

The Hartree-Fock method

Let us consider an atom with n electrons. The Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + \sum_{i < j}^n \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}}$$

or, in atomic units

$$H = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \quad \text{where } r_{ij} = |\vec{r}_i - \vec{r}_j|$$

Z is the charge of the nucleus

In the variational treatment of the helium atom, which we did previously, we approximated the wave function as a product of hydrogenlike orbitals. In the case of n electrons it would take the form

$$\Psi(\vec{r}_1, \dots, \vec{r}_n) = f_1(\vec{r}_1) \dots f_n(\vec{r}_n)$$

where f are hydrogen-like functions. As we demonstrated for He, the use of an "effective" nuclear charge gives considerable improvement, but we are still a little far from having an accurate wave function. The next step in improving the situation is to employ a variation wave function that has a form similar to the one given above, but in which functions $f_i(r)$ are not restricted to hydrogen-like orbitals. Instead one can vary $f_i(r)$ arbitrarily to minimize the energy functional

$$E = \int \dots \int \Psi^* H \Psi d\vec{r}_1 \dots d\vec{r}_n$$

This task is harder than in previous variational calculations, where we only had to adjust some parameter(s). Here we have to vary the functions f_i . Note that even if we find the best possible functions f_i , our wave function will still be only an approximate one. The many-electron Schrödinger equation is not separable and the exact wave function cannot be represented as a product of n single-electron functions. Yet we can expect a significant improvement over the previous treatment.

The procedure of computing f_i 's in the above product is called the Hartree self-consistent field method.

Suppose we know a reasonable initial guess to functions f_i . Then the probability density of electron i

is
$$p_i(r) = |f_i(r)|^2 \quad \left(\begin{array}{l} \text{we assume all } f_i\text{'s} \\ \text{are normalized} \end{array} \right)$$

Let us now turn our attention to electron 1 and regard electrons 2, ..., n as being smeared out to form an effective (and fixed) distribution of electric charge with which electron 1 interacts.

The potential energy of interaction between point charges Q_1 and Q_2 is $V_{12} = \frac{Q_1 Q_2}{r_{12}}$ (in atomic units).

If, instead of a point-like Q_2 we have a smeared out charge distribution p_2 then V_{12} becomes

$$V_{12} = \int \frac{Q_1 p_2}{r_{12}} d\vec{r}_2 = Q_1 \int \frac{|f_2(\vec{r}_2)|^2}{r_{12}} d\vec{r}_2$$

Summing up the interactions of electron 1 with all other electrons we get

$$V_{12} + V_{13} + \dots + V_{1n} = \sum_{j=2}^n \int \frac{|f_j(\vec{r}_j)|^2}{r_{1j}} d\vec{r}_j$$

The potential energy of interaction between electron 1 and all particles in the system (including nucleus) is then

$$V_1^{\text{eff}}(\vec{r}_1) = \sum_{j=2}^n \int \frac{|f_j(\vec{r}_j)|^2}{r_{1j}} d\vec{r}_j - \frac{Z}{r_1}$$

This V_1 we can now use as the potential energy in a single-electron Schrödinger equation,

$$\left[-\frac{1}{2} \nabla_{\vec{r}_1}^2 + V_1^{\text{eff}}(\vec{r}_1) \right] f_1(\vec{r}_1) = \epsilon_1 f_1(\vec{r}_1)$$

and solve for function $f_1(\vec{r})$

While the above equation looks like a simple single-electron eigenvalue problem, there is one essential complication. $V_1^{\text{eff}}(\vec{r}_1)$ depends on f_2, f_3, \dots, f_n . We can write similar equations for all orbitals f_j :

$$\left[-\frac{1}{2} \nabla^2 + V_j^{\text{eff}}(\vec{r}) \right] f_j(\vec{r}) = \epsilon_j f_j(\vec{r}) \quad j=1, \dots, n \quad (*)$$

This is essentially a system of coupled implicit nonlinear equations with respect to f_j . They are nonlinear because f_j 's are buried in V_i^{eff} . It turns out the problem can be solved iteratively by the self-consistent field method. In this approach we pick a reasonable guess for $f_1^{(0)}, \dots, f_n^{(0)}$, then evaluate $V_j^{(0)}$. Then we solve equations (*) and call the solutions $f_j^{(1)}$. Then we take $f_j^{(1)}$ and evaluate $V_j^{(1)}$ again, solve (*) again and obtain $f_j^{(2)}$

We repeat the cycle until functions $f_j^{(k)}$ no longer change (within predefined numerical accuracy). Usually such self-consistent procedure converges, although sometimes additional numerical "tricks" are required (e.g. at each iteration it may be better to mix the "old" and "new" density rather than replace "old" with "new").

