a little simpler we are going to use atomic units where mass is the mass of an electron unit of mass is mass of an electron unit of charge is charge of an electron, unit of angular momentum is our good old h cross, unit of permittivity is 4 pi epsilon 0 electric potential has unit as potential of an electron in the first Bohr orbit and I have not corrected this m to n yet perils of copy paste.

And Bohr magneton is the unit of magnetic moment energy unit is hartree remember and 1 har tree again I am stressing this because it is very easy to lose sight of this 1 hartree is actually 27.21 electron volt substantial in atomic scales. So, when you use all this Hamiltonian for helium atom that we have written earlier boils down to something simpler in atomic units. But while doing this please do not forget that this m h cross square 4 pi epsilon 0 they are all there.

If you want it in if you want to write it in the expanded form you should not forget which goes where of course when we calculate energy then we do not have to worry because we have this conversion 27.21 electron volt is equal to 1 hartree all right.

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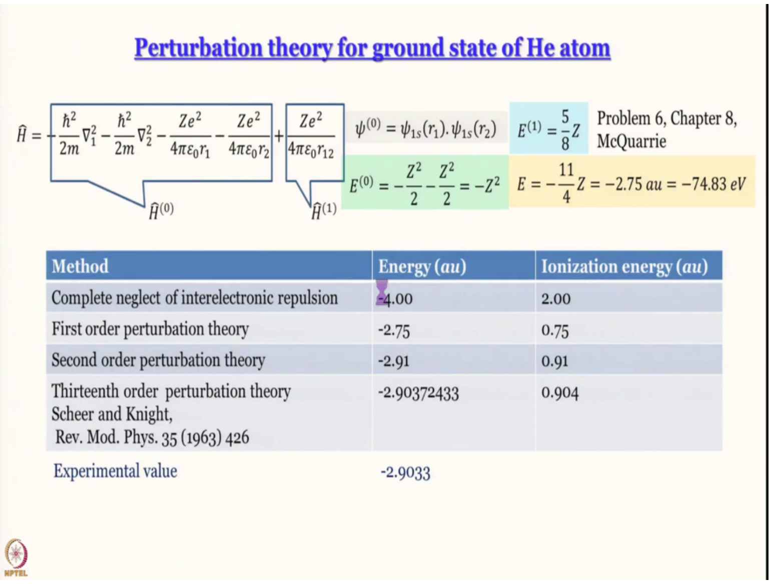

Perturbation theory for ground state of He atom

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

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

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

Problem 6, Chapter 8, McQuarrie

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

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

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	

And with that background I have kept this same as what we had written earlier from next slide onwards you will see that we have written it in atomic units. So, we discuss a perturbation theoretical treatment for ground state of helium atom where the sum of the 1 electron Hamiltonians is taken as the unperturbed Hamiltonian and the term involving electron-electron repulsion is taken as the first order correction to Hamiltonian.

The uncorrected wave function or 0th order wave function is taken as the product of the 2, 1s orbitals you talk about helium so 2, 1s orbitals so again we are working within the ambit of orbital approximation and then we said that first of all E 0th is z square by 2 - z square by 2 that is equal to - z square in hartree and we said that we just go through this problem 6 of chapter 8 of Macquarie quantum chemistry you will get to learn that the first order correction to energy is 5 8 of z in hartree.

So energy in hartree is -2.75 which translates to -74.83 electron volt remember what was the value experimentally -78.99 is not it 78.99 so that is where it is we are not really we are not really there yet and then we said that this is only first order correction you can work on second order correction higher order correction and thirteenth order correction more or less gets close to the value.

