

Lecture #28: Hartree Fock Self-Consistent Field Method

I. Terminology

Orbitals - an orbital is a one-electron wave function usually designated by $\phi(r)$. Wavefunctions in general may involve several electrons $\Psi(r_1, r_2, r_3, \dots)$, and thus by orbital approximation: $\Psi(r_1, r_2, r_3, \dots) = \phi(r_1) \phi(r_2) \phi(r_3) \dots$

Slater Orbitals - $S_{nlm}(r, \mathbf{q}, \mathbf{f}) = N_{nl} r^{n-1} e^{-V r} Y_l^m(\mathbf{q}, \mathbf{f})$

$\zeta \neq Z/n$ but is arbitrary used to take into account **effective Z, due to shielding**. These functions may be utilized as basis set as for trial functions with ζ and n as a variational parameters: $\psi_{nlm} = S_{nlm}(r_1, \theta_1, \phi_1) S_{nlm}(r_2, \theta_2, \phi_2)$

Hartree-Fock Limit/approximation - If you use some flexible trial function $\Psi(r_1, r_2) = \phi(r_1) \phi(r_2)$ we will ultimately reach a limit of the best energy eigenvalue obtained if this is composed of orbitals: this is the Hartree-Fock limit. Differs from true energy by an amount called **correlation energy**.

Correlation Energy: Energy stabilization due to the interaction of electron spins. Hartree Fock calculations neglect this. Correlation Energy (CE) = $E_{\text{true}} - E_{\text{HF}}$ = a negative no.

II. Hartree-Fock Self Consistent Field Method

Overview of Hartree Fock Approximation:

<http://www.shodor.org/chemviz/overview/hfa.html>

Description of the HF-SCF Method

This is an approximation that seeks to optimize a polyelectronic wave function utilizing only (1) **orbital wave functions** and (2) these **functions need not be restricted** to any family of functions. Once the optimized orbitals are obtained individually, the total wavefunction is obtained (the product of orbitals). Finally the variational method is applied to \mathbf{H} whose e-e repulsion term depends on the optimized orbitals utilizing the total wave function to obtain energy eigenvalues. For convenience we may let the orbitals be represented by a linear superposition of slater orbitals. This is a reiterative procedure that terminates when the coefficients of the orbital in question barely change (converge), i.e. when the orbitals are self-consistent.

Hartree Fock SCF procedure for a polyelectronic atom in general

1. Define trial wavefunction via orbital approximation: $Y(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = f(\mathbf{r}_1) f(\mathbf{r}_2) \dots f(\mathbf{r}_n)$

usually with each $\phi(r_j) = \sum c_i S_{nlm}(n_i, \zeta_i)$ thus variational parameters (c_i, n_i, ζ_i)

2. Compute many $V_j^{\text{eff}}(r_j)$ (**mean repulsion field** for the jth electron) by the sum of the electron-electron pairwise potentials:

$$V_j^{\text{eff}}(r_j) = \sum_k \iiint \sin q \, dq d\mathbf{f} \, \mathbf{f}_k^*(r_k) \frac{e^2}{4\pi\epsilon_0 r_{jk}} \mathbf{f}_k(r_k) r_k^2 dr_k \quad (2)$$

This is the weighted average of the potential experienced by electron j from electron k where the

weights are $\mathbf{f}_k^*(r_k) \mathbf{f}_k(r_k) r_k^2 dr_k$

Note $r_{jk} = \sqrt{(r_j^2 + r_k^2 - 2r_j r_k \cos \mathbf{q})}$ so we need not fix r_{jk} distance since we integrate over θ, r_k to get an expression in r_j .

$$\int \frac{r_k^2}{r_{jk}} dr_k = \int \frac{r_k^2}{\sqrt{r_k^2 - 2r_j r_k \cos \mathbf{q} + r_j^2}} dr_k \text{ may be evaluated by formulae}$$

2.261 & 2.264 of "Table of Integrals, Series, and Products" by I.S. Gradshteyn/I.M. Ryzhik 1980:

$$R = cx^2 + bx + a = r_k^2 - 2r_j r_k \cos \mathbf{q} + r_j^2 \rightarrow c=1, x=r_k, b=-2r_j \cos \mathbf{q}, a=r_j^2$$

$$2.261 \int \frac{dx}{\sqrt{R}} = \int \frac{dr_k}{\sqrt{cx^2 + bx + a}} = \int \frac{dr_k}{\sqrt{r_k^2 + (-2r_j \cos \mathbf{q})r_k + r_j^2}} = \frac{1}{\sqrt{c}} \ln(2\sqrt{cR} + 2cx + b) \text{ for } c > 0$$

$$2.264 \int \frac{x^2 dx}{\sqrt{R}} = \int \frac{r_k^2 dr_k}{\sqrt{r_k^2 + (-2r_j \cos \mathbf{q})r_k + r_j^2}} = \left(\frac{x}{2c} - \frac{3b}{4c^2} \right) \sqrt{R} + \left(\frac{3b}{8c^2} - \frac{a}{2c} \right) \int \frac{dx}{\sqrt{R}}$$

3. Solve many 1-electron Schrodinger equations via variational method and secular determinant (Lect 23) for all j^{th} electrons to obtain improved orbitals $\mathbf{f}(\mathbf{r}_j)$ with new (c_i, n_i, ζ_i) specified (usually use variation method, i.e. expectation value in ϕ_j of resulting \mathbf{H}_j).

$$\mathbf{H}_j = \left[-\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{Ze^2}{4\pi\epsilon_0 r_j} + V_j^{\text{eff}}(r_j) \right]$$

$$\langle E \rangle = \text{approximate Energy in } \mathbf{f}_j \text{ basis} = \frac{\int \mathbf{f}_j^* \mathbf{H}_j \mathbf{f}_j dt}{\int \mathbf{f}_j^* \mathbf{f}_j dt}$$

$$\left(\frac{\partial E_{\text{apprx}}}{\partial c_1} \right) = 0 \quad \left(\frac{\partial E_{\text{apprx}}}{\partial c_2} \right) = 0 \quad \left(\frac{\partial E_{\text{apprx}}}{\partial c_3} \right) = 0$$

With these new values of c_1, c_2, c_3, \dots we get $\{\phi_j\}$ orbitals: $\{\phi(r_1), \phi(r_2), \phi(r_3), \dots, \phi(r_j), \phi(r_n)\}$

4. REITERATE: Keep cycling through steps 2-3 until the output function $\phi(r_j)$ and previous input function $\phi(r_j)$ are sufficiently close or *self-consistent*. (coefficients c_1, c_2, \dots don't change)

5. Once optimization of orbitals achieved compute the total energy of the energy level by adding the orbital energies computed in parts 2-4. This will need to be corrected for the redundant repulsion energies.