

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?

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

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

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