8 Many Electron Atoms

When we come to the point of dealing with the Helium atom, you will find that we cannot solve the problem exactly due to the inter-electronic repulsion term. We must therefore use approximation techniques such as perturbation theory and the variational principle.

The helium atom problem takes on special importance because the methods that are used to treat helium and the concepts that emerge will be applicable to atoms with more electrons.

Before I apply the techniques of perturbation theory and the variational principle to helium, I would like to make a brief digression and introduce a system of units called ***atomic units***. The Schrödinger equation for atoms becomes quite simple if we write it in atomic units.

First, let us write out the helium atom Hamiltonian explicitly (here we explicitly assume that we can neglect the kinetic energy associated with the nuclear motion):

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Now let us choose a set of units such that

$$m_e = 1 \quad , \quad \hbar = 1 \quad , \quad e = 1 \quad , \quad 4\pi\varepsilon_0 = 1$$

If we do this the helium atom Hamiltonian becomes

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

We no longer have to include any physical constants in our Schrödinger Equation. These units are called **atomic units**, and all other physical quantities can be expressed in terms of these four. Certain quantities related to atoms become "natural units".

Quantity	Natural Unit	SI unit equivalent
Mass	$m_e = 1$	9.1×10^{-31} kg
Charge	$\lvert e \rvert = 1$	1.6×10^{-19} C
Angular momentum	$\hbar=1$	1.05×10^{-34} Js
Permittivity constant	$4\pi\varepsilon_0 = 1$	1.1126×10^{-10} C^2 J^{-1} m^{-1}

These are the four basic units. Others follow from these:

Quantity	Natural Unit	SI unit equivalent
Length	$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ = 1 (Bohr)	5.3×10^{-11} m (about 0.5 Å)
Energy	$\frac{e^2}{4\pi\varepsilon_0 a_0}$ = 1 (Hartree)	4.35×10^{-18} J

Note that one Bohr is the radius of the hydrogen atom in its lowest state. Also note that one Hartree is twice the ionization energy of the ground state energy of the hydrogen atom.

8.1 Perturbation Treatment of Helium

We want to solve the Schrödinger equation for helium. If we use perturbation theory, we can write the zeroth-order Hamiltonian as

$$\hat{H}^{(0)} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}$$

As we have done before, we could further break this up into two one-electron Hamiltonians.

We can write the zeroth-order wave function for the ground state as

$$\psi^{(0)}(\mathbf{r}_1,\mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$$

Where the ψ_{1s} functions are the hydrogen-like 1*s* wave functions for electron 1 and electron 2.

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

In atomic units, the ground state energy of the hydrogen-like atom is:

$$E_1 = -\frac{Z^2}{2}$$

You can take the formula that I gave you for the hydrogen atom energy levels and put it in atomic units to verify this. The zeroth-order energy can therefore be given by

$$E_1^{(0)} = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2$$

The perturbation part of the Hamiltonian is just

$$\hat{H}' = \frac{1}{r_{12}}$$

so the first order correction to the energy is

$$E_1^{(1)} = H'_{11} = \int\int \psi_1^{(0)*}(\mathbf{r}_1,\mathbf{r}_2)\hat{H}'\psi_1^{(0)*}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1\,d\mathbf{r}_2$$

$$= \int\int \psi_{1s}^*(\mathbf{r}_1)\psi_{1s}^*(\mathbf{r}_2)\left(\frac{1}{r_{12}}\right)\psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)d\mathbf{r}_1\,d\mathbf{r}_2$$

Note that the integration is over the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Thus each of these integral signs above represents a triple integral, one for each coordinate of each particle (that is $d\mathbf{r}_1$ is $dx_1\,dy_1\,dz_1$ and similarly for $d\mathbf{r}_2$)

Remember, that the first order correction in perturbation theory is simply the average value of the perturbation. Thus, this integral represents the average inter-electronic repulsion (calculated with the zeroth-order wave functions).

