9.7: The Self-Consistent Field Approximation (Hartree-Fock Method)

In this section we consider a method for finding the best possible one-electron wavefunctions that was published by Hartree in 1948 and improved two years later by Fock. For the Schrödinger equation to be solvable, the variables must be separable. The variables are the coordinates of the electrons. In order to separate the variables in a way that retains information about electron-electron interactions, the Coulomb repulsion term, e.g. $\dfrac{e^2}{4\pi\epsilon_0 r_{12}}$ for helium, must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in an average way. The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible one-electron functions.

The best possible one-electron wavefunctions, by definition, will give the lowest possible total energy for a multi-electron system when combined into a Slater determinant and used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the Hartree-Fock wavefunctions and the calculated total energy is the Hartree-Fock energy of the system. Application of the variational method to the problem of minimizing the total energy leads to the following set of Schrödinger-like equations called Hartree-Fock equations,

$$\hat{F}\varphi_i = \epsilon_i \varphi_i \tag{9.7.1}$$

where $\hat{F}$ is called the Fock operator. The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 9.7.1. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving 9.7.1 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of atomic and molecular orbitals. The full antisymmetrized wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{9.7.2}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. For electron 1 in helium, for example,

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \tag{9.7.3}$$

The second term in Equation 9.7.2, $\sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$, accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we'll call electron 1 throughout the following discussion), and the average field created by all the other electrons in the system is built in terms of the coordinates of a generic "other electron" (which we'll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals.

The operators $\hat{j}$ and $\hat{K}$ result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy, $\dfrac{e^2}{4\pi\epsilon_0 r_{12}}$, which in atomic units simplifies to $1/r_{12}$. Atomic units are used in the rest of this discussion to simplify the notation by removing fundamental constants.

The operators $\hat{J}$ and $\hat{K}$ are most conveniently defined by examining how they operate on a wavefunction, φ_i, which describes electron 1.

$$\hat{J}_j(1)\varphi_i(1) = \left[\int \varphi_i^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_i(1) \tag{9.7.4}$$

$$\hat{K}_j(1)\varphi_i(1) = \left[\int \varphi_j^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_j(1) \tag{9.7.5}$$

$\hat{J}$ is called a Coulomb operator. As mentioned above, the specific coordinates 1 and 2 are used here to underline the fact that $\hat{J}$ operates on a function of one electron in an orbital (here, electron 1 in φ_i using the results of an expectation value integral over the coordinates of a different electron (electron 2 in φ_j. The second electron can be described by the same spatial orbital (if i = j) or by a different spatial orbital (if i ≠ j). $\hat{J}$ takes the complex conjugate of an orbital describing electron 2, $\varphi_j^*(2)\varphi_j(2)$, multiplies by 1/r12, and integrates over the coordinates of electron 2. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)$ represents the charge distribution in space due to electron 2 in orbital j. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)\frac{1}{r_{12}}$ thus represents the potential energy at r_1 due to the charge density at r_2 where r_{12} is the distance between r_1 and r_2. Evaluation of the integral gives the total potential energy at r1 due to the overall, or average, charge density produced by electron 2 in orbital j. Since the part of the Fock operator containing $\hat{J}$ involves a sum over all the orbitals, and a multiplicative factor of 2 to account for the presence of two electrons in each orbital, solution of the Hartree-Fock equation produces a spatial orbital φ_i that is determined by the average potential energy or Coulomb field of all the other electrons.

The other operator under the summation in the Fock operator is $\hat{K}$, the exchange operator. Equation 9.7.5 reveals that this operator involves a change in the labels on the orbitals. In analogy with the Coulomb operator, $d\tau_2\varphi_j^*(2)\varphi_i(2)\frac{1}{r_{12}}$ represents the potential energy at r_1 due to the overlap charge distribution at r_2 associated with orbitals i and j. The integral is the potential energy due to the total overlap charge density associated with electron 2. The term exchange operator is used because the electron is exchanged between the two orbitals i and j. This overlap contribution to the charge density and potential energy is a quantum mechanical effect. It is a consequence of the wave-like properties of electrons. Wave-like properties means the electrons are described by wavefunctions. While difficult to understand in a concrete physical way, the effects of the exchange operator are important contributors to the total energy of the orbitals and the system as a whole. There is no classical analog to this interaction energy, and a classical theory is unable to calculate correctly the energies of multi-electron systems.