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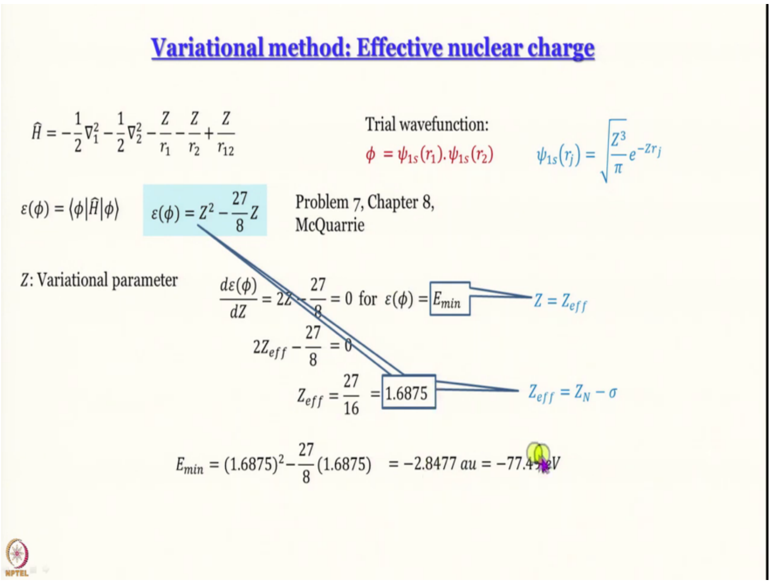

Variational method: Effective nuclear charge

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

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

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

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

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

$E_{min} = (1.6875)^2 - \frac{27}{8}(1.6875) = -2.8477\ au = -77.4$[illegible]$V$

Today now we are going to talk about variational method for treating this many electron atom problems. We are going to talk about helium atom and we are going to arrive at what we had talked about earlier this effective nuclear charge here I have written the Hamiltonian in atomic units half del 1 square - half del 2 square - z by r 1 - z by r 2 + z by r 1 2 of course half del 1 square - z by r 1 that is the Hamiltonian for electron number 1 half del 2 square - z by r 2 is the Hamiltonian for electron number 2 and this z by r 1 2 is a term for which we have to do so much of discussion the electron-electron repulsion term.

What is the trial wave function we start with the same trial wave function but of course we will play around with it as you will see. Same trial wave function we take 2 1s orbitals I hope you remember that 1 is orbital is of this form root over z cube by a by pi multiplied by e to the power - z r j this is the 1s orbital written in terms of the jth electron if you do not remember the coefficient it is but one thing you should know is that this 1s orbital is essentially an exponential decay in r all so this is my trial wave function I start from there.

Trial wave function again is the same wave function that we had in our orbital approximation 1 electron hydrogenic wave function orbital. Next thing to do in variation method as we know is to find out this functional epsilon of phi which is the similar expression as energy just instead of the exact wave function psi we are using the trial wave function phi. So, we will work with this function epsilon of phi integral of phi star h hat phi over all function space.

In this case over all values of r j and phi star is equal to phi in this case we are talking about 1s orbital. Now what is the variational parameter? What we will do is; well even before that now when we talked about time dependent perturbation theory we had referred to problem 6 now we refer to problem 7 of the same chapter. If you go through this if you work it out you will get this expression for epsilon of phi z square - 27 z by 8.

So then looking at this expression and also looking at the expression of psi if you think what is the handle that we have what is the parameter that we can play around it what can be our variational parameter can we play around with r j makes no sense r j in any case and we have to formulate the problem that way. So, the only thing that is left really is that nuclear charge and it makes sense to use z as a variational parameter because as we have discussed qualitatively already that this nuclear charge is not really the charge that is felt by an electron.

An electron feels an effective nuclear charge which is nuclear charge minus some shielding constant sigma and essentially we are trying to find out sigma. So, one way of finding out sigma is to keep changing the value of z vary the value of z and see for which value of z we get an minimum in the value of the functional epsilon we will call it E min as usual and that is going to set an upper limit to the energy of the system.

So, z will be the variational parameter also wherever we get the energy minimum that is going to be the effective nuclear charge. So, I am not really calculating sigma I am calculating effective nuclear charge and I will I can find sigma by subtracting the effective nuclear charge from the actual whole nuclear charge that is there in case of helium it is 2. We are talking about helium do not forget. So, z is my variation parameter this is the expression for the functional so what is the next thing to do I want to find the minimum of the epsilon of the function on epsilon.

So I have to take the first derivative with respect to z equal to 0. What is the first derivative 2 z - 27 by 8 first derivative of epsilon with respect to z is 2 z - 27 by 8 very easy and that is going to be equal to 0 for us to get the minimum value of the functional epsilon. As I said that would be the upper limit of the energy calculated for the system. And as we have also said correspondingly the z value for which the minimum is obtained that is going to be z effective.