I will not take the time to do this integral explicitly here. The result from the integral is

$$E_1^{(1)} = \frac{5}{8}Z$$

So corrected to first order, the energy of the helium atom is

$$E_1 = E_1^{(0)} + E_1^{(1)} = -Z^2 + \frac{5}{8}Z$$

For helium, $Z = 2$, so

$$E_1 = -\frac{11}{4} = -2.75$$

The actual value is -2.9033 au, so this result is about 5% in error.

If we were to take the is to second order we would find $E_1 = -2.91$ au

To third order one would get $E_1 = -2.9037$ au, in excellent agreement with the experimental value.

Recall that there is no restriction that the perturbation theory estimate approaches the true energy as an upper limit. This only holds for the variational method.

8.2 Variational Treatment of Helium

We can also use the variational method to estimate the energy of the ground state of helium. We will take our trial function to be the same as our zeroth-order perturbation theory wave function

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$$

Where

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

except that we can treat the nuclear charge Z as a variational parameter.

Thus

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi} e^{-Z(r_1 + r_2)}$$

We now have to evaluate the variational function given by

$$E_\varphi = \int \Phi^*(\mathbf{r}_1, \mathbf{r}_2) \hat{H} \Phi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 \, d\mathbf{r}_2$$

where we are omitting the normalization integral in the denominator because we chose 1*s* functions which were initially normalized.

The Hamiltonian for the helium atom is the same whether you use perturbation theory or the variational principle, however in the latter, you must include the entire Hamiltonian in the integral rather than just the perturbation part when calculating the integrals.

Recall that the Hamiltonian for helium is

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

We can rewrite this as

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

(It should be clear that this is the same as the original.)

If we put the Hamiltonian and the wave functions into the variational function we get

$$E_\varphi(Z) = \int \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{r_{12}} \right) \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

We can now simplify this by noting that

$$\left(-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j} \right) \sqrt{\frac{Z^3}{\pi}} e^{-Zr_j} = -\frac{Z^2}{2} \sqrt{\frac{Z^3}{\pi}} e^{-Zr_j}$$

This is just the Schrödinger Equation for a one-electron atom with charge Z.

We can write one of these equations for electron 1 and another for electron 2. The fact that the wave function is a product of functions for electron 1 and 2 makes no difference, since the electron 1 Laplacian does not operate on the electron two part of the wave function and vice versa. We can therefore simplify the variational function to obtain:

$$E_\varphi(Z) = -\frac{Z^2}{2} - \frac{Z^2}{2} + \int \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{r_{12}} \right) \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

We can simplify the remaining integral in the following way

$$\int \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{r_{12}} \right) \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}\, d\mathbf{r}_1\, d\mathbf{r}_2 = 2\frac{Z^3}{\pi} \int \frac{Z-2}{r_1} e^{-2Zr_1} d\mathbf{r}_1 \int \frac{Z^3}{\pi} e^{-2Zr_2} d\mathbf{r}_2 + \left(\frac{Z^3}{\pi}\right)^2 \int \frac{1}{r_{12}} e^{-2Z(r_1+r_2)} d\mathbf{r}_1 d\mathbf{r}_2$$

(factor of 2 comes from two identical terms.)

Notice that the last integral is the same integral we had to evaluate in first order perturbation theory. The result equaled 5/8 *Z*.

The second integral in the first term is just the normalization integral for a 1*s* wave function and equals 1. We are left with

$$2\frac{Z^3}{\pi} \int \frac{Z-2}{r_1} e^{-2Zr_1} d\mathbf{r}_1 = 2(Z-2)\frac{Z^3}{\pi} \int \frac{1}{r_1} e^{-2Zr_1} d\mathbf{r}_1 = 2(Z-2)Z$$

where the last step was evaluated by looking up the integral.

