

1. In solving the canonical Hartree-Fock equations, it is common to use eigenfunctions of the core Hamiltonian as starting guesses for the canonical molecular orbitals. This eigenvalue equation looks as follows

$$\hat{h}\phi_p = \epsilon_p\phi_p$$

where ϕ_p is a spatial function. Project this equation by χ_μ and then expand ϕ_p as a linear combination of atomic orbitals, $\phi_p = \sum_\nu \chi_\nu C_{\nu p}$, in order to arrive at the following matrix equation for the core guess.

$$\mathbf{HC} = \mathbf{SC}\epsilon \quad (\mathbf{H})_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle \quad (\mathbf{S})_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \quad (\mathbf{C})_{\mu p} = C_{\mu p} \quad (\epsilon)_{pq} = \epsilon_p \delta_{pq}$$

For extra credit, you may also briefly answer the following question in words: For an open-shell system, why do we end up with different spatial orbitals for different spins, even though the initial core-guess orbitals are the same for each spin?

Answer:

$$\left. \begin{aligned} \langle \chi_\mu | \hat{h} | \phi_p \rangle &= \sum_\nu \langle \chi_\mu | \hat{h} | \chi_\nu \rangle C_{\nu p} = (\mathbf{HC})_{\mu p} \\ \langle \chi_\mu | \phi_p \rangle \epsilon_p &= \sum_\nu \langle \chi_\mu | \chi_\nu \rangle C_{\nu p} \epsilon_p = (\mathbf{SC}\epsilon)_{\mu p} \end{aligned} \right\} \implies \mathbf{HC} = \mathbf{SC}\epsilon$$

Since there are different numbers of occupied α and β orbitals, the α and β density matrices will differ even for matching MO coefficients. This results in different exchange fields for \hat{f}_α and \hat{f}_β , breaking the orbital degeneracy.

2. Derive the expansion of H_e in terms of Φ -normal-ordered excitations.

Answer:

$$\begin{aligned}
& \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r \\
&= \sum_{pq} h_{pq} (\colon a_p^\dagger a_q \colon + \colon \overline{a_p^\dagger a_q} \colon) \\
&+ \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \left(\colon a_p^\dagger a_q^\dagger a_s a_r \colon + \colon \overline{a_p^\dagger a_q^\dagger a_s a_r} \colon + \colon \overline{a_p^\dagger a_q^\dagger a_s} a_r \colon + \colon a_p^\dagger \overline{a_q^\dagger a_s a_r} \colon + \colon a_p^\dagger \overline{a_q^\dagger a_s} a_r \colon + \colon \overline{a_p^\dagger a_q^\dagger a_s} a_r \colon + \colon \overline{a_p^\dagger a_q^\dagger a_s a_r} \colon \right) \\
&= \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{pr} \gamma_{qs} - \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{ps} \gamma_{qr} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \colon a_p^\dagger a_q^\dagger a_s a_r \colon + \sum_{pq} h_{pq} \colon a_p^\dagger a_q \colon \\
&- \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{ps} \colon a_q^\dagger a_r \colon + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{pr} \colon a_q^\dagger a_s \colon + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{qs} \colon a_p^\dagger a_r \colon - \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \gamma_{qr} \colon a_p^\dagger a_s \colon \\
&= \underbrace{\sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle \gamma_{pr} \gamma_{qs} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \colon a_p^\dagger a_q^\dagger a_s a_r \colon}_{E_{\text{ref}}} + \underbrace{\sum_{pq} (h_{pq} + \sum_{rs} \langle pr || qs \rangle \gamma_{rs}) \colon a_p^\dagger a_q \colon}_{f_{pq}}
\end{aligned}$$

In the final step, we have relabeled summation indices and made use of the antisymmetry of $\langle pq || rs \rangle$ in order to combine the second and third terms as well as the last four terms.

3. Derive the second Slater rule using Wick's theorem, and explain why this matrix element evaluates to zero for canonical Hartree-Fock orbitals.

$$\langle \Phi | H_e | \Phi_i^a \rangle = ?$$

Answer: Note that $a_a^\dagger a_i = :a_a^\dagger a_i:$, since this pair is already in Φ -normal order.

$$\begin{aligned} \langle \Phi | H_e :a_a^\dagger a_i: | \Phi \rangle &= E_{\text{ref}} \langle \Phi | :a_a^\dagger a_i: | \Phi \rangle + \sum_{pq} f_{pq} \langle \Phi | :a_p^\dagger a_q: :a_a^\dagger a_i: | \Phi \rangle + \frac{1}{4} \sum_{pq} \langle pq || rs \rangle \langle \Phi | :a_p^\dagger a_q^\dagger a_s a_r: :a_a^\dagger a_i: | \Phi \rangle \\ &= \sum_{pq} f_{pq} :a_p^\dagger \overline{a_q^\dagger a_a^\dagger} a_i: \\ &= \sum_{pq} f_{pq} \gamma_{pi} \eta_{qa} \\ &= f_{ia} \end{aligned}$$

On the right-hand side of the first line, term one vanishes because $a_a^\dagger a_i$ is in Φ -normal order and term three vanishes because there are no complete cross-contractions between two strings with different numbers of operators.

Projecting the canonical Hartree-Fock equation by some ψ_q leads to

$$f_{pq} = \langle \psi_q | \hat{f} | \psi_p \rangle = \epsilon_p \langle \psi_q | \psi_p \rangle = \epsilon_p \delta_{qp}$$

due to spin-orbital orthonormality, showing that the Fock matrix is diagonal and $f_{ia} = 0$.