

The self-consistent field equations (SCF)

Here's a derivation of the SCF equations, which turn 1 Schrödinger equation for N electrons into N Schrödinger equations for 1 electron each, to be iterated. This process allows us to optimize the orbital functions $\phi_i=f_i$ to yield the lowest variational energy. You do not need to study this for the exam. The idea of SCF: for an N degree of freedom Hamiltonian in variables x_i , find the best product wavefunction $\varphi = A_N \prod f_i(x_i)$. The procedure of SCF: by the variational principle, the exact energy E_0 will always be lower than the trial energy $E_\varphi = \langle \varphi | H | \varphi \rangle$, so the best φ can be found by letting $\partial E / \partial \varphi = 0$. This yields N 1-dimensional equations for each f_i , which can be iterated until the f_i converge to self-consistency. What follows below is for those who can't resist the full mathematics, and already know the basics of Lagrange multipliers.

In the specific Hartree-Fock case, $E_0 \leq \langle \varphi | H | \varphi \rangle$ for any determinantal φ consisting of orthonormal f_i 's. As the f_i 's are varied, they may lose orthonormality $\langle f_i | f_j \rangle = \delta_{ij}$, so it must be enforced as a Lagrange-multiplier: if $y(x_i)$ is to be minimized subject to constraints $z_k(x_i)=0$, then one must minimize $y(x_i) - \sum_k \lambda_k z_k(x_i)$, where $\{\lambda\}$ is a set of Lagrange multipliers (appendix A). In this specific case,

$$\mathcal{F} = \langle \varphi | H_e | \varphi \rangle - \sum_{i,j} \lambda_{ij} (\langle f_i | f_j \rangle - \delta_{ij}) \quad 7-45$$

must therefore be minimized. Taking a small variation $\delta \mathcal{F}$ in \mathcal{F} due to variations δf_i in the functions,

$$\delta \mathcal{F} = \sum_i \delta \langle f_i | h^{(1)} | f_i \rangle + \sum_{i,j < i} \delta \langle f_i f_j | h^{(2)} | f_i f_j \rangle - \delta \langle f_i f_j | h^{(2)} | f_j f_i \rangle - \sum_{i,j} \lambda_{ij} \delta \langle f_i | f_j \rangle \quad 7-46$$

the first three terms arise from the one and two electron integrals in E_{HF} , while the last assures orthonormality. Using the product rule (only the one electron operator complex conjugate is shown explicitly),

$$\begin{aligned} &= \sum_i \langle \delta f_i | h^{(1)} | f_i \rangle + \langle f_i | h^{(1)} | \delta f_i \rangle + \sum_{i,j < i} \{ \langle \delta f_i f_j | h^{(2)} | f_i f_j \rangle + \langle f_i \delta f_j | h^{(2)} | f_i f_j \rangle + c.c. \} \\ &\quad - \{ \langle \delta f_i f_j | h^{(2)} | f_j f_i \rangle + \langle f_i \delta f_j | h^{(2)} | f_j f_i \rangle - \sum_{i,j} \lambda_{ij} \{ \langle \delta f_i | f_j \rangle + \langle f_i | \delta f_j \rangle \}. \end{aligned} \quad 7-47$$

Diagonal $J_{ii} - K_{ii}$ terms cancel, so one can sum over all j and divide by two:

$$\begin{aligned} &= \sum_i \langle \delta f_i | h^{(1)} | f_i \rangle + cc + \frac{1}{2} \sum_{i,j} \{ \langle \delta f_i f_j | h^{(2)} | f_i f_j \rangle + \langle f_i \delta f_j | h^{(2)} | f_i f_j \rangle + cc \} \\ &\quad - \{ \langle \delta f_i f_j | h^{(2)} | f_j f_i \rangle + \langle f_i \delta f_j | h^{(2)} | f_j f_i \rangle + cc \} - \sum_{i,j} \lambda_{ij} \{ \langle \delta f_i | f_j \rangle + \langle f_i | \delta f_j \rangle \}. \end{aligned} \quad 7-48$$

