Hartree-Fock Exercises Part II

1. Starting from the 1st Slater-Condon rule:
$$E = \sum_{i}^{N} \langle \psi_i^i | \hat{h}(i) | \psi_i^i \rangle + \sum_{i<j}^{N} \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_i^i \psi_j^j \rangle - \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_j^i \psi_i^j \rangle$$
derive the form of the above energy expression for the special case of a closed-shell molecular system with $N = 2n$ electrons in n doubly-occupied spatial orbitals. Explicitly integrate out the spin functions to arrive at an expression in terms of just the spatial orbitals:
$$E = 2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i}^{N/2} \sum_{j}^{N/2} 2 \langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle$$
2. a. Beginning from the restricted-determinant form for the 1st Slater-Condon rule (derived above), expand each spatial orbital as a linear combination of atomic orbitals:
$$\langle \phi_i | = \sum_{p} \langle \chi_p | C_{pi}^* \quad | \phi_i \rangle = \sum_{q} | \chi_q \rangle C_{qi} \quad \langle \phi_j | = \sum_{r} \langle \chi_r | C_{rj}^* \quad | \phi_j \rangle = \sum_{s} | \chi_s \rangle C_{sj}$$
to derive the energy expression for LCAO-MO RHF.

   b. Convert the two-electron integrals from the result in part a from physicist's notation to chemist's notation.

   c. Write out NumPy code to evaluate the expression in part b using a sum of `np.einsum` calls.
3. Explain how our typically non-orthogonal atomic orbital basis functions are transformed to an orthonormal basis in the Roothaan-Hall scheme. Why is it okay to compute the electronic energy in the non-orthonormal AO basis, despite the energy expression being derived under the assumption of orbital orthonormality?
4. Define the Hartree-Fock optimization problem in one sentence.
5. Starting from the Hartree-Fock equations, expand the spatial orbitals in a basis of atomic orbitals $\phi_i = \sum_{q} \chi_q C_{qi}$ and multiply each side on the left by χ_p and integrate both sides to arrive at the Roothaan-Hall equations.
6. Describe the algorithm for solving the Roothaan-Hall equations