How do we obtain the total energy of an atom in the Hartree method? It might be tempting to simply sum up the orbital energies of all electrons, $\epsilon_1 + \epsilon_2 + \dots + \epsilon_n$. However, this is wrong. The potential energy in (*) for $j=1$ includes, in an average way, the repulsion energy between electrons 1&2, 1&3, ..., 1&n. Similarly, for $j=2$ we include the repulsion between 2&1, 2&3, ..., 2&n. So if we simply sum up all ϵ_i 's then we effectively double count all interelectron repulsions. To obtain the total energy E in the proper way we evaluate $\langle H \rangle$:

$$\begin{aligned}
 E = \langle H \rangle &= \int \psi^* H \psi \, d\vec{r}_1 \dots d\vec{r}_n = \\
 &= \int \prod_{p=1}^n f_p^*(\vec{r}_p) \left[-\frac{1}{2} \sum_{i=1}^n \nabla_{\vec{r}_i}^2 - \sum_{i=1}^n \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \right] \prod_{a=1}^n f_a(\vec{r}_a) \, d\vec{r}_1 \dots d\vec{r}_n = \\
 &= \sum_{i=1}^n \int f_i^*(\vec{r}_i) \left[-\frac{1}{2} \nabla_{\vec{r}_i}^2 - \frac{Z}{r_i} \right] f_i(\vec{r}_i) \, d\vec{r}_i + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \iint f_i^*(\vec{r}_i) f_j^*(\vec{r}_j) \frac{1}{r_{ij}} f_i(\vec{r}_i) f_j(\vec{r}_j) \, d\vec{r}_i \, d\vec{r}_j \\
 &= \sum_{i=1}^n \int f_i^*(\vec{r}_i) \left[-\frac{1}{2} \nabla_{\vec{r}_i}^2 - \frac{Z}{r_i} + \underbrace{\sum_{j=1}^n \int f_j^*(\vec{r}_j) \frac{1}{r_{ij}} f_j(\vec{r}_j) \, d\vec{r}_j}_{V_i^{\text{eff}}(\vec{r}_i)} \right] f_i(\vec{r}_i) \, d\vec{r}_i -
 \end{aligned}$$

$$-\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \iint f_i^*(\vec{r}_i) f_j^*(\vec{r}_j) \frac{1}{r_{ij}} f_i(\vec{r}_i) f_j(\vec{r}_j) d\vec{r}_i d\vec{r}_j =$$

$\underbrace{\hspace{10em}}_{J_{ij}} \leftarrow \text{Coulomb integral}$

$$= \sum_{i=1}^n \epsilon_i - \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} J_{ij} = \sum_{i=1}^n \epsilon_i - \sum_{i < j} J_{ij}$$

When we solve the Hartree equations we get all ϵ_i 's. The Coulomb integrals can also be evaluated given f_i 's.

If we examine our original ansatz,

$$\Psi = f_1(\vec{r}_1) f_2(\vec{r}_2) \dots f_n(\vec{r}_n)$$

we can notice one serious issue. The Hartree product of f_i 's does not satisfy the Pauli principle. Fock suggested that an antisymmetrized product of spin-orbitals should be used instead. A fully antisymmetric product can be written as a Slater determinant

$$\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(n) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(1) & \phi_n(2) & \dots & \phi_n(n) \end{vmatrix}$$

where the arguments $(1, 2, \dots)$ of the functions refer to both spatial coordinates \vec{r} of the corresponding particle and its spin degrees of freedom.

The requirement of antisymmetrization makes things a little more complicated and we will skip algebra further. We will just write the

final result — the differential equations for finding the Hartree-Fock orbitals. They actually have the same general form as the equations for Hartree orbitals:

$$\hat{F} \phi_i = \epsilon_i \phi_i \quad i=1, \dots, n$$

Here \hat{F} is called the Fock operator. Essentially it is some effective Hamiltonian and ϵ_i is the orbital energy. The Fock operator has extra terms as compared with the effective Hartree Hamiltonian. The effective potential is no longer local. Also, the expression for the total energy, in addition to the Coulomb integrals, involves the so called exchange integrals K_{ij}

$$K_{ij} = \iint \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) \frac{1}{r_{12}} \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

In atomic and molecular physics it is customary to define the correlation energy as

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

where E_{HF} is the total energy obtained within the Hartree-Fock approximation

For example, in the case of He atom

$$E_{\text{corr}} = \underbrace{(-2.9037)}_{\text{exact energy}} + \underbrace{2.8617}_{\text{HF energy}} = -0.0420 \text{ a.u.} = 1.14 \text{ eV}$$