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Hartree-Fock Theory

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Bibliography :

- A. Szabo and N. S. Ostlund : *Modern Quantum Chemistry.*
- F. A. Cotton : *Chemical Applications of Group Theory.*
- J. C. Slater : *Quantum Theory of Molecules and Solids.*

Notation : orbitals are noted φ_a or for simplicity a.

1. Basis set orthogonalization

Consider a non-orthogonal basis set consisting of N functions $\{\varphi_i\}_{i=1,N}$.

(a) Express the overlap matrix elements S_{ij} of $\mathbf{S}$.

(b) What are the properties of $\{S_{ij}\}$?

(c) If $\mathbf{s} = \{s_{ij}\}$ is the diagonal matrix, what is the relation between the $\mathbf{S}$ and $\mathbf{s}$ matrices ?

(d) Löwdin orthogonalization: define and show that $\mathbf{X} = \mathbf{S^{-1/2}}$ is an orthogonalizing transformation matrix.

2. Slater rules - Hartree-Fock energy

Let us start with a $\{\varphi_i\}$ orthonormalized basis set and consider a N-electron Slater determinant $|\Psi\rangle = |\varphi_a\varphi_b\cdots|$. Let us recall that Ψ can be written as :

$$|\Psi\rangle = (N!)^{-1/2}\sum_{n=1}^{N!}(-1)^{\sigma(n)}\mathcal{P}_n[\varphi_a(1)\varphi_b(2)\cdots\varphi_c(N)]$$

where $\sigma(n)$ is the number of transpositions that generates the permutation $\mathcal{P}_n$. Let $|\Psi'\rangle = |\varphi'_a\varphi'_b\cdots\varphi'_c\rangle$ be another N-electron Slater determinant constructed on the same set of orbitals (for clarity though, the orbitals are primed).

(a) Express $\langle\Psi|\Psi'\rangle$.

(b) Show that $\langle\Psi|\Psi'\rangle = 0$ unless $|\Psi\rangle = |\Psi'\rangle$.

(c) Any one-electron operator $\hat{\mathcal{O}}_1$ can be written as :

$$\hat{\mathcal{O}}_1 = \sum_{i=1,N} \hat{h}(i)$$

Show that

$$\langle\Psi|\hat{\mathcal{O}}_1|\Psi\rangle = \sum_a \langle a|h|a\rangle$$

(d) Let $|\Psi_a^r\rangle = |\varphi_r\varphi_b\cdots|$ be a single excitation on the reference Ψ. Use the second quantification to show that

$$\langle\Psi|\hat{\mathcal{O}}_1|\Psi_a^r\rangle = \langle a|h|r\rangle$$

(e) Show that $\langle\Psi|\hat{\mathcal{O}}_1|\Psi_{ab}^{rs}\rangle = 0$, where $|\Psi_{ab}^{rs}\rangle = |\varphi_r\varphi_s\cdots|$ is a double-excitation.

(f) Let $\hat{\mathcal{O}}_2$ be a two-electron operator. Show that

$$\langle\Psi|\hat{\mathcal{O}}_2|\Psi\rangle = \frac{1}{2}\sum_a\sum_b[(aa,bb)-(ab,ba)]$$

3. Unitary transformation

Let us consider the impact of a unitary transformation on a Slater determinant.

(a) Let $\{\varphi_i'\}$ be a set of spin-orbitals obtained from $\{\varphi_i\}$ by a unitary transformation $\mathbf{U}$. Express φ_j' as a function of the $\{\varphi_i\}$ and the matrix elements of $\mathbf{U}$.

(b) If $\mathbf{A}$ is a square matrix the determinant of which represents the wave function $|\Psi_0\rangle$, express **A'** using the new spin-orbitals.

(c) Show that $|\Psi_0'\rangle = e^{i\theta}|\Psi_0\rangle$.

4. Hartree-Fock equations

In the Hartree-Fock procedure, the wave function is written as a single determinant $\Psi = |\varphi_a\varphi_b\cdots|$. We will concentrate on the restricted Hartree-Fock procedure for an even number of electrons N, *i.e.* $N_\alpha = N_\beta = N/2$. The constraints on the orbitals call for Lagrange multipliers so that the occupied orbitals are varied independently. The Lagrangian thus reads

$$\mathcal{L} = \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle - \sum_a\sum_b \epsilon_{ba}[\langle\varphi_a|\varphi_b\rangle - \delta_{ab}]$$

and one should impose $\delta\mathcal{L} = 0$ whatever $\delta\varphi_a$.

(a) What properties the ϵ matrix should satisfy ?

(b) Express $\delta\mathcal{L}$ using the matrix elements calculations rules.

(c) Recast the Hartree-Fock equation, defining the Fock operator.

(d) Using the previous elements to show that the Lagrange multipliers matrix can be brought into a diagonal form.

5. Brillouin and Koopmans theorems

Let us start with the canonical orbitals $\{\varphi_i\}$ defined along the Hartree-Fock procedure, with $\Psi_0 = |\varphi_a \bar{\varphi}_a \cdots|$.

(a) Show that $\langle \Psi_a^r | \hat{\mathcal{H}} | \Psi_0 \rangle = 0$. This is Brillouin's theorem.

(b) Use the definition of the eigen-values of the Fock operator to show the Koopmans theorem, say IP$= {}^{N-1}E - {}^{N}E = -\epsilon_a$, where φ_a is an occupied orbitals.