

Hartree approximation

N-electron wavefunction constructed from the product of N one electron wavefunctions

$$\psi^H(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

$$H\psi^H = E\psi^H$$
$$H = \sum_{i=1}^N h(i) \quad \leftarrow \quad \text{Effective one electron Hamiltonian}$$

$$h(i)\chi_j(\mathbf{x}_i) = \epsilon_j\chi_j(\mathbf{x}_i)$$

$$E = \epsilon_i + \epsilon_j + \dots + \epsilon_k$$

Mean field approach: single particle in an effective field

Drawback : Fermionic nature of electrons is not considered in Hartree approximation

$$|\psi^H(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$$
$$= |\chi_i(\mathbf{x}_1)|^2 d\mathbf{x}_1 |\chi_j(\mathbf{x}_2)|^2 d\mathbf{x}_2 \dots |\chi_k(\mathbf{x}_N)|^2 d\mathbf{x}_N$$

Uncorrelated probabilities

Electrons are distinguishable !!!!!

Slater determinant

Electron 1 in χ_i and electron 2 in χ_j

$$\psi_{12}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)$$

Electron 2 in χ_i and electron 1 in χ_j

$$\psi_{21}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)$$

Take a linear combination

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)]$$

Ensures that $\psi(\mathbf{x}_1, \mathbf{x}_2) = -\psi(\mathbf{x}_2, \mathbf{x}_1)$

If both electrons occupy the same orbital, the wavefunction is zero
: **Pauli exclusion principle**

For a 2 electron system, the wave function is

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

Slater determinant

For an N electron system, the wave function is

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \dots & \dots & \chi_k(\mathbf{x}_1) \\ \cdot & \dots & \dots & \cdot \\ \cdot & \dots & \dots & \cdot \\ \cdot & \dots & \dots & \cdot \\ \chi_i(\mathbf{x}_N) & \dots & \dots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

Rows: electrons

Columns: orbitals

Coulomb and Fermi correlation

A 2-electron Slater determinant

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle$$

Case I: 2 electrons with opposite spins

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2)$$

Probability of finding electron 1 in $d\mathbf{r}_1$ and electron 2 in $d\mathbf{r}_2$ simultaneously is obtained after integrating out the spin degree of freedom is

$$\text{For } \psi_1 = \psi_2 \quad P(\mathbf{r}_1, \mathbf{r}_2) = |\psi_1(\mathbf{r}_1)|^2|\psi_1(\mathbf{r}_2)|^2$$

$$\text{For } \mathbf{r}_1 = \mathbf{r}_2 \quad P(\mathbf{r}_1, \mathbf{r}_1) \neq 0$$

(Coulomb correlation, neglected in HF theory)

Case II: 2 electrons with same spins

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\beta(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2)$$

$$P(\mathbf{r}_1, \mathbf{r}_1) = 0 \quad (\text{Fermi correlation, included in HF theory})$$

Summary: Single Slater determinant (HF), electrons with parallel spins are correlated whereas electrons with opposite spins are uncorrelated.

Hartree-Fock approximation

The wave function is a Slater determinant Φ_{SD}

Goal: find out the best Slater determinant that gives the lowest energy

Evaluate the integral

$$\begin{aligned} E_{HF} &= \langle \Phi_{SD} | \hat{H} | \Phi_{SD} \rangle \\ &= \sum_{i=1}^N (i | \hat{h}_i | i) + \frac{1}{2} \sum_i^N \sum_j^N [(ii | jj) - (ij | ji)] \end{aligned}$$

One electron term

$$(i | \hat{h}_i | i) = \int \chi_i^*(\mathbf{x}_1) \left[-\frac{1}{2} \nabla^2 - \sum_A^M \frac{Z_A}{|\mathbf{r}_{iA}|} \right] \chi_i(\mathbf{x}_1) d\mathbf{x}_1$$

Two electron terms

Coulomb intergral (direct term)

$$(ii | jj) = \int \int |\chi_i(\mathbf{x}_1)|^2 \frac{1}{|\mathbf{r}_{12}|} |\chi_j(\mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2$$

Exchange intergral

$$(ij | ji) = \int \int \chi_i(\mathbf{x}_1) \chi_j^*(\mathbf{x}_1) \frac{1}{|\mathbf{r}_{12}|} \chi_j(\mathbf{x}_2) \chi_i^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$E_{HF} = E[\{\chi_i\}]$$

Variational freedom → choice of orbitals

Introduce Lagrange multipliers, leads to Hartree-Fock equation

$$\hat{f}\chi_i = \epsilon_i \chi_i$$

↑
Fock operator

$$\hat{f} = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{|\mathbf{r}_{iA}|} + V_{HF}(i)$$

↗
Hartree-Fock potential

HF potential: average potential experienced by i^{th} electron

$$V_{HF}(i) = \sum_j^N [\hat{J}_j(\mathbf{x}_1) - \hat{K}_j(\mathbf{x}_1)]$$

Coulomb term

$$\hat{J}_j(\mathbf{x}_1) = \int |\chi_j(\mathbf{x}_2)|^2 \frac{1}{|\mathbf{r}_{12}|} d\mathbf{x}_2$$

Exchange term

$$\hat{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \int \chi_j^*(\mathbf{x}_2) \frac{1}{|\mathbf{r}_{12}|} \chi_i(\mathbf{x}_2) d\mathbf{x}_2 \chi_j(\mathbf{x}_1)$$

Exchange term exists only for the electrons with parallel spin. In case of antiparallel spins, the integral is zero as spin functions are orthogonal

Hartree-Fock method is **self interaction free**.