For the ground state of helium, electrons 1 and 2 are both described by spatial orbital φ_i, so N = 1 and the sum in Equation 9.7.2 includes only j = 1. Furthermore, since i = j = 1, the exchange and Coulomb integrals are identical in this case. As a result, the summation in the Fock operator takes a very simple form and the complete Fock operator for electron 1 in helium is given by

$$\hat{F}(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} + \hat{U}(1) \tag{9.7.6}$$

where $\hat{U}(1)$ is given by the summation in the Fock operator.

$$\hat{U}(1) = \sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2 \tag{9.7.7}$$

> ### Exercise 9.7.30
>
> Show that $\sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2$ by substituting the definitions of $\hat{J}(1)$ and $\hat{K}(1)$ for helium into the summation and evaluating the summation over the only occupied spatial orbital.

The interaction of electron 1 with electron 2 is averaged over all positions of electron 2 to produce $\hat{U}(1)$. By integrating over the coordinates of electron 2, the explicit dependence of the potential energy on the coordinates of electron 2 is removed. This approach makes it possible to account for the electron-electron repulsion in terms of the spatial distribution of the two electrons using only single-electron terms in the Fock operator and one-electron wavefunctions.

Since both electrons in helium are described by the same spatial wavefunction, the Fock equation given by 9.7.8 and 9.7.6 describes either electron equally well. Solving the Fock equation therefore will give us the spatial wavefunction and the one-electron energy associated with either of the electrons.

The energy of an electron in the spatial orbital φ_1 can be calculated either by solving the Fock equation

$$\hat{F}(1)\varphi_1(1) = \epsilon_1(1)\varphi_1(1) \tag{9.7.8}$$

or by using an expectation value expression.

$$\epsilon_1(1) = \int \varphi_1^*(r_1)\hat{F}(r_1)\varphi_1(r_1)d\tau \tag{9.7.9}$$

In order to solve either of these equations for the energy ϵ_1, we need to evaluate the potential energy function $\hat{U}(1)$ that is part of the Fock operator $\hat{F}(1)$. In order to evaluate $\hat{U}(1)$, the forms of all of the occupied spatial orbitals, $\varphi_i(2)$ must be known. For the simple case of helium, only the $\varphi_1(2)$ function is required, but for larger multi-electron systems, the forms of occupied orbitals ϵ_1, ϵ_2 etc. will be needed to specify $\hat{U}(1)$. For helium, we know that $\varphi_1(2)$ will have the same form as $\varphi_1(1)$, and the φ_1 functions can be obtained by solving the Fock equation (9-58). However, we are now caught in a circle because the Fock operator depends upon the φ_1 function.

The problem with solving Equation 9.7.8 to obtain the Fock orbitals is that the Fock operator, as we have seen, depends on the Fock orbitals. In other words, we need to know the solution to this equation in order to solve the equation. We appear to be between a rock and a hard place. A procedure has been invented to wiggle out of this situation. One makes a guess at the orbitals, e.g. one inserts some adjustable parameters into hydrogenic wavefunctions, for example. These orbitals are used to construct the Fock operator that is used to solve for new orbitals. The new orbitals then are used to construct a new Fock operator, and the process is repeated until no significant change in the orbital energies or functions occurs. At this end point, the orbitals produced by the Fock operator are the same as the orbitals that are used in the Fock operator to describe the average Coulomb and overlap (or exchange) potentials due to the electron-electron interactions. The solution therefore is self-consistent, and the method therefore is called the self-consistent field (SCF) method.

The objective of the Hartree-Fock method is to produce the best possible one-electron wavefunctions for use in approximating the exact wavefunction for a multi-electron system, which can be an atom or a molecule. So what kind of guess functions should we write to get the best possible one-electron wavefunctions? Answers to this question have spawned a huge area of research in computation chemistry over the past 40 years, including a Nobel Prize in 1998. In Chapter 10 we examine in detail the various alternatives for constructing one-electron wavefunctions from basis functions.

> **Exercise 9.7.31**
>
> Write a paragraph without using any equations that describes the essential features of the Hartree-Fock method. Create a block diagram or flow chart that shows the steps involved in the Hartree-Fock method.

