

Hartree-Fock-Roothan Self-Consistent Field Method

1. Helium

Here is a summary of the derivation of the Hartree-Fock equations presented in class. First consider the ground state of He and start with with a variational trial wave-function written as a product of 1-electron orbitals, $\phi(i)$; that is

$$\Psi(1, 2) = \phi_\alpha(1)\phi_\beta(2), \quad (1)$$

where the orbitals, $\phi_{\alpha/\beta}$, (called Fock orbitals) are unknown. For notational simplicity only, we assume that they are real but not necessarily normalized, and use "1" and "2" to denote the coordinates of electron 1 or 2. We also added a subscript to each of the orbitals, as that extra bit of notation will be useful later when considering multi-electron atoms.

The energy bound corresponding to Eq. (1), as usual, is

$$E[\phi] = \frac{\int d(1)d(2) \phi_\alpha(1)\phi_\beta(2)H\phi_\alpha(1)\phi_\beta(2)}{\int d(1)d(2) |\phi_\alpha(1)|^2|\phi_\beta(2)|^2}, \quad (2)$$

where $d(i)$ denotes an integration over the position and possibly electronic spin coordinates of particle i . At this point, assume we have the orbital functions and consider how $E[\phi]$ changes under an arbitrary change in the orbital functions, that is we let

$$\phi_\alpha(1) \rightarrow \phi_\alpha(1) + \delta\phi_\alpha(1), \quad (3)$$

etc., where $\delta\phi_\alpha(1)$ is an arbitrary, small, function. By using this in Eq. (2), we have

$$E[\phi + \delta\phi] = \frac{\int d(1)d(2) [\phi_\alpha(1) + \delta\phi_\alpha(1)][\phi_\beta(2) + \delta\phi_\beta(2)]H[\phi_\alpha(1) + \delta\phi_\alpha(1)][\phi_\beta(2) + \delta\phi_\beta(2)]}{\int d(1)d(2) |\phi_\alpha(1) + \delta\phi_\alpha(1)|^2|\phi_\beta(2) + \delta\phi_\beta(2)|^2} \quad (4)$$

We now expand all the products and discard all the terms that have quadratic or higher powers in the $\delta\phi$'s. This gives

$$\begin{aligned} \delta E \equiv E[\phi + \delta\phi] - E[\phi] = & \left\{ \int d(1)d(2) \delta\phi_\alpha(1)\phi_\beta(2)H\phi_\alpha(1)\phi_\beta(2) + \phi_\alpha(1)\delta\phi_\beta(2)H\phi_\alpha(1)\phi_\beta(2) \right. \\ & + \phi_\alpha(1)\phi_\beta(2)H\delta\phi_\alpha(1)\phi_\beta(2) + \phi_\alpha(1)\phi_\beta(2)H\phi_\alpha(1)\delta\phi_\beta(2) \\ & \left. - 2E[\phi] \int \phi_\alpha(1)\delta\phi_\alpha(1)|\phi_\beta(2)|^2 + |\phi_\alpha(1)|^2\phi_\beta(2)\delta\phi_\beta(2) \right\} \\ & \div \int d(1)d(2) |\phi_\alpha(1)|^2|\phi_\beta(2)|^2, \quad (5) \end{aligned}$$

where we have moved the first-order terms from the denominator by noting that

$$\frac{1}{A + \delta A} = \frac{1}{A} - \frac{\delta A}{A^2} + \frac{\delta A^2}{A^3} - \dots \quad (6)$$

We can rewrite Eq. (5) by using the fact that H is Hermitian in the 3rd and 4th terms to move H onto the factors to its right. This just gives the first two terms and thus:

$$\delta E = \frac{2 \left\{ \int d(1)d(2) \delta\phi_\alpha(1)\phi_\beta(2)(H - E[\phi])\phi_\alpha(1)\phi_\beta(2) + \phi_\alpha(1)\delta\phi_\beta(2)(H - E[\phi])\phi_\alpha(1)\phi_\beta(2) \right\}}{\int d(1)d(2) |\phi_\alpha(1)|^2 |\phi_\beta(2)|^2} \quad (7)$$

Since we are looking for the orbitals that minimize the variational bound, a necessary condition is that δE , being linear in the $\delta\phi$'s, must vanish for arbitrary $\delta\phi$ (at least arbitrary small $\delta\phi$'s). From Eq. (7) we see that this requires that

$$\int d\mathbf{r}_2 \phi_\beta(2)(H - E[\phi])\phi_\alpha(1)\phi_\beta(2) = 0, \quad (8)$$

where notice that we have dropped one of the integrations. An similar equation is obtained for $\phi_\beta(2)$.

