Hartree-Fock method

Based on the Ritz variational principle:

$|\Psi\rangle$ - trial (variational) wave function. Should be as rich and realistic as possible

$$\delta \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 0$$

Energy of the system is minimized

In the Hartree-Fock method, the trial wave function is the particle-number conserving product state. That's it!

$$|\tilde{Z}\rangle = \exp\left(\sum_{ph} \tilde{Z}^*_{ph} a^+_p a_h\right) a^+_1 \dots a^+_A |0\rangle$$

(M-A)A complex variables (<< size of the Hilbert space)

$$\delta E_{\mathrm{HF}} = 0 \qquad E_{\mathrm{HF}} \equiv \frac{\langle \tilde{Z} | \hat{H} | \tilde{Z} \rangle}{\langle \tilde{Z} | \tilde{Z} \rangle}$$

variation: $\delta \equiv \sum_{ph} \delta \tilde{Z}^*_{ph} \frac{\partial}{\partial \tilde{Z}^*_{ph}}$

$$|\delta \tilde{Z}\rangle \equiv \delta |\tilde{Z}\rangle$$

Hartree-Fock equations

Let us consider two-body Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V} = \sum_{\mu\nu} T_{\mu\nu} a_\mu^+ a_\nu + \tfrac{1}{4} \sum_{\mu\lambda\nu\pi} V_{\mu\lambda\nu\pi} a_\mu^+ a_\lambda^+ a_\pi a_\nu$$

The corresponding HF energy is

$$E_{\mathrm{HF}} = \sum_{\mu\nu} T_{\mu\nu} \rho_{\nu\mu} + \frac{1}{2} \sum_{\mu\lambda\nu\pi} V_{\mu\lambda\nu\pi} \rho_{\nu\mu} \rho_{\pi\lambda}$$

Density matrix of the product state $|\tilde{Z}\rangle$

The variation of the HF energy can be written as:

$$\delta E_{\mathrm{HF}} = \frac{\langle \tilde{Z} | \hat{H} | \delta_\perp \tilde{Z} \rangle}{\langle \tilde{Z} | \tilde{Z} \rangle}$$

where

$$|\delta_\perp \tilde{Z}\rangle \equiv |\delta \tilde{Z}\rangle - \frac{\langle \tilde{Z} | \delta \tilde{Z} \rangle}{\langle \tilde{Z} | \tilde{Z} \rangle} |\tilde{Z}\rangle$$

Note that

$$\langle \tilde{Z} | \delta_\perp \tilde{Z} \rangle = 0$$

Since

$$|\delta\tilde{Z}\rangle = \sum_{ph} \delta\tilde{Z}^*_{ph} a^+_p a_h |\tilde{Z}\rangle$$

one gets

$$|\delta_\perp\tilde{Z}\rangle = \sum_{ph} \delta\tilde{Z}^*_{ph} \left(a^+_p a_h - \rho_{hp}\right) |\tilde{Z}\rangle$$

In the HF minimum

$$\langle\tilde{Z}_0|\hat{H}\left(a^+_p a_h - \rho_{0hp}\right)|\tilde{Z}_0\rangle = 0$$

The above condition is equivalent to

$$\langle\tilde{Z}_0|\hat{H}a^+_\mu a_\nu|\tilde{Z}_0\rangle - \rho_{0\nu\mu}\langle\tilde{Z}_0|\hat{H}|\tilde{Z}_0\rangle = 0$$

which does not depend on the definition of the reference state. Using the Wick's theorem, the above expression can be written as:

$$\langle\tilde{Z}|\hat{H}a^+_\mu a_\nu|\tilde{Z}\rangle - \rho_{\nu\mu}\langle\tilde{Z}|\hat{H}|\tilde{Z}\rangle = (\rho h(1-\rho))_{\nu\mu}$$

where

$$h_{\mu\nu} \equiv T_{\mu\nu} + \Gamma_{\mu\nu}$$

Single-particle (HF) Hamiltonian

$$\Gamma_{\mu\nu} \equiv \sum_{\lambda\pi} V_{\mu\lambda\nu\pi}\rho_{\pi\lambda}$$

Single-particle potential

Γ is an average one-body potential that depends on the density matrix

Of course

$$\Gamma^+ = \Gamma,$$
$$h^+ = h$$

The variational equation is equivalent to

$$(\rho_0 h_0 (1-\rho_0))_{\nu\mu} = 0$$

All particle-hole matrix elements of HF hamiltonian in the HF state must vanish!

or

$$[h_0, \rho_0] = 0$$

HF equations

$$[h_0(\rho_0), \rho_0] = 0$$

self-consistent s.p. hamiltonian

self-consistent density matrix

In the canonical basis:

$$\rho_0 = \begin{bmatrix} 1 & & 0 & \\ & 1 & & \\ 0 & & 0 & \\ & & & 0 \end{bmatrix}$$

A x A

$$\bar{h}_{0hp} = 0$$

In the canonical basis, the HF hamiltonian can be written as

$$\bar{h}_{0\mu\nu} = \epsilon_{0\mu}\delta_{\mu\nu}$$

$$\hat{h}_0 \equiv \sum_{\mu\nu} h_{0\mu\nu} a^+_\mu a_\nu$$

$$\hat{\Gamma}_0 \equiv \sum_{\mu\nu} \Gamma_{0\mu\nu} a^+_\mu a_\nu$$

$$\hat{h}_0 = \hat{T} + \hat{\Gamma}_0$$

$$\hat{h}_0 |\lambda\rangle = \epsilon_{0\lambda}|\lambda\rangle \quad \text{for} \quad |\lambda\rangle = \bar{a}^+_\lambda |0\rangle$$

$$\hat{h}_0 \bar{a}^+_{\lambda_1} \ldots \bar{a}^+_{\lambda_A} |0\rangle = E_{0\lambda_1 \ldots \lambda_A} \bar{a}^+_{\lambda_1} \ldots \bar{a}^+_{\lambda_A} |0\rangle$$

$$E_{0\lambda_1 \ldots \lambda_A} = \sum_{h=1}^{A} \epsilon_{0\lambda_h}$$

h is an independent-particle hamiltonian

$$E_{\mathrm{HF}} = \frac{1}{2}\mathrm{Tr}(\hat{T}\rho) + \frac{1}{2}\mathrm{Tr}(\hat{h}\rho)$$

$$E_{\mathrm{HF}} = \frac{1}{2}\sum_{h=1}^{A} (T_{hh} + \epsilon_h)$$

The lowest (HF) energy corresponds to occupation of A lowest canonical states, but is is not the sum of A-lowest s.p. energies!