

Lecture 19: The Hartree-Fock Method

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The HF Energy Functional

$$\begin{aligned} E^{\text{HF}}[\{\phi_i\}] &= \langle \Phi | \hat{H} | \Phi \rangle = E_1[\Phi] + E_2[\Phi] \\ &= \sum_i \frac{\langle \phi_i | \hat{h}_{\text{core}} | \phi_i \rangle}{\langle \phi_i | \phi_i \rangle} + \frac{1}{2} \sum_{ij} \frac{\langle ij || ij \rangle}{\langle \phi_i | \phi_i \rangle \langle \phi_j | \phi_j \rangle} \end{aligned}$$

- Minimize with respect to all occupied orbitals $\{\phi_i\}$ subject to normalization
- Necessary condition:

$$\frac{\delta E^{\text{HF}}[\{\phi_i\}]}{\delta \langle \phi_k |} = 0 \quad \forall k = 1, \dots, N$$

Functional Derivatives

- Normalization:

$$\frac{\delta \langle \phi_i | \phi_i \rangle}{\delta \langle \phi_k |} = \delta_{ik} |\phi_k\rangle$$

- One-electron integrals:

$$\frac{\delta \langle \phi_i | \hat{h}_{\text{core}} | \phi_i \rangle}{\delta \langle \phi_k |} = \delta_{ik} \hat{h} |\phi_k\rangle$$

- Two-electron integrals:

$$\begin{aligned} \frac{\delta \langle ij || ij \rangle}{\delta \langle \phi_k |} &= \frac{\delta}{\delta \langle \phi_k |} (\langle \phi_i | \langle \phi_j | \hat{v}_{ee} | \phi_i \rangle | \phi_j \rangle - \langle \phi_i | \langle \phi_j | \hat{v}_{ee} | \phi_j \rangle | \phi_i \rangle) \\ &= \delta_{ik} (\langle 2 : \phi_j | \hat{v}_{ee} | \phi_k \rangle | \phi_j \rangle - \langle 2 : \phi_j | \hat{v}_{ee} | \phi_j \rangle | \phi_k \rangle) \\ &\quad + \delta_{jk} (\langle 1 : \phi_i | \hat{v}_{ee} | \phi_i \rangle | \phi_k \rangle - \langle 1 : \phi_i | \hat{v}_{ee} | \phi_k \rangle | \phi_i \rangle) \end{aligned}$$

Canonical HF Equations

- Necessary condition for minimum:

$$\frac{\delta E^{\text{HF}}[\{\phi_i\}]}{\delta \langle \phi_k |} = (\hat{F}[\{\phi_i\}] - \epsilon_k) \frac{|\phi_k\rangle}{\langle \phi_k | \phi_k \rangle} = 0$$

- Canonical HF equations:

$$\hat{F}[\{\phi_i\}] |\phi_k\rangle = \epsilon_k |\phi_k\rangle$$

- Fock operator:

$$\hat{F}[\{\phi_i\}] = \hat{h}_{\text{core}} + \hat{J}[\{\phi_i\}] + \hat{K}[\{\phi_i\}]$$

\hat{F} is Hermitian/selfadjoint, but depends on its eigenvectors:
Iterative “selfconsistent field” solution required

- Canonical HF orbital energies:

$$\epsilon_k = \langle \phi_k | \hat{F} | \phi_k \rangle$$

Hartree and Exchange Potentials

- Coulomb operator or Hartree potential:

$$\hat{J} = \hat{V}^H = \sum_j \frac{\langle 2:\phi_j | \hat{v}_{ee} | 2:\phi_j \rangle}{\langle \phi_j | \phi_j \rangle}$$

Local multiplicative, *repulsive* potential generated by the electron density:

$$V^H(x) = \int dx' \frac{\rho(x')}{|\mathbf{r} - \mathbf{r}'|}$$

Average or “mean field” effective electron interaction; classical electrostatic potential of the charge density.

- Exchange operator:

$$\hat{K} = \hat{V}^X = - \sum_j \frac{\langle 1:\phi_j | \hat{v}_{ee} | 2:\phi_j \rangle}{\langle \phi_j | \phi_j \rangle}$$

Nonlocal, *attractive* exchange potential between same-spin electrons:

$$V^X(x, x') = - \frac{\gamma(x, x')}{|\mathbf{r} - \mathbf{r}'|}$$

Physical Meaning of HF Orbitals

- “Canonical” occupied HF orbitals diagonalize the Fock matrix and hence the matrix

$$\epsilon_{ij} = \langle \phi_i | \hat{F} | \phi_j \rangle$$

- Similarly, canonical virtual HF orbitals diagonalize

$$\epsilon_{ab} = \langle \phi_a | \hat{F} | \phi_b \rangle .$$

- *Koopmans’ Theorem*: The energies of occupied HF orbitals approximate negative ionization potentials, and the energies of virtual orbitals approximate electron affinities. Canonical HF orbitals approximate Dyson orbitals
- Energies of occupied orbitals must be negative, otherwise the ground state wavefunction corresponds to an unbound state that cannot be normalized (“continuum state”)

Brillouin Condition

- The HF determinant and thus the total energy do not depend on occ-occ or virt-virt unitary transformations!
- Non-canonical (e.g. localized) HF orbitals still can minimize the energy as the *Brillouin condition*

$$\epsilon_{ai} = \langle \phi_a | \hat{F} | \phi_i \rangle = 0$$

is satisfied.