Combining all the terms in our variational function one gets

$$E_\varphi(Z) = -\frac{Z^2}{2} - \frac{Z^2}{2} + 2Z\left(Z-2\right) + \frac{5}{8}Z$$

$$= Z^2 - \frac{27}{8}Z$$

If we now take the derivative and set it equal to zero (to minimize the energy with respect to our variational parameter *Z*, we find that

$$\frac{\partial E_\varphi(Z)}{\partial Z} = 2Z - \frac{27}{8} = 0$$

Consequently we have

$$Z_{\min} = \frac{27}{16}$$

Putting this back into the expression for $E_\varphi(Z)$ gives

$$E_{\min} = \left(\frac{27}{16}\right)^2 - \frac{27}{8}\frac{27}{16} = -2.848$$

Note that $Z_{\min} < 2$, the charge on the nucleus. This can be interpreted as partial screening of the full nuclear charge by the other electron (that is each electron partially screens the other). This is a physically reasonable result.

At first glance, the value for the energy, -2.848 au, seems to be in excellent agreement with the experimental value, *i.e.*, within 1.8%. One must take a closer look at this agreement, however. While in a relative sense, the percent agreement with the experimental value is good, even a small percentage of the total energy is still a significant amount of energy in an absolute sense, particularly compared to typical chemical bond energies.

The difference equals:

-2.848 - (-2.9033) =0.0553 au

Knowing that

1 au (hartree) = 2625.5 kJ/mol

this difference of 0.0553 au equals 145.19 kJ/mol

This amount of energy is comparable to a weak chemical bond (it is about 1/3 of a typical CH bond energy). Clearly, this will not do if we want to use quantum mechanics for more complicated molecular systems.

Part of the problem is that we restricted ourselves to a trial function, which was a product of one-electron functions. We did this for two reasons:

- This type of function is the zeroth-order function that we used in perturbation theory. Physically this means that it would be the true wave function if there were not any inter-electronic repulsion. We then consider the inter-electronic repulsion as a small perturbation on the system and might not expect the true functions to be much different.

- We do this because the concepts of electron orbitals shape the way we think about chemistry. (This is the way we like to think about chemistry.)

Think back to first year chemistry. We write the electronic configuration for the ground state of an atom like carbon as $\mathbf{1}\boldsymbol{s}^2\mathbf{2}\boldsymbol{s}^2\mathbf{2}\boldsymbol{p}^2$ for example.

The periodic behavior of the elements in the periodic table results from filling electrons into such one-electron orbitals. This is the way the periodic table is organized. What are we doing when we write that?

Basically we are saying that the wave function for the carbon atom is the product of 2 1*s* wave functions, 2 2*s* wave functions and 2 2*p* wave functions.
The whole concept of electrons going into orbitals assumes the wavefunction is a product of one electron wavefunctions.

What we are in effect doing when we write down an electronic configuration such as this is writing down the zeroth-order perturbation theory wave function. Thus, it helps us think about electrons going into individual orbitals. This, in turn, has great predictive power about chemical bonding! This notation, which you may have thought about in first year chemistry as being somewhat mysterious, really has its root in quantum mechanics.

One more related point:
Remember from first year chemistry that the sequence in which orbitals fill as you go to atoms of higher atomic number is not quite the same as the energies of the H atom orbitals.

The order of the H atom wave functions depend only upon the quantum number *n*

So **1*s* < 2*s*, 2*p* < 3*s*, 3*p*, 3*d* < 4*s*, 4*p*, 4*d*, 4*f* < 5*s* . . .**

But remember the order of orbitals in many electron atoms is

1*s* < 2*s* < 2*p* < 3*s* < 3*p* < 4*s* < 3*d* < 4*p* < 5*s* < 4*d* . . .

This is because in writing individual one-electron orbitals, we are neglecting inter-electronic repulsion. We are neglecting shielding of one electron from others.

When we include inter-electronic repulsion, the energies of the different orbitals change since some are screened more than others. Recall the radial distributions that I showed for the hydrogen atom wavefunctions. Some orbitals had little lumps of probability near the nucleus. This influences the amount of screening.

Let us now get back to our discussion of the variational estimate for the ground state of helium. If we don't restrict our functions to products of one electron functions we can get essentially the exact answer for the energy of helium, however, we lose the physical interpretation of one electron orbitals which so much shapes our thinking about chemistry.

