The Hartree-Fock method for He atom

Let us consider the helium atom with the Hamiltonian

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

or, in atomic units

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

One possible way to approximate the two-electron wave function is to write it as a product of "orbitals"

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\psi(\vec{r}_2)$$

The two functions on the right are the same because the Pauli exclusion principle allows up to 2 electrons in the same orbital (due to different spins). The probability distribution of electron 2 is $|\psi(\vec{r}_2)|^2$. We can interpret it as a charge density which yields some effective potential energy that electron 1 experiences due to electron

$$V_1^{eff}(\vec{r}_1) = \int \psi^*(\vec{r}_2)\frac{1}{r_{12}}\psi(\vec{r}_2)d\vec{r}_2$$

With that we can define an effective one-electron Hamiltonian as

$$H_1^{eff}(\vec{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + V_1^{eff}(\vec{r}_1)$$

The Schrödinger equation that corresponds to this effective Hamiltonian is

$$H_1^{eff}\psi(\vec{r}_1) = \varepsilon_1\psi_1(\vec{r}_1) \qquad \leftarrow \text{Hartree-Fock eqn. for He}$$

There is also a similar equation for $\psi(\vec{r}_2)$. While we used a physical argument of a charge density of electron 2 to obtain the HF equation above, i is possible to derive it directly by applying th

Variational principle to the energy of a helium atom in an orbital approximation

$$E = \iint d\vec{r_1} d\vec{r_2} \; \Psi^*(\vec{r_1}) \Psi^*(\vec{r_2}) H \Psi(\vec{r_1}) \Psi(\vec{r_2})$$

assuming that Ψ is normalized. We will find that

$$E = I_1 + I_2 + J_{11} \quad \text{where} \quad I_j = \int \Psi^*(\vec{r_j}) \left(-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j} \right) \Psi(\vec{r_j}) \, d\vec{r_j}$$

and $\quad J_{ij} = \iint \Psi^*(\vec{r_1}) \Psi(\vec{r_1}) \frac{1}{r_{12}} \Psi^*(\vec{r_2}) \Psi(\vec{r_2}) \, d\vec{r_1} \, d\vec{r_2}$

Integral J_{ij} is called the Coulomb integral as it can be interpreted as the interaction between two charge distributions. The HF equation can be obtained by minimizing E with respect to Ψ.

While the HF looks like a simple 1-electron eigenvalue problem there is one essential complication. $V_1^{eff}(\vec{r_1})$ depends on $\Psi(\vec{r_2})$. Thus we must know the solution before we can determine $H_1^{eff}(\vec{r_1})$. It turns out the problem can be solved iteratively by the self-consistent field method. We can first guess $\Psi(\vec{r})$ then use it to evaluate $V_i^{eff}(\vec{r_1})$ and then solve the HF equation for an updated $\Psi(\vec{r})$. This cycle is repeated until $\Psi(\vec{r})$ no longer changes (within certain predefined threshold). The solutions $\Psi(\vec{r})$ are called the Hartree-Fock orbitals.

To find the physical interpretation of ε_1 let us note that

$$\int \Psi^*(\vec{r_1}) H_1^{eff} \Psi(\vec{r_1}) \, d\vec{r} = \varepsilon_1$$

using $H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - V_i^{eff}(\vec{r_1})$ and the definitions of I_i and J_{11} we obtain $\varepsilon_1 = I_1 + J_{11}$

The total energy of He is not the sum of its orbital energies because

$$\varepsilon_1 + \varepsilon_2 = (I_1 + J_{11}) + (I_2 + J_{11}) \neq E \quad (\text{recall } E = I_1 + I_2 + J_{11})$$

We see that

$$\varepsilon_1 = E - I_2$$

According to the definition of I_j, I_2 is the energy of He ion computed with the helium HF orbital. Thus, the above equation suggests that

$$I.E. \approx -\varepsilon_1$$

that is the negative of ε_1 is approximately the ionization energy of He atom. This approximation is called the Koopman approximation. For He atoms it has been determined by numerical calculations that $-\varepsilon_1 = 0.9179$ a.u. while the experimental ionization energy is 0.904 a.u.

It is customary in atomic and molecular physics and quantum chemistry to define the so called correlation energy as
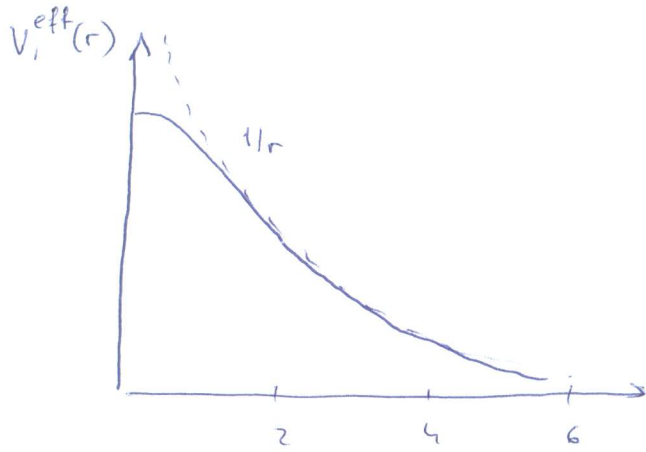
$$E_{corr} = E_{exact} - E_{HF}$$

For He

$$E_{corr} = \left(-2.9037 + \underbrace{2.8617}_{\text{HF energy}} \right) = -0.0420 \text{ a.u.}$$

In practical calculations, the HF orbitals are usually expanded in terms of some basis functions (e.g. Slater orbitals):

$$\psi(\vec{r}) = \sum c_i \phi_i(\vec{r}) \qquad \phi_i(\vec{r}) = A \, r^{n-1} e^{-\zeta r} Y_\ell^m(\theta, \varphi)$$

The effective HF potential $V_1^{eff}(r)$ looks as follows

$V_1^{eff}(r)$

1/r

2   4   6

At large r the electron sees the He nucleus completely screened by the other electron. Thus V_1^{eff} approaches $\frac{1}{r}$ at large r.