Quantum Chemistry

Lecture 17

Extension of Hartree-Fock Theory
to Open Shell Systems

NC State University

Restricted Hartree-Fock

There are two basic types of Hartree-Fock (HF) calculations, restricted and unrestricted. These terms refer to the restrictions on the spin orbitals, α and β. In a restricted HF calculation the spin orbitals are confined to the same spatial orbital. In essence, this is the case of a closed shell molecule, in which all of the electrons are spin paired. Subsequently, we can consider the case of unpaired electrons, which is the province of unrestricted HF methods. These methods are essential for many metal ions and, of course, for radicals.

A restricted set of spin orbitals has the form:

$$\phi_i(q) = \begin{Bmatrix} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega) \end{Bmatrix}$$

where $\Psi(r)$ and $\alpha(\omega)$ or $\beta(\omega)$ are the spatial and spin parts.

Closed shell single determinant wave functions

The closed shell restricted ground state is given by

$$\Psi_0 = |\phi_1 \phi_2 \cdots \phi_{N-1} \phi_N >$$
$$= |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \psi_{N/2-1} \bar{\psi}_{N/2-1} \psi_{N/2} \bar{\psi}_{N/2} >$$

which represents a single-determinant wave function. The equations are:

$$f(q_1)\phi_i(q_1) = \varepsilon_i \phi_i(q_1)$$

- The spin orbital ϕ will either be spin up (α) or spin down (β). In a closed shell molecule the same result must be obtained for both α and β.

The

Closed shell Fock operator

Therefore, arbitrarily choosing α, the Fock equations become:

$$f(q_1)\psi_j(r_1)\alpha(\omega_1) = \varepsilon_i\psi_j(r_1)\alpha(\omega_1)$$

We left multiply by $\alpha^*(\omega_1)$

$$\left[\int d\omega_1\, \alpha^*(\omega_1) f(q_1)\alpha(\omega_1)\right]\psi_j(r_1) = \varepsilon_i\psi_j(r_1)$$

If we let $f(r_1)$ be the closed shell Fock operator

$$f(r_1) = \int d\omega_1\, \alpha^*(\omega_1) f(q_1)\alpha(\omega_1)$$

Integration over spin variables

$$f(r_1)\psi_j(r_1) = h(r_1)\psi_j(r_1)$$

$$+\sum_c \int d\omega_1 dq_2\, \alpha^*(\omega_1)\phi_c^*(q_2) r_{12}^{-1} \phi_c(q_2)\alpha(\omega_1)\psi_j(r_1)$$

$$-\sum_c \int d\omega_1 dq_2\, \alpha^*(\omega_1)\phi_c^*(q_2) r_{12}^{-1} \phi_c(q_1)\alpha(\omega_1)\psi_j(r_2)$$

$$= \varepsilon_j \psi_j(r_1)$$

A closed shell calculation implies an equal sum over the other electron. Thus, we should integrate over ω_2 as well.

Compact form for the closed shell Fock operator

When we carry out the integration over the spin variables, the last term vanishes due to spin orthogonality. Thus, we have

$$f(r_1)\psi_j(r_1) = h(r_1)\psi_j(r_1)$$

$$+2\sum_{c}^{N/2}\left[\int dr_2\, \psi_c^*(r_2) r_{12}^{-1} \psi_c(r_2)\right]\psi_j(r_1) - \sum_{c}^{N/2}\left[\int dr_2\, \psi_c^*(r_2) r_{12}^{-1} \psi_j(r_2)\right]\psi_c(r_1)$$

