

Excercises: Hartree Fock Part I

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1. Suppose you have a system with 3 electrons in 3 molecular spin orbitals ($\psi_1^1\psi_2^2\psi_3^3$). "Antisymmetrize" this product wavefunction by forming a Slater determinant using the definition of a Slater Determinant. Explicitly expand all permutations in two ways:

- Permuting the electron labels
- Permuting the MO labels

Show these two expansions are equivalent by labeling equivalent terms.

2. Suppose you perform a linear transformation A of N molecular spin orbitals describing an N -electron system, collected in a vector $\psi = [\psi_1, \psi_2, \dots, \psi_N]$ to form a new set of spin orbitals ψ' :

$$\psi' = \psi A$$

show that for the corresponding Slater determinants built from these spin orbital sets that the following is true:

$$\Phi' = \Phi \det(A)$$

3. Show that for an orthonormal set of spin orbitals, the Slater determinant composed of them is normalized,

$$\langle \Phi | \Phi \rangle = \int \Phi^* \Phi d\tau = 1$$

Hint: use the definition of a Slater determinant combined with tricks used in our derivation of the first Slater-Condon rule (see lecture notes).

4. Derive the first Slater-Condon rule for the value of the energy for a Slater determinant wavefunction,

$$E = \sum_i \langle \psi_i^i | h(i) | \psi_i^i \rangle + \sum_{i < j} \langle \psi_i^i \psi_j^j | g(i, j) | \psi_i^i \psi_j^j \rangle - \langle \psi_i^i \psi_j^j | g(i, j) | \psi_j^i \psi_i^j \rangle$$

Begin from the time-independent Schrodinger equation, the Slater determinant definition of the wavefunction, and the following simplified electronic Hamiltonian:

$$\hat{H} = \sum_i \hat{h}(i) + \sum_{i < j} \hat{g}(i, j)$$

5. Explain in your own words how one gets from the time-independent Schrodinger equation to the Hartree-Fock equations (NOT the Roothaan-Hall or Pople-Nesbet equations). Include a brief description of each of the following:
- the Hamiltonian
 - the nature of the wavefunction and its components
 - how the best electronic energy is obtained for this wavefunction
 - how the Hartree-Fock equations relate to this wavefunction