So it is well formulated very easy algebra it is all right done what is the value of z? Here this z is z effective as we said we write z effective 2z - 27 by 8 equal to 0, so a class 5, class 6 students can work out that z effective in this case is 27.16. What is 27.16 its 1.6875 I hope I have got the division please work it out yourself in case it is wrong I do not think it is wrong it is fine. So, the point is it is less than 2 what is the actual nuclear charge? It is 2.

What we see is we have calculated a value of z effective which is less than the actual nuclear charge and from here we can calculate the value of sigma shielding constant to be 2 – 1.6875 that will come to how much 0.3125 is not it yeah 3125 0.3125 that is the value of sigma that we get from this very simple variational treatment of the helium atom ground state problem. So, we know how to find the energy minimum which is the upper limit of energy actually do not get confused because I am saying energy minimum and upper limit.

Energy minimum means minimum of epsilon the functional epsilon that sets the upper limit of the energy calculated by this method remember upper limit theorem. So, we have not only been able to find the energy that we are looking for we have also been able to determine the effective nuclear charge and there is a great. Now what will we do to find the value of this epsilon we take this effective nuclear charge and plug it in there not to find the value of epsilon sorry to find the value of E min.

So we know z defective we plug the value of z effective in the expression for epsilon to find E min let us do that mean turns out to be 1.6875 square - 27 by 8, 1.687575 that turns out to be – 2.8477 which translates as 77.49 electron volt, so, getting close but perhaps not close enough there is a problem close but not that close also.

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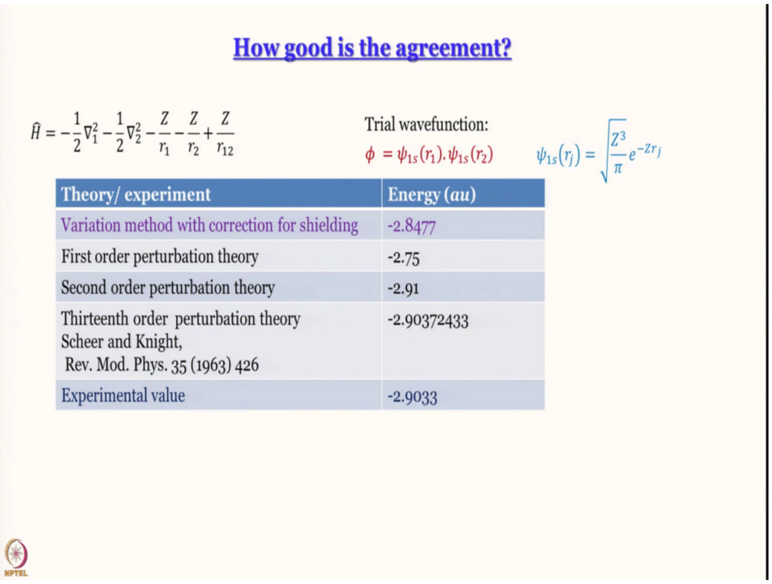

How good is the agreement?

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

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
Second order perturbation theory	-2.91
Thirteenth order perturbation theory Scheer and Knight, Rev. Mod. Phys. 35 (1963) 426	-2.90372433
Experimental value	-2.9033

So to understand the problem let us have a look and let us compare with what we get – 2.8477 this value is perhaps wrong but anyway first order perturbation theory gives me a value of – 2.75 second order perturbation theory gives me value of – 2.91, 13th order perturbation theory no its gives me a value of – 2.90372433 and so on and so forth. So, this is where we should get and so what we see is by the simple variation method that we have used here we are doing better than first order perturbation theory but not as good as second order perturbation theory and definitely not go as good as 13th order perturbation theory.

So this is definitely not the end of the road this is definitely not the end of the story and also to make a point that whatever we have discussed first order or variation method they are not all that great that comes out nicely if you look at another molecular atomic property and that is ionization energy.