Finally, we can write the closed shell Fock operator in abbreviated form as:

$$f(r_1) = h(r_1) + 2\sum_{c}^{N/2} J_a(r_1) - \sum_{c}^{N/2} K_a(r_1)$$

Unrestricted Hartree Fock

Up to this point HF theory has been derived exclusively for closed shell (spin paired) systems. The restriction in "restricted Hartree Fock" refers to the requirement for spin pairing. For systems with unpaired electrons, there is a modification of the theory that removes the restriction. We will assume that we can treat the α and β spins separately. The so-called unrestricted HF (UHF) calculation starts with a one-electron operator for the α spins:

$$f^{\alpha}(1) = h(1) + \sum_{a}^{N^{\alpha}} [J_a^{\alpha} - K_a^{\alpha}] + \sum_{a}^{N^{\beta}} J_a^{\beta}$$

Unrestricted Hartree Fock

There can be no exchange between electrons of different spin so there is no exchange integral between α and β. There is a similar equation for the β spins.

$$f^{\beta}(1) = h(1) + \sum_{a}^{N^{\beta}} \left[J_a^{\beta} - K_a^{\beta} \right] + \sum_{a}^{N^{\alpha}} J_a^{\alpha}$$

The definition of the Coulomb and exchange integrals is the same as we have seen previously, with the addition of an index showing whether the operator can be applied to α or β spins.

Unrestricted Fock operator

The kinetic energy terms are:

$$h_{ii}^{\alpha} = \langle \phi_i^{\alpha} | h | \phi_i^{\alpha} \rangle \qquad h_{ii}^{\beta} = \langle \phi_i^{\beta} | h | \phi_i^{\beta} \rangle$$

The Coulombic interaction of two electrons of different spin are given by:

$$J_{ij}^{\alpha\beta} = J_{ij}^{\beta\alpha} = \langle \phi_i^{\alpha} \phi_i^{\alpha} | \phi_j^{\beta} \phi_j^{\beta} \rangle$$

The Coulomb terms between atoms that possess the same spin are given by:

$$J_{ij}^{\alpha\alpha} = \langle \phi_i^{\alpha} \phi_i^{\alpha} | \phi_j^{\alpha} \phi_j^{\alpha} \rangle$$

for α with an analogous equation for β. However, the exchange integrals exist only between atoms of the same spin.

$$K_{ij}^{\alpha\alpha} = \langle \phi_i^{\alpha} \phi_j^{\alpha} | \phi_j^{\alpha} \phi_i^{\alpha} \rangle$$

The Total Energy in Unrestricted Hartree Fock

The total unrestricted energy can be written as:

$$E_0 = \sum_a^{N^\alpha} h_{aa}^{\alpha}(1) + \sum_a^{N^\beta} h_{aa}^{\beta}(1)$$

$$+\frac{1}{2}\sum_a^{N^\beta}\sum_b^{N^\beta}\left[J_{ab}^{\beta} - K_{ab}^{\beta}\right] + \frac{1}{2}\sum_a^{N^\alpha}\sum_b^{N^\alpha}\left[J_{ab}^{\alpha} - K_{ab}^{\alpha}\right] + \sum_a^{N^\alpha}\sum_b^{N^\beta} J_{ab}^{\alpha\beta}$$

The occupation numbers N^α and N^β refer to the number of occupied orbitals of each spin. The factors of 1/2 in front of the third and fourth terms prevent double counting of the electron interactions.

Parallel SCF Equations in Unrestricted Hartree Fock

The introduction of a basis set involves two separate sums of atomic orbitals, one of each spin:

$$|\Psi_i^{\alpha}> = \sum_{\mu=1}^{N^{\alpha}} c_{\mu i}^{\alpha} \phi_{\mu} \qquad |\Psi_i^{\beta}> = \sum_{\mu=1}^{N^{\beta}} c_{\mu i}^{\beta} \phi_{\mu}$$

From this point forward, there will be two sets of equations leading to two separate Fock matrices, one for each spin.

$$\mathbf{H}^{\alpha}\mathbf{c}^{\alpha} = E\mathbf{S}^{\alpha}\mathbf{c}^{\alpha} \qquad \mathbf{H}^{\beta}\mathbf{c}^{\beta} = E\mathbf{S}^{\beta}\mathbf{c}^{\beta}$$