

Problem set 4: Hartree-Fock and (some) Density Functional Theory (due November 21).

Chapter 3 in S&O discusses Hartree-Fock . It is good to read pages 108-152, and 205-229. The sections on basis sets and results in S&O are dated. In class I will also discuss a little bit of DFT. I will be posting a paper on the web site, I myself wrote on DFT, that discusses the fundamentals, and some issues regarding these fundamentals.

Problems:

1. S&O: 3.3, 3.5, 3.6, 3.8
2. S&O: 3.9, 3.15, 3.17
3. Completing the derivation of Hartree-Fock-Roothaan equations

In my class notes I derive the stationarity equation

$$\frac{\partial F}{\partial C_{\lambda d}} = \sum_{\mu, \nu} h_{\mu\nu} \frac{\partial D_{\nu\mu}}{\partial C_{\lambda d}} + \sum_{\mu, \nu, \sigma, \tau} \langle \mu\nu || \sigma\tau \rangle D_{\tau\nu} \frac{\partial D_{\sigma\mu}}{\partial C_{\lambda d}} - \sum_{a, b} \epsilon_{ba} \frac{\partial}{\partial C_{\lambda d}} (\sum_{\mu, \nu} C_{\mu a} S_{\mu\nu} C_{\nu b})$$

as well as

$$\frac{\partial D_{\mu\nu}}{\partial C_{\lambda d}} = \delta_{\mu\lambda} C_{\nu d} + \delta_{\nu\lambda} C_{\mu d}$$

a) Use this to derive the equation

$$\sum_{\nu} [h_{\lambda\nu} + \sum_{\sigma, \tau} \langle \lambda\sigma || \nu\tau \rangle D_{\tau\sigma}] C_{\nu d} - \sum_{b, \nu} S_{\lambda\nu} C_{\nu b} \epsilon_{bd} + \sum_{\mu} C_{\mu d} [h_{\mu\lambda} + \sum_{\sigma, \tau} \langle \mu\sigma || \lambda\tau \rangle D_{\tau\sigma}] - \sum_{a, \nu} \epsilon_{da} S_{\lambda\nu} C_{\nu a} = 0$$

b) Assuming the symmetry of the Lagrangian multipliers $\epsilon_{ab} = \epsilon_{ba}$, and the symmetry of the density matrices and integrals (as discussed in the notes), show that the second line in the above equation equals the first line. Therefore the first line should vanish by itself. In the literature it is usually said (correctly) that the second line equals the complex conjugate of the first line. This is true if basis functions / coefficients might be complex. We have assumed real basis functions.

4. Formal Density Functional Theory

A crucial ingredient of the proof of the famous Hohenberg-Kohn theorem is showing that the ground states for two Hamiltonians that differ in the nuclear potential only, necessarily have a different ground state density.

a) Let us first reiterate the proof:

Consider two Hamiltonians and their corresponding ground states

$$H_a = T + v_a + w, \quad H_a \Psi_a = E_a \Psi_a, \quad \rho_a$$

$$H_b = T + v_b + w, \quad H_b \Psi_b = E_b \Psi_b, \quad \rho_b$$

Then

$$(\langle \Psi_b | H_a | \Psi_b \rangle - E_a) + (\langle \Psi_a | H_b | \Psi_a \rangle - E_b) > 0$$

Explain why this should be true.

By substituting expectation values for E_a, E_b and rearranging show that this expression can be reduced to

$$\int (v_a(\mathbf{r}) - v_b(\mathbf{r}))(\rho_b(\mathbf{r}) - \rho_a(\mathbf{r})) d^3r > 0$$

This can only be true if $\rho_b(\mathbf{r})$ is different (at least somewhere) from $\rho_a(\mathbf{r})$. From this argue that the density hence determines the potential and hence the Hamiltonian and the ground state energy. This is the Hohenberg-Kohn theorem.

b) The variational principle is also valid for the Hartree-Fock groundstate. Follow the same steps to argue that the densities of Hartree-Fock states corresponding to Hamiltonians a and b above *have* to be different. Hence the Hartree-Fock density determines the nuclear (or external) potential v , the Hamiltonian and the Hartree-Fock energy: You have now proven that the Hartree-Fock energy is a functional of the Hartree-Fock density, (not just the density matrix, which we use to derive HF equations)!

c) Extend the argument to show that the *exact* total energy is also a functional of the Hartree-Fock density! This is a well-known but little discussed result in the literature.