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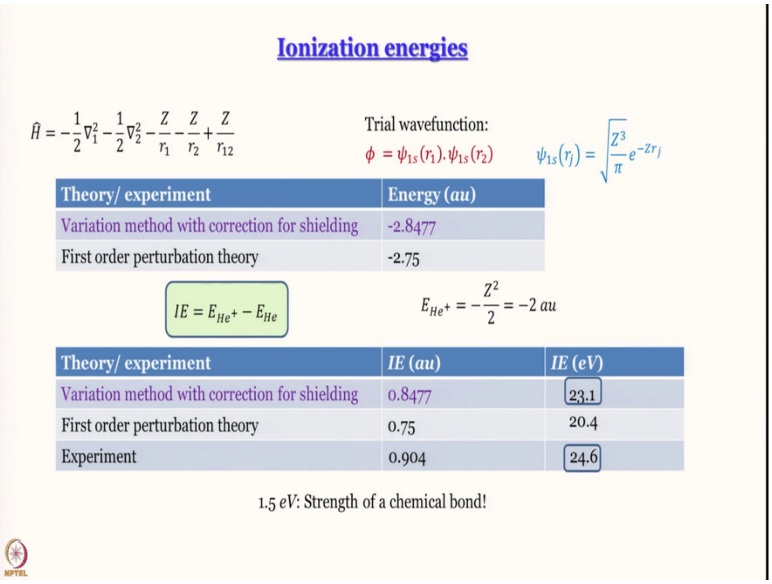

Ionization energies

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

Trial wavefunction:

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

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!

We all know what ionization energy is, in gas phase the energy difference between the iron helium plus and the uncharged atom helium that is ionization energy. So, now what we will do is we will work out ionization energy that is calculated using variation method as well as first order perturbation theory. Now energy of helium plus is very easy to calculate. As helium plus means it is a 1 electron system 1 electron system will have an energy of - z square by 2 where z is equal to 2 there is no question of effective nuclear charge anymore.

There is no question of shielding, there is only 1 electron. So, it feels the entire nuclear charge that is there so 2 square by 2 - 2 square by 2 that gives you - 2 atomic unit so energy of helium plus is - 2 atomic unit ionization energy then would be - 2 - - 2.8477 in case of your variation method 2.75 in case of perturbation theory and these are the values that you get. And you appreciate the picture properly when we take it to electron volt.

Remember electron volt is larger number is not it 1 atomic unit is 27.2 electron volt. So, if I translate that we see it better that is all you might not think that 0.84, 0.75 in our minds everything that is little less than 1 what is the difference. Of course if I told you 7500 and 8477 you would have seen the difference but let us see the difference in electron volt multiply by this 227.2 the numbers you get are 20.4 for first order perturbation theory and 23.1 for variation method.

So you see significant difference is there between the 2 calculations and then when you look at the experimental value 0.904 this is the correct value then you get an ionization energy of 24.6. So, 20.4 electron volt is definitely very, very far away from 24.6 electron volt ionization energy is 23.1 close enough well definitely better than 20.4 but see the difference between 23.1 and 24.6 the number calculated from variation method and the number obtained experimentally is 1.5 electron volt.

1.5 evolt is not a small number in this context because typically this 1.5 electron volt would be of the order of the bond strength, strength of a chemical bond would be about 1.5 electron volt or little more little less. So, since we are talking about atomic and molecular systems this difference is not really small ok this is sufficiently large so we have miles to go before we sleep we need to do better than this simple variation method that we have adopted. And to just convey how long it has taken to do better we will show you some timelines shortly.

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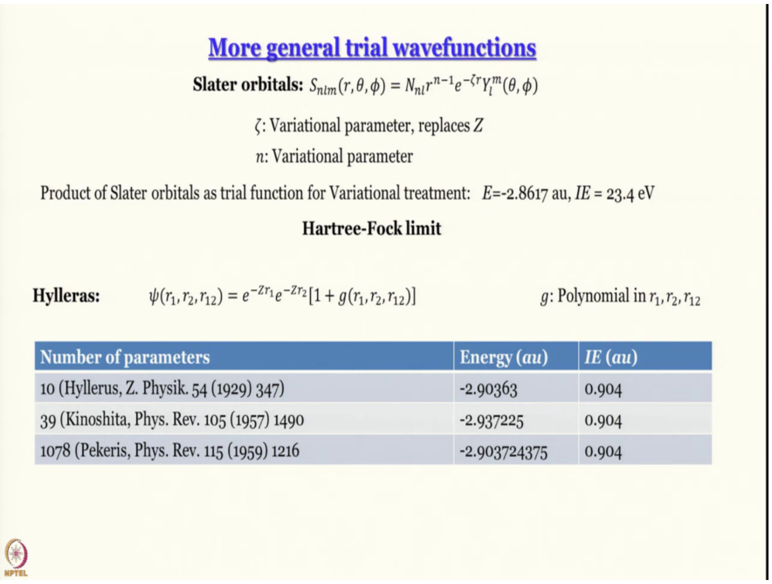