In order to proceed further, we have to consider the explicit form of the Hamiltonian, which for helium is just

$$H = H_1 + H_2 + \frac{1}{r_{12}}, \quad (9)$$

in atomic units, where

$$H_i \equiv -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \quad (10)$$

is the Hamiltonian for the noninteracting electrons (i.e., of a singly ionized helium atom ($Z=2$)). In addition, we now assume that the individual orbital functions are normalized. We can thus rewrite Eq. (8) as

$$[H_1 + U_\beta^{eff}(1)]\phi_\alpha(1) = \varepsilon_\alpha \phi_\alpha(1), \quad (11)$$

where

$$U_\beta^{eff}(1) \equiv \int d(2) \frac{|\phi_\beta(2)|^2}{r_{12}} \quad (12)$$

and

$$\varepsilon_\alpha \equiv E[\phi] - I_\beta, \quad (13)$$

with

$$I_\beta \equiv \int d(2) \phi_\beta^*(2) H_2 \phi_\beta(2). \quad (14)$$

Equation (11) is known as the Hartree-Fock equation, and its solution will give the lowest energy bound possible with an orbital form for the two-electron wave-function, i.e., with Eq. (1). It is very similar to the one-electron Schrodinger equations we have considered before, with one important difference. Notice how the electron-electron repulsion term appears in $U_{\beta}^{eff}(1)$. Since $|\phi_{\beta}(2)|^2$ is the probability density for finding electron 2 at a given position, Eq. (12) gives the average electron-electron repulsion for a fixed position of electron 1. In this sense, the orbital assumption is referred to as a *mean-field* approximation and neglects correlations between the actual positions of the electrons.

In addition to the errors associated with the orbital assumption, the Hartree-Fock equations are considerably more difficult to solve than the usual one-electron problems we've encountered since the effective potential depends on the solution. What is done in practice is to choose a form for the orbitals, e.g., by using a hydrogenic 1s orbital, calculating the effective potentials, and solving the resulting one electron problem. The orbitals thus obtained are then used to recalculate the effective potentials and the entire procedure is repeated until self-consistency is obtained.

The eigenvalues ε_{α} are called the *orbital energies*. There are many ways in which the total energy of the atom can be expressed in terms of the orbital energies, e.g.,

$$E[\phi] = \varepsilon_{\alpha} + I_{\beta}, \quad (15)$$

cf. Eq. (13). Another, equivalent, expression can be obtained by using Eqs. (9), (10) directly in Eq. (2), namely

$$E[\phi] = I_{\alpha} + I_{\beta} + J_{\alpha,\beta}, \quad (16)$$

where the I 's are given by Eq. (14) and

$$J_{\alpha,\beta} \equiv \int d(1)d(2) \frac{|\phi_{\alpha}(1)|^2 |\phi_{\beta}(2)|^2}{r_{12}} = \int d(1) \phi_{\alpha}^*(1) U_{\beta}^{eff}(1) \phi_{\alpha}(1) \quad (17)$$

is called a Coulomb integral (and is just the mean electron-electron repulsion energy in the orbital approximation). By using Eq. (11) it follows that $\varepsilon_{\alpha} = I_{\alpha} + J_{\alpha,\beta}$, which implies that $\varepsilon_{\alpha} + \varepsilon_{\beta} \neq E[\phi]$, cf. Eq. (16)!

Notice that to the extent that the orbitals are close to those of the helium ion, the integrals $I_{\alpha(\beta)}$ are approximately the corresponding energies of the ion in state $\alpha(\beta)$. To the extent that this is true, Eq. (13) shows that

$$E_{He^+} - E_{He} \approx -\varepsilon_{\alpha} \quad (18)$$

which is known as Koopmans' theorem. This can be extended to other problems and is useful in estimating the ionization energy in cases where the energy of the ion is not well known.

The Hartree-Fock equations give $E[\phi] = -2.8617 au$ compared with an exact answer of $-2.9037 au$ which is correct to 1.4%. The remaining $-0.0420 au$ of energy is known as the correlation energy and is equivalent to 110.24 kJ/mol which is about 25% of the energy in a C-H bond. Thus, as good as the orbital approximation is, one still often needs more accuracy for many applications.