The expectation value of the Fock operator gives us the energy of an electron in a particular orbital.

$$\epsilon_i(1) = \int d\tau_1 \varphi_i^*(1)\hat{F}(1)\varphi_i(1) \tag{9.7.10}$$

Using the definition of the Fock operator and representing the integrals with bracket notation gives

$$\epsilon_i(1) = \langle H_i^0 \rangle + \sum_{j=1}^{N}(2J_{ij} - K_{ij}) \tag{9.7.11}$$

where

$$\langle H_i^0 \rangle = \left\langle \varphi_i| -\frac{1}{2}\nabla_1^2|\varphi_i \right\rangle - \left\langle \varphi_i|\frac{Z}{r_1}|\varphi_i \right\rangle \tag{9.7.12}$$

The kinetic and potential energy terms in the operator $\hat{H}^0$, defined in Equation 9.7.3, are written here in atomic units for simplicity of notation. The sum involving the Coulomb and exchange integrals, J and K, accounts for the electron-electron interaction energy between the electron in orbital i and all the other electrons in the system. We now want to examine the meaning and the nature of the sum over all the orbitals in Equation 9.7.11.

> **Exercise 9.7.32**
>
> Describe the contributions to the orbital energy or single-electron energy *epsilon* in words as represented by Equation 9.7.11.

For the case j = k one has for $2J_{ik} - K_{ik}$

$$2\left\langle \varphi_i(1)\varphi_k(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_k(2)\right\rangle - \left\langle \varphi_i(1)\varphi_k(2)|\frac{1}{r_{12}}|\varphi_k(1)\varphi_i(2)\right\rangle \qquad (9.7.13)$$

The first term with the factor of 2 is the average potential energy due to the charge distribution caused by an electron in orbital i with the charge distribution caused by the two electrons in orbital k. The factor of 2 accounts for the two electrons in orbital k. The second term is the average potential energy due to the overlap charge distribution caused by electrons 1 and 2 in orbitals i and k. The second term appears only once, i.e. without a factor of 2, because only one of the electrons in orbital k has the same spin as the electron in orbital i and can exchange with it. The minus sign results from the wavefunction being antisymmetric with respect to electron exchange.

Exercise 9.7.33

Rewrite Equation 9.7.13 including the spin functions α and β explicitly for each electron. Since these two spin functions form an orthonormal set and factor out of the spatial integrals, show that that the exchange integral is zero if the two electrons have different spin.

For the case j = i one has

$$2\left\langle \varphi_i(1)\varphi_i(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_i(2)\right\rangle - \left\langle \varphi_i(1)\varphi_i(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_i(2)\right\rangle \qquad (9.7.14)$$

revealing that $J_{ii} = K_{ii}$, and $2J_{ii} - K_{ii} = J_{ii}$, which corresponds to the *Coulomb repulsion* between the two electrons in orbital i. Because these electrons have opposite spin, there is no exchange energy. This was the case for our helium example, above.

If the single-electron orbital energies are summed to get the total electronic energy, the Coulomb and exchange energies for each pair of electrons are counted twice: once for each member of the pair. These additional $2J - K$ contributions to the single-electron energies must be subtracted from the sum of the single-electron energies to get the total electronic energy, as shown in Equation 9.7.15. The factor of 2 accounts for the fact that two electrons occupy each spatial orbital, and ε_i, is the energy of a single electron in a spatial orbital.

$$E_{elec} = \sum_{i=1}^{N}\left[2\epsilon_i - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \qquad (9.7.15)$$

Exercise 9.7.34

Use Equations 9.7.11 and 9.7.15 to show that the total electronic energy also can be expressed in the following

$$E_{elec} = \sum_{i=1}^{N}\left[2\left\langle H_i^0\right\rangle - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \qquad (9.7.16)$$

$$E_{elec} = \sum_{i=1}^{N}\left(\epsilon_i + \left\langle H_i^0\right\rangle\right) \qquad (9.7.17)$$

forms.

Exercise 9.7.35

Write out all the terms in Equation 9.7.15 for the case of 4 electrons in 2 orbitals with different energies.

As we increase the flexibility of wavefunctions by adding additional parameters to the guess orbitals used in Hartree-Fock calculations, we expect to get better and better energies. The variational principle says that any approximate energy calculated using the exact Hamiltonian is an upper bound to the exact energy of a system, so the lowest energy that we calculate using the Hartree-Fock method will be the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single Slater determinant wavefunction. This limit is called the Hartree-Fock limit, the energy is the Hartree-Fock energy, the orbitals producing this limit are by definition the best single-electron orbitals that can be constructed and are called Hartree-Fock orbitals, and the Slater determinant is the Hartree-Fock wavefunction.

Contributors and Attributions

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")