More general trial wavefunctions

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

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

Hylleras: $\psi(r_1,r_2,r_{12}) = e^{-Zr_1}e^{-Zr_2}[1 + g(r_1,r_2,r_{12})]$ g: Polynomial in r_1, r_2, r_{12}

Number of parameters	Energy (*au*)	*IE* (*au*)
10 (Hyllerus, Z. Physik. 54 (1929) 347)	-2.90363	0.904
39 (Kinoshita, Phys. Rev. 105 (1957) 1490	-2.937225	0.904
1078 (Pekeris, Phys. Rev. 115 (1959) 1216	-2.903724375	0.904

So now what we do is we start thinking of more general trial wave functions remember our previous discussion of variation method we had said that you can actually use any function to construct the wave function that is there. Remember the elephant that I showed in the opening slide, to get the elephant I can use whatever function whatever polynomial whatever exponential I want as long as it finally gives me the shape of the elephant.

So there is no need for us to stick to hydrogen atom wave function. So, we introduce the first wave function which is sort of a deviation from hydrogen atom wave function sort of but not a very far deviation when you do any theory you do not do something in white today and tomorrow you do something in black that can take you very, very far away from reality. So, we always take baby steps and the baby step we are talking about is that of Slater orbital.

Let us have a look at this form of Slater orbital here. We are writing s for Slater S it is characterized by nlm three quantum numbers very much like your hydrogen atom wave functions or vitals atomic orbitals and it is a function of r theta phi if you work in spherical polar coordinates. The expression for Slater orbital is the normalization constant which is a function of n and l multiplied by r to the power n - 1 very similar to what we had for atomic orbitals hydrogen atom wave functions, one electron wave functions multiplied by well I read the last factor first multiplied by Y l m of theta and phi this is familiar to us the angular part of the wave function form might be different that will see.

And the second factor is E to the power - zeta r what would that function have been in case of atomic orbital it would have been E to the power - z r is not it. So, z is your nucleus charge atomic number so instead of z we are using a variation and parameter zeta it replaces z in the expression for an for a hydrogen atom wave function and again to think of it we have already done this. What did we do in our previous treatment of variation method for helium atom?

We use z as a variational parameter did not we so essentially we use z as zeta we just did not call it zeta we still called it z here Slater called it zeta that is one. But is that all as we saw just by using this z or zeta as variation and parameter we do not get very close to the real value. We do not get very close to the reality, so what Slater did was that he introduced one more variation parameter used n as variational parameter as well.

Now this might sound counter intuitive we know what n is for hydrogen atom n is the principal quantum number it has to be 1 2 3 4 so on and so forth. How can I use it as a variational parameter and get something like 0.9, 0.8, 1.2 what sense does it make well the sense it makes is this we are not dealing with one electron systems any longer we are trying to stick to one electron wave functions as long as we can because they are familiar to us we know how to handle them.

And also many electron wave function is sort of a it builds up on 1 electron wave functions we can think that you start with 1 electron wave function then add some complication you get many electron wave function many electron atom starting from 1 electron atom but it is not completely uncorrelated is it there has to be some kind of a correlation there has to be some kind of a gradual evolution from a 1 electron system to a many electron system.

So we want to go gradually as well all right. The problem is we cannot write the exact form so the things to have do have done perhaps is to have added a term we do not know which term to add. So, what we are doing is we are essentially scaling the wave function by a variational parameter we are multiplying by a factor to arrive at a wave function that gives us the correct energy. Right now we only bother about energy ok.

We do not worry about how exactly we get the wave function it is a and ends justify the means sort of approach you if you want to call it that and again we have said this earlier I will just remind you again it is sort of using sort of like using the activity coefficient and pretending as if not all of the concentration of a react of a molecule is available for doing reactions whereas the reality is that all of the concentration is available is just that they run slower.