However, even if thinking about wavefunctions as products as one-electron functions is only approximate, it has great predictive power and thus is practical. There are ways that we can keep this useful picture of electrons in individual orbitals and get a better estimate of the energy. One way to do this is to introduce one-electron orbitals that are more general functions than the hydrogen atom one-electron functions. One set of such orbitals are called **Slater Orbitals** since they were introduced by John Slater. They have the form

$$S_{nlm}(r,\vartheta,\varphi) = N_{nl} r^{n-1} e^{-\xi r} Y_l^m(\vartheta,\varphi)$$

I will not discuss these in detail, but the angular parts are spherical harmonics and the radial parts are similar to the H atom eigenfunctions. The parameter ξ is taken to be arbitrary and is not necessarily equal to *Z*/*n* as in the hydrogen atom wave functions.

Even if we have an extremely flexible one-electron function, there is still a theoretical limit to the accuracy that one can achieve in a variational calculation if one assumes the form of the wave function to be a product of one-electron functions.

A procedure called the ***Hartree-Fock Self-Consistent Field method*** gives a procedure by which we can calculate the best wave function which is restricted to a product of one electron functions. In another words, if we are going to restrict ourselves to one-electron functions, a Hartree-Fock calculation is the best we can do.

8.3 Hartree-Fock SCF Method

I will first explain the application of this approach for Helium. We will generalize it later.

The Hartree-Fock approach starts by writing the wavefunction as a product of one-electron functions or one-electron orbitals.

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$$

One typically chooses these one electron functions to be hydrogenlike orbitals but with somewhat more flexibility. In practice one chooses a linear combination of Slater type orbitals for each function. No matter what the functional form of these orbitals, they retain their identity as one-electron functions.

The basic physics of the Hartree-Fock method is that it takes into consideration the inter-electronic repulsion in an average way.

Consider the fact that the potential between two point charges is given by

$$U(r)=\frac{q_1q_2}{4\pi\varepsilon_0 r}=\frac{e^2}{4\pi\varepsilon_0 r}$$

Rather than considering the inter-electronic repulsion as an interaction between two point charges, consider it as the interaction of a single point charge with a continuous charge distribution. This approach makes sense inasmuch as the quantum mechanical wave function for an electron gives us its probability distribution.

The potential energy for the interaction of a point charge with some continuous charge distribution is

$$dU(r_{12})=\frac{q_1\rho_2}{4\pi\varepsilon_0 r_{12}}d\mathbf{r}_2$$

where ρ_2 is the charge per unit volume for electron 2 and dr_2 is the volume element. $\rho_2\ dr_2$ is the differential charge, dq_2

To get the full potential one must integrate over the volume element $d\mathbf{r}_2$.

$$U(r_{12})=\int\frac{q_1\rho_2}{4\pi\varepsilon_0 r_{12}}d\mathbf{r}_2$$

However, we know the probability distributions from the one-electron wave functions.

If $\varphi(\mathbf{r}_2)$ is the orbital (wave function) for electron 2, then the probability distribution for electron 2 is given by

$$\rho_2 d\mathbf{r}_2=-e\varphi^*(\mathbf{r}_2)\varphi(\mathbf{r}_2)d\mathbf{r}_2$$

where d$\mathbf{r}_2$ is the volume element of electron.

Since this is a probability distribution for an electron we can also interpret this as a charge distribution for electron 2. We can therefore write the potential energy that electron 1 experiences from its interaction with electron 2 as

$$U_1^{eff}(\mathbf{r}_1) = \int \varphi^*(\mathbf{r}_2)\frac{1}{r_{12}}\varphi(\mathbf{r}_2)\,d\mathbf{r}_2$$ (Note: the change to atomic units)

We can therefore write an effective one electron potential

$$\hat{H}_1^{eff}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(\mathbf{r}_1)$$

The Schrödinger equation corresponding to this effective Hamiltonian is

$$H_1^{eff}(\mathbf{r}_1)\varphi(\mathbf{r}_1) = \varepsilon_1\,\varphi(\mathbf{r}_1)$$

where $\varphi(\mathbf{r}_1)$ is a one electron orbital and ε_1 is the orbital energy.