2. Beyond Helium

We were able to ignore spin and the anti-symmetry of the wave-function for helium because we account for all of that in the spin wave-function (essentially by having an antisymmetric spin wave-function corresponding to one spin up and one spin down). Matters are more complicated for the rest of the periodic table. As was mentioned when we introduced spin and the symmetry requirements of the wave-function an elegant way to account for this is by writing the wave-function as a *Slater determinant*; namely,

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_1(2) & \cdot & u_1(N) \\ u_2(1) & u_2(2) & \cdot & u_2(N) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ u_N(1) & u_N(2) & \cdot & u_N(N) \end{vmatrix}, \quad (19)$$

were the u_i are the orbital functions, including spin. The factor of $1/\sqrt{N!}$ is the normalization constant assuming that the individual orbital functions are all normalized. By using the properties of determinants, it is easy to see that the Slater determinant changes sign if we interchange the particle labels on any pair of particles (i.e., this corresponds to interchanging two columns of the determinant) and vanishes if any pair of orbitals, u_i and u_j , are the same (i.e., the determinant will have two equal rows). This last property is just the Pauli exclusion principle.

As an example, consider helium; according to Eq. (19)

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [u_1(1)u_2(2) - u_2(1)u_1(2)], \quad (20)$$

which is obviously anti-symmetric. In addition, if we write $u_1(i) = \phi(i)|\uparrow\rangle_i$ and $u_2(i) = \phi(i)|\downarrow\rangle_i$, where $|\uparrow\rangle_i$ and $|\downarrow\rangle_i$ are the spin wave functions corresponding to a spin up and spin down state for electron i [†], Eq. (20) becomes

$$\Psi(1, 2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \frac{|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2}{\sqrt{2}} \quad (21)$$

which is equivalent to what we used above (for the ground state of He).

For atoms with more than two electrons, the Pauli exclusion principle requires that some of the space parts of the orbital functions be different. For example, for a closed shell atom containing $2N$ spin-paired electrons, we could write

$$\Psi(1, 2, \dots, 2N) = \frac{1}{\sqrt{2N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1)|\uparrow\rangle_1 & \phi_1(\mathbf{r}_2)|\uparrow\rangle_2 & \cdot & \phi_1(\mathbf{r}_{2N})|\uparrow\rangle_{2N} \\ \phi_1(\mathbf{r}_1)|\downarrow\rangle_1 & \phi_1(\mathbf{r}_2)|\downarrow\rangle_2 & \cdot & \phi_1(\mathbf{r}_{2N})|\downarrow\rangle_{2N} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \phi_N(\mathbf{r}_1)|\uparrow\rangle_1 & \phi_N(\mathbf{r}_2)|\uparrow\rangle_2 & \cdot & \phi_N(\mathbf{r}_{2N})|\uparrow\rangle_{2N} \\ \phi_N(\mathbf{r}_1)|\downarrow\rangle_1 & \phi_N(\mathbf{r}_2)|\downarrow\rangle_2 & \cdot & \phi_N(\mathbf{r}_{2N})|\downarrow\rangle_{2N} \end{vmatrix}, \quad (22)$$

[†]McQuarrie uses $\alpha(i)$ and $\beta(i)$ to denote the spin up and spin down states.

which corresponds to an electronic configuration in which each of the N orbitals is doubly occupied. For non-closed shell atoms, one typically uses a linear combination of Slater determinants corresponding to the possible electronic configurations consistent with the exclusion principle and with coefficients that are chosen to minimize the trial function's energy as usual.

In order to compute the trial function's energy, we need to be able to write out a general determinant, namely, for a matrix M

$$\det(M) = \sum_{i,j,k,\dots} \varepsilon^{i,j,k,\dots} M_{i,1} M_{j,2} M_{k,3} \dots, \quad (23)$$

where $\varepsilon^{i,j,k,\dots}$ is zero if any of the indices are the same, +1 if the indices can be obtained from an even number of permutations of 1,2,3... and -1 otherwise. You may have seen this in your linear algebra course, but if not, you needn't worry; you're not responsible for this part of the derivation. A nice exercise in combinatorics is to use Eq. (23) to obtain the normalization constant used for the Slater determinants.

