Solution to 10.675 Assignment #1

1. Derive an expression for the total ground state energy of a two-electron system using Hartree-Fock theory. This should be done