This is called the ***Hartree-Fock Equation*** for helium.

One can use the variational principle to solve this equation and get the best values of the parameters in $\varphi(\mathbf{r}_1)$ that will minimize the energy ε_1.

Here one is applying the variational principle to a one-electron problem!! That is, one calculates the variational function, $E_{\square}$, using the one electron functions and the *effective* one-electron Hamiltonian. One then minimizes the variational function by varying the parameters in the trial functions. This gives an estimate of the energy ε_1, and a new wavefunction (new variable parameters in the linear combination of Slater orbitals).

Let me first talk first about these wave functions and then about the orbital energy ε_1.

Recall that we started with a wave function $\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$

The one-electron functions $\varphi(\mathbf{r}_1)$ and $\varphi(\mathbf{r}_2)$ have the same functional form and have one or several variable parameters. We then calculated the average effective potential $U_1^{eff}(\mathbf{r}_1)$ that electron 1 experiences using the function $\varphi(\mathbf{r}_2)$. That in turn gives us an effective one-electron Hamiltonian $\hat{H}_1^{eff}(\mathbf{r}_1)$ which in turn gives us a new function $\varphi(\mathbf{r}_1)$ and thus also $\varphi(\mathbf{r}_2)$ as the parameters in both $\varphi(\mathbf{r}_1)$ and $\varphi(\mathbf{r}_2)$ vary in the same way. We then use this $\varphi(\mathbf{r}_2)$ to calculate a new effective potential and then another effective one-electron Hamiltonian which gives us another function $\varphi(\mathbf{r}_2)$.

Schematically we can write this

$$\begin{tikzcd}
\varphi(\mathbf{r}_2) \arrow[r] & U_1^{eff}(\mathbf{r}_1) \arrow[r] & \hat{H}_1^{eff}(\mathbf{r}_1) \arrow[r, "\text{Var. Princ.}"] & \varphi(\mathbf{r}_1) \arrow[d] \\
{} \arrow[u] & & & {} \arrow[lll]
\end{tikzcd}$$

One continues in this cyclic process until the functions $\varphi(\mathbf{r})$ no longer change. When that is the case, the resulting orbitals are called ***Hartree-Fock Orbitals.***

This is why the procedure is called the ***Hartree-Fock Self Consistent Field Method*** because the wave functions which are calculated are self consistent - *i.e.* the average field one would calculate from them will produce a Hamiltonian which will yield a wave function which is the same as the original.

This procedure is fairly simple to visualize for helium, since although there are two electrons and two one-electron wave functions, the functions are the same. Remember from first year chemistry that one can put two electrons in each orbital. For many electron atoms, one can still have a wave function that is the product of one-electron functions, but there must be one distinct function for every two electrons.
In the case of many electrons, one calculates the average potential experienced by electron 1 from all the other electrons in the atom. One then constructs an effective one electron Hamiltonian and solves for a new one-electron function for electron 1. One then moves on to electron 2. In calculating the average potential for electron 2, one uses the new function for electron 1. One then gets a new function for electron 2. You move down the line repeating this for each of the electrons. When one is done you go back to the beginning and start all over again. You continue to iterate until the functions change no more.

Let us get back to the case of Helium. When you have found the optimum Hartree-Fock Orbitals, you find the energy by taking its expectation (average) value using the full Hamiltonian and the full wave function (which is a product of the optimized Hartree-Fock Orbitals)

$$E = \int\int \varphi^*(\mathbf{r}_1)\varphi^*(\mathbf{r}_2)\hat{H}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

where you may recall that for helium,

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

If we substitute this into the variational function we get

$$E = I_1 + I_2 + J_{12}$$

where

$$I_j = \int \varphi^*(\mathbf{r}_j)\left[-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j}\right]\varphi(\mathbf{r}_j)d\mathbf{r}_j$$

Note that this is just the average energy of an electron in the Hartree-Fock orbitals neglecting inter-electronic repulsion.

and

$$J_{12} = \int\int \varphi^*(\mathbf{r}_1)\varphi^*(\mathbf{r}_2)\left[\frac{1}{r_{12}}\right]\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

which is called the coulomb integral. This looks like the average value of the inter-electronic repulsion in the Hartree-Fock orbitals.