Now the Hamiltonian for a multi-electron atom is just

$$H = \sum_i H_i + \sum_{i<j} \frac{1}{r_{i,j}}, \quad (24)$$

where

$$H_i \equiv -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}, \quad (25)$$

cf. Eq. (10).

When a Slater determinant is used to compute the energy bound, Eqs. (19) and (23) can be used to show that

$$E[\phi] = \sum_{i=1}^N 2I_i + \sum_{\substack{i,j \\ 1}}^N (2J_{i,j} - K_{i,j}), \quad (26)$$

where

$$I_i \equiv \int d\mathbf{r}_1 \phi_i^*(\mathbf{r}_1) H_1 \phi_i(\mathbf{r}_1), \quad (27a)$$

$$J_{i,j} \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2), \quad (27b)$$

and

$$K_{i,j} \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1). \quad (27c)$$

The first two integrals are the same as encountered above, cf. Eqs. (14) and (17). The last one is new and is called an *exchange integral*. Note that in the case where the orbital functions are the same, $K_{i,j} = J_{i,j}$ and the contribution to the energy bound is identical to what was found for helium.

Finally, if we vary the orbital functions as we did for helium and set the first order variation to zero, we obtain the following equations:

$$F_i \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i), \quad i = 1, \dots, N \quad (28)$$

where

$$F_i \equiv -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_j (2J_j - K_j) \quad (29)$$

with

$$J_j \phi_i(\mathbf{r}_1) \equiv \phi_i(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_j(\mathbf{r}_2) \quad (30)$$

and

$$K_j \phi_i(\mathbf{r}_1) \equiv \phi_j(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2), \quad (31)$$

F is known as the Fock operator.

Equations (28)–(31) generalize the Hartree-Fock equations obtained for helium above. They suffer from the same problem, namely, they are self-consistent equations, and the effective potential terms require us to know the orbitals. As with helium, this is dealt with iteratively. In practice, the Fock orbitals are expressed as linear combinations of Slater orbitals, with adjustable coefficients and exponential parameters which are then determined variationally. This scheme was developed by Roothan, and hence, the method is sometimes called the Hartree-Fock-Roothan method.

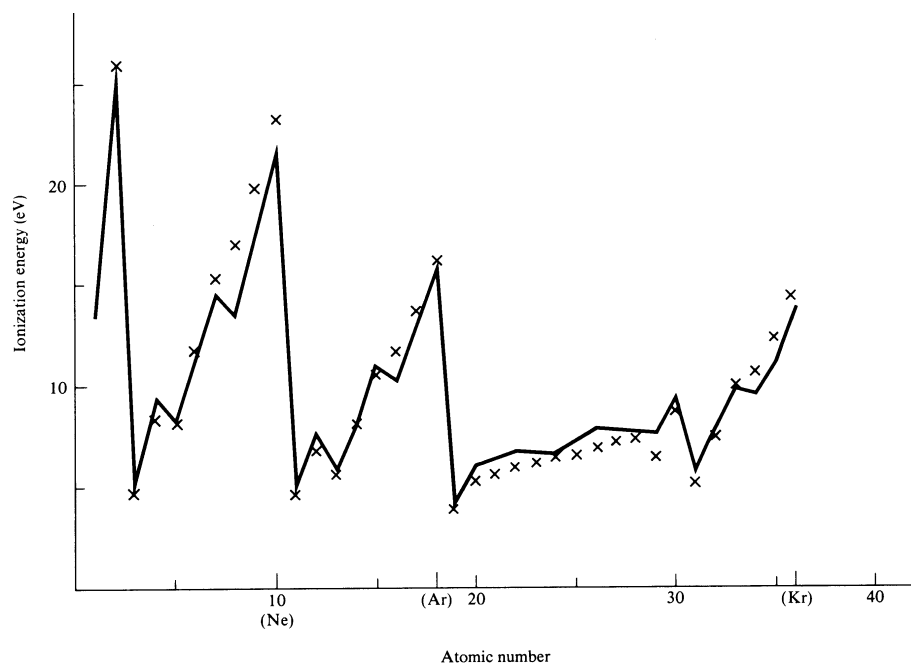


Figure 8-1. The ionization energies of neutral atoms of hydrogen through krypton plotted versus atomic number. The dots connected by straight lines are experimental data and the crosses are calculated according to Koopmans' theorem.

From McQuarrie, Quantum Chemistry, p 310.