The sum is over all i and j, so the second terms in curly brackets simply replicate the first. Furthermore, $\langle f_i | \delta f_j \rangle = \langle \delta f_j | f_i \rangle^*$, and $\lambda_{ij} = \lambda_{ji}^*$ if we allow only *real* variations in \mathcal{F} (it is after all an energy functional). The last term is therefore also just a c.c. of the preceding term:

$$= \sum_i \langle \delta f_i | h^{(1)} | f_i \rangle + \sum_{i,j} \{ \langle \delta f_i f_j | h^{(2)} | f_i f_j \rangle - \langle \delta f_i f_j | h^{(2)} | f_j f_i \rangle \} - \sum_{i,j} \lambda_{ij} \langle \delta f_i | f_j \rangle + c.c. \quad 7-49$$

By requiring $\delta \mathcal{F}$ to be real, the matrix λ must therefore be Hermitian. Pulling $\langle \delta f_i |$ out of the entire expression, we finally obtain

$$\delta F = \sum_i \langle \delta f_i | \{ h^{(1)} | f_i \rangle + \sum_{j=1}^N \langle f_j | h^{(2)} | f_j \rangle | f_i \rangle - \langle f_j | h^{(2)} | f_i \rangle | f_j \rangle - \lambda_{ij} | f_j \rangle \} + c.c. = 0. \quad 7-50$$

$\delta F = 0$ at the minimum. If it is to remain zero for arbitrary infinitesimal variations $\langle \delta f_i |$, the term in curly brackets must vanish (and its complex conjugate also, but this contains no new information). The result is the Hartree-Fock SCF equation

$$\{ h^{(1)} + \sum_{j=1}^N \hat{J}_j - \hat{K}_j \} | f_i(1) \rangle = \sum_{j=1}^N \lambda_{ij} | f_j(1) \rangle \quad 7-51$$

or

$$\hat{F} | f_i \rangle = \sum_{j=1}^N \lambda_{ij} | f_j \rangle, \quad 7-52$$

where F is the Fock operator. Explicitly, the coulomb and exchange operators are

$$\hat{J}_j f_i(1) = \left\{ \int d\tau_2 f_j^*(2) \frac{e^2}{r_{12}} f_j(2) \right\} f_i(1) \quad 7-53$$

and

$$\hat{K}_j f_i(1) = \left\{ \int d\tau_2 f_j^*(2) \frac{e^2}{r_{12}} f_i(2) \right\} f_j(1). \quad 7-54$$

The exchange operator K switches the functions of f_i and f_j in the integration, as its name suggests.

In matrix notation,

$$F(\mathbf{f}) \cdot \mathbf{f} = \Lambda \mathbf{f}. \quad (\Lambda \text{ is Hermitian.}) \quad 7-55$$

Applying a unitary transformation on both sides (U^\dagger on left and an inserted identity)

$$U^\dagger F U U^\dagger \mathbf{f} = U^\dagger \Lambda U U^\dagger \mathbf{f} \text{ or} \\ F' \mathbf{f}' = \varepsilon \mathbf{f}'. \quad 7-56$$

where $F' = U^\dagger F U$ and $\mathbf{f}' = U^\dagger \mathbf{f}$ in the new basis set. We can choose the matrix U such that ε is diagonal in the new basis \mathbf{f}' . The SCF equation then has the form of a standard eigenvalue problem. Very conveniently, the form of $F' = U^\dagger (h^{(1)} + \sum J_i - K_i) U$ is the same as the form of F . The reason: $h^{(1)}$, J_i and K_i commute with U :

i) Clearly $h^{(1)'} = U^\dagger h^{(1)} U = U^\dagger U h^{(1)} = h^{(1)}$ since $h^{(1)}$ does not depend on the f_i ;

$$\text{ii) } \sum_k \hat{J}'_k = \sum_k \langle f'_k | h^{(2)} | f'_k \rangle = \sum_k \langle f_k | U h^{(2)} U^\dagger | f_k \rangle + \sum_k \langle f_k | U U^\dagger h^{(2)} | f_k \rangle \\ = \sum_k \langle f_k | h^{(2)} | f_k \rangle = \sum_k \hat{J}_k$$

since $h^{(2)}$ is independent of the basis functions f_k .

$$\text{iii) } \sum_k \hat{K}'_{k-k} = \sum_k \langle f'_k | h^{(2)} | f'_n \rangle_{-k} = \sum_k \langle f_k | U h^{(2)} U^\dagger | f_n \rangle_{-k} + \sum_k \langle f_k | U U^\dagger h^{(2)} | f_n \rangle_{-k} \\ = \sum_k \langle f_k | h^{(2)} | f_n \rangle_{-k} = \sum_k \hat{K}_{k-k}$$

since $h^{(2)}$ is independent of the basis functions f_k . In iii), a transformation U must also be applied to the placeholder $_$.