Note that in this determination of the total energy, one simply uses the optimized Hartree-Fock orbitals and does not vary their parameters. The optimization has already been done.

It turns out that the total energy of the Helium atom is not simply the sum of the orbital energies. We can show this if we go back to the one-electron Schrödinger equation that we had written

$$H_1^{eff}(\mathbf{r}_1)\varphi(\mathbf{r}_1) = \varepsilon_1\varphi(\mathbf{r}_1)$$

If we multiply this on both sides by $\varphi^*(\mathbf{r}_1)$ and integrate we get

$$\varepsilon_1 = \int \varphi^*(\mathbf{r}_1) H_1^{eff}(\mathbf{r}_1)\varphi(\mathbf{r}_1)\, d\mathbf{r}_1$$

If we were to substitute in our expression for the effective one-electron Hamiltonian we could easily show that

$$\varepsilon_1 = I_1 + J_{12}$$

If we then take the sum of the orbital energies we get

$$\varepsilon_1 + \varepsilon_2 = I_1 + J_{12} + I_2 + J_{12} \neq E \qquad \text{(this counts } J_{12} \text{ twice)}$$

However, if we compare the orbital energy to the expression we had for *E* before we can see that

$$\varepsilon_1 = E - I_2$$

If we look at the expression for the integral I_2 we had earlier, you can see that it simply looks like the average energy of a one-electron atom with charge *Z* (in this case *Z*=2 for helium) calculated with the Hartree-Fock orbital. This is just an approximation to the energy of a helium ion. ε_1 is then the difference between the energy of the helium atom and the energy of the helium ion. That is it the energy needed to remove an electron from that particular orbital. This is what we know as the ***Ionization energy***.

Thus $\quad IE \cong -\varepsilon_1$

This is called **Koopman's Theorem** and can be (and has been) verified experimentally using spectroscopy.

If we were to go through all the mechanics of the Hartree-Fock Procedure and calculate the energy of helium we would get

E = -2.8617 au.

This is to be compared to the exact energy

E = -2.9037 au (experimental).

Remember, this procedure yields the best estimate of the energy in the approximation that we can represent the wave function as a product of one-electron functions. The closeness of this result to the exact energy tells us that it is ok to think of electrons in separate orbitals to a fairly high degree of approximation. While this result is almost within 1% of the exact energy, as we stated earlier, even a small percentage error can be a big absolute error.

The question is why isn't this better. What have we left out which might contribute to the energy?Well, in the basic approach of the Hartree-Fock method, the electrons are assumed to be independent of each other, interacting through some average or effective potential. This is the assumption that the motion of the electrons is uncorrelated. We know in reality, the motion of the electrons must be correlated, that is the motion of one electron will effect that of the other.

We can define a **correlation energy** as

$$E_{corr} = E_{exact} - E_{HF}$$

Although Hartree-Fock gets almost 99% of the exact energy, the difference is about 100 kJ/mole, which is comparable to chemical bond energies.

The calculation of correlation energies and the inclusion of electron correlations into the wave functions is an area of active interest.

Let us now move on to Lithium, which has three electrons. If we follow along the lines that we have been proceeding, it might seem *natural* to start by writing the wave function as a product of 1s orbitals

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)\psi_{1s}(\mathbf{r}_3)$$

However, most of you probably recall from first year chemistry that you cannot put 3 electrons in a 1*s* orbital. To understand why, I need to discuss the subject of Electron spin and Pauli Principle.

Tjalling Koopmans