Assignment-1: Many-Electron Systems (12/05/2024)

1. Given a set of K orthonormal spatial functions, $\{\psi_i^\alpha(r)\}$, and another set of K orthonormal functions, $\left\{\psi_i^\beta(r)\right\}$, such that the first set is not orthogonal to the second set, that is,

$$\int dr\psi_i^{\alpha*}(r)\psi_j^\beta(r) = S_{ij}$$

   where S is an overlap matrix, show that the set $\{\chi_i\}$ of $2K$ spin orbitals, formed by multiplying $\psi_i^\alpha(r)$ by the α spin function and $\psi_i^\beta(r)$ by the β spin function, that is,

$$\chi_{2i-1}(x) = \psi_i^\alpha(r)\alpha(\omega)$$

$$\chi_{2i}(x) = \psi_i^\beta(r)\beta(\omega)$$

   for all $i = 1, 2, \dots, k$ is an orthonormal set.
2. Show that the Hartree product is an eigenfunction of the non-interacting Hamiltonian defined as

$$H^{NI} = \sum_{i=1}^{N} h(r_i)$$

3. Show that the function, defined as,

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

   is normalized
4. Suppose that the spin orbitals χ_i and χ_j are eigenfunctions of a one-electron operator h with eigenvalues ε_i and ε_j. Show that the Slater determinant is an eigenfunction of the independent-particle Hamiltonian $H^{NI} = h(r_1) + h(r_2)$.
5. For the Slater determinants $|K\rangle = |\chi_i\chi_j\rangle$ and $|L\rangle = |\chi_k\chi_l\rangle$, show that, $\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$.
6. Show that the molecular orbitals formed in a minimal basis treatment of the hydrogen molecule form an orthonormal set.
7. For the systems given below, calculate the total number of possible determinants that can be formed, and the number of singly and doubly excited determinants for a minimal basis description: (a) hydrogen molecule, (b) 1, 3 butadiene, (c) cyclobutadiene and (d) benzene.
8. Determine the values of the integrals $\langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle$ and $\langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle$. What is the relation between $\langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle$ and $\langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_0\rangle$?