Thus, the Fock operator written in terms of the \mathbf{f}' acting on the \mathbf{f}' yields the same result as the Fock operator written in terms of the \mathbf{f} acting on the \mathbf{f} . Dropping the 'primes, we therefore write the final form of the Fock equation as:

$$\hat{F}|i\rangle = \varepsilon_i |i\rangle \quad 7-57$$

where $|i\rangle$ is a set of functions diagonalized by U^\dagger , and ε_i can now be recognized as the energy for the orbital $|i\rangle$ (or f_i). Although it looks like a simple eigenvalue problem, the Fock operator *depends* on its solution functions $|i\rangle$, and the HF-SCF equation is a set of N integro-differential equations which can be solved iteratively:

- i) guess the $|i\rangle$'s (see section c)
- ii) calculate $\hat{F}(|i\rangle)$ using the newest $|i\rangle$'s
- iii) solve the HF equations to obtain new ε_i and $|i\rangle$
- iv) if the new ε_i and $|i\rangle$ have not converged, repeat ii), else stop.

When self-consistency has been reached, $|i\rangle$ are the "nonlinear" eigenfunctions of the Fock operator, which is now diagonalized. Notice that E_{HF} , the molecular energy we seek, is not simply the sum of the orbital energies ε_i :

$$\begin{aligned} \sum_i \varepsilon_i &= \sum_i \langle i|\hat{F}|i\rangle = \sum_i \langle ih^{(1)}|i\rangle + \sum_{i,j} \langle ij|h^{(2)}|ij\rangle - \langle ij|h^{(2)}|ji\rangle \\ &= E_{HF} + \frac{1}{2} \sum_{i,j} \langle ij|h^{(2)}|ij\rangle - \langle ij|h^{(2)}|ji\rangle \end{aligned} \quad 7-58$$

Adding up orbital energies counts the electronic repulsion terms twice. Therefore

$$E^{HF} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i,j} \langle ij|h^{(2)}|ij\rangle - \langle ij|h^{(2)}|ji\rangle \quad 7-59$$

Similarly, the restricted HF energy yields

$$\hat{F} = h^{(1)} + \sum_{k=1}^{N/2} 2\hat{J}_k - \hat{K}_k \Rightarrow 2 \sum \varepsilon_\ell = 2 \sum \langle \ell|\hat{F}|\ell\rangle + 2 \sum_{\ell,k}^{N/2} \langle \ell k|h^{(2)}|\ell k\rangle - \langle \ell k|h^{(2)}|k \ell\rangle \quad 7-60$$

and

$$E_{HF} = 2 \sum_{\ell}^{N/2} \varepsilon_\ell - \sum_{\ell,k}^{N/2} 2 \langle \ell k|h^{(2)}|\ell k\rangle - \langle \ell k|h^{(2)}|k \ell\rangle. \quad 7-61$$

What exactly is the meaning of the individual orbital energies? If we remove one electron from its orbital,

$$E_{N-1}^{HF} = \sum_{i \neq m} \langle ih^{(1)}|i\rangle + \frac{1}{2} \sum_{i \neq m} \sum_{j \neq m} \langle ij|h^{(2)}|ij\rangle - \langle ij|h^{(2)}|ji\rangle; \quad 7-62$$

therefore

$$E_{N-1}^{HF} - E_N^{HF} = - \langle mh^{(1)}|m\rangle - \sum_j \langle mj|h^{(2)}|mj\rangle + \langle mj|h^{(2)}|jm\rangle = -\varepsilon_m. \quad 7-63$$

Thus, the orbital energies ε_i ; are just the negative HF ionization potentials (Koopman's theorem). Note that the same HF orbitals are used for the molecule and ion. In reality, the ion has its own optimized orbitals that lie lower in energy, so Koopman's IP is an upper limit to the real IP.