Exercises: Hartree Fock Part I

January 15, 2020

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 $\boldsymbol{A}$ of N molecular spin orbitals describing an N-electron system, collected in a vector $\boldsymbol{\psi} = [\psi_1, \psi_2, ..., \psi_N]$ to form a new set of spin orbitals $\boldsymbol{\psi'}$:

   $$\boldsymbol{\psi'} = \boldsymbol{\psi}\boldsymbol{A}$$

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

   $$\Phi' = \Phi \det(\boldsymbol{A})$$

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-indepedent 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