Solve the HF equation by self-consistent field procedure

Interpretation of HF orbital energies

Koopman's theorem: HF orbital energy is an approximation of minus the ionization energy associated with the removal of an electron from that particular orbital χ_i

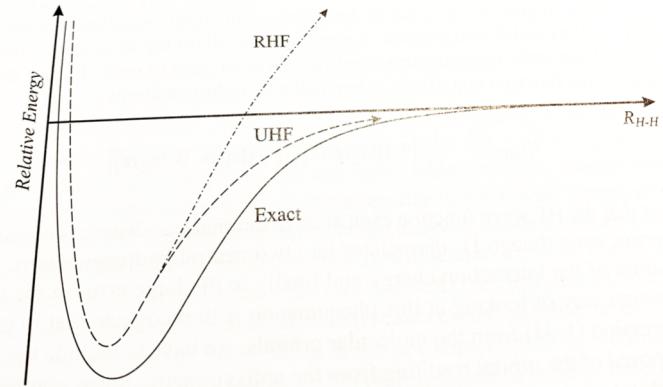
$$\epsilon_i = E_N - E_{N-1}^i = -IE(i)$$

Electron correlation (H_2 molecule)

Correlation is neglected in HF.

Correlation energy:

$$E_C^{HF} = E_0 - E_{HF}$$



Dynamical correlation: short-ranged effect, electron movement

Static correlation: arising from other Slater determinants

At equilibrium separation, correlation error $\sim 0.04 E_h$

At large separation, error $\sim 0.25 E_h$

(not due to dynamical correlation)

$$\Phi_{GS} = \frac{1}{\sqrt{2}} \det \{ \sigma_g(\mathbf{r}_1) \alpha(\omega_1) \sigma_g(\mathbf{r}_2) \beta(\omega_2) \}$$
$$\sigma_g = \frac{1}{\sqrt{2}} \{ 1s_L + 1s_R \}$$

Expand

$$\Phi_{GS} = \frac{1}{2} [\det \{ 1s_L \alpha 1s_R \beta \} + \det \{ 1s_L \beta 1s_R \alpha \} \\ + \det \{ 1s_L \alpha 1s_L \beta \} + \det \{ 1s_R \alpha 1s_R \beta \}]$$

All have equal probabilities !!!!

OK for equilibrium separation, not OK for large separation
where the ionic contribution should be zero

In the dissociation limit,

$$\Phi_{DISS} = \frac{1}{\sqrt{2}} [det\{1s_L\alpha 1s_R\beta\} + det\{1s_L\beta 1s_R\alpha\}]$$

We have to include determinant composed of orbitals resulting from antisymmetric linear combination of atomic orbitals

$$\sigma_u = \frac{1}{\sqrt{2}} \{1s_L - 1s_R\}$$

The antisymmetric Slater determinant

$$\Phi_{AS} = \frac{1}{\sqrt{2}} det\{\sigma_u(\mathbf{r}_1)\alpha(\omega_1)\sigma_u(\mathbf{r}_2)\beta(\omega_2)\}$$

The correct wave function at the dissociation limit is

$$\Phi_{DISS} = \frac{1}{\sqrt{2}} \{\Phi_{GS} + \Phi_{AS}\}$$

Therefore, static correlation:
linear combination of Slater determinants

Electron density

Exchange-correlation hole is defined as

$$h_{XC}(\mathbf{x}_1; \mathbf{x}_2) = \frac{\rho_2(\mathbf{x}_1; \mathbf{x}_2)}{\rho(\mathbf{x}_1)} - \rho(\mathbf{x}_2)$$

Pair density

Integrate

$$\int h_{XC}(\mathbf{x}_1; \mathbf{x}_2) d\mathbf{x}_2 = N - 1 - N = -1$$

(exactly the charge of 1 electron)

Composed of exchange and correlation holes

$$h_{XC}(\mathbf{r}_1; \mathbf{r}_2) = h_X^{\sigma_1=\sigma_2}(\mathbf{r}_1; \mathbf{r}_2) + h_C^{\sigma_1, \sigma_2}(\mathbf{r}_1; \mathbf{r}_2)$$

Fermi hole
(treated in HF)

Coulomb hole
(neglected in HF)

Fermi hole

$$\int h_X(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$$
$$h_X(\mathbf{r}_1; \mathbf{r}_2) < 0$$

Coulomb hole

$$\int h_C(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = 0$$

since $\int h_{XC}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$