A similar kind of a scaling problem so nothing very new this has been used for a long time so since we cannot work with one parameter we are trying to compensate by playing around with another that is why so do not we do not feel it is a sacrilege that we are going to get non integral values of n and the problem is I think I wanted to show you a value of n that we get after optimization but I have forgotten to write it.

Well if I remember I will show it the next day otherwise just read Macquarie's book please it is given that when you get n something like 0.995 for helium. So, using this and this is where you get n equal to 0.995. So, you use the product of Slater orbitals instead of wave functions and you vary n as well as psi zeta sorry when you do that you get energy of – 2.8617 atomic unit ionization energy of 23.4 electron volt which is a little amount of improvement from ahah 23.1 electron volt or something that we got earlier.

So this is sort of a limit which is called Hartree Fock limit and for the first time in this course we take the name of Hartree and Fock and in the next 1 or 2 modules we are actually going to discuss in as much detail as we can the Hartree Fock approach to this multi electron problem many electron problem ok for now let us just say that this is the hartree referred limit that one can reach using this kind of an approach.

And again what kind of a problem is it, it is a minimization or an optimization problem I have 2 parameters zeta is 1 n is the other I need to minimize z so minimize energy with respect to zeta as well as n. So, you know how to do it take derivative in this case partial derivative equate to 0. In many cases it will not be able we will not be able to do it like that we have to do it numerically as we have briefly mentioned earlier perhaps we will come back to it in more detail when we discuss Hartree Fock in the next modules.

So this is what is called Slater orbital and using it you can get little bit of improvement but not really what you want. So, you want to try out other forms of orbitals and now that we have opened the flood gate we have said that we do not have to stick to hydrogen atom wave functions then there is actually no need to even retain the form. Here the rough framework of hydrogen atom wave function is retained with the introduction of the variational parameter.

So, in the subsequent kinds of orbitals and we will discuss maybe a couple of more in the next class but today let me show you at least one more hilarious for example use this kind of a wave function which is a function of r 1 r 2 and r 1 2 the inter nuclear separation. And the functional form that we use was product of 2 exponential functions one in r 1 one in r 2 multiplied by 1 + a function g a polynomial g in terms of these three independent variables that it took g is a polynomial.

Now see you can play around with the number of terms in polynomial each term will be associated with the coefficient each coefficient will be a variational parameter and of course you can play around with z and arrive at what effective nuclear charge you get the only issue with that is that some of this correction for effective nuclear charge might go in the coefficients of g. So, it becomes a numerical problem and you need computation you need to do you need good computers to handle systems like this because you try to do it by hand.

You will go grow very old before you can solve even the helium problem so as you see as computational power grew from 1929 to 1957 to 1959 this was a timeline I was talking about earlier Hyllerous use 10 terms he could use only 10 I do not know what kind of computer Hyllerous had if at all perhaps he did everything by hand. He got an energy of – 2.9063 an ionization energy of 0.904 which is a remarkable improvement over what we had earlier remember. Then Kinoshita in 1957 published this result with 39 parameters and you get – 2.937225 for energy atomic units ionization energy remains 0.904. Pekeres used 1078 parameters that means 1078 terms and published this result in 1959.

You see at this huge increase in number of terms and the improvement is there – 2.903 I think I missed the 0 here I am sorry about that it is not -2.90372525 it is -2.9379037225 so you get something like this so what we see is that you keep on increasing the number of terms at one point of time it is going to saturate it is not going to get any better it will get as good as it gets ok and you cannot it makes no sense to increase the number of terms beyond that I mean you can no harm done.

Because upper limit theorem tells us that in any case you will stop at the actual value of energy you stop a little more than that you will never go beyond. So, the chance of overshooting is not there but if you increase the number of terms the question is how good a computer you have? What is your computational power? So that is always the trade-off more number of terms gets us closer to the realistic value but it becomes computationally more expensive.

If you have better computers I would be my guest use as many terms as you want does not matter. So, with that I do not know why I have animated this with that the field is set for us to now try to see how we can draw this elephant. Well elephant is allegorical of course how we can generate whatever wave function we need using the Hartree Fock method. And since we are running out of time and not elaborate.

Now next day we will also learn that Hartree Fock method uses something called a self consistent field model very exciting challenging and opens up the field for addressing more complicated problems like molecules at later time that is what we are going to discuss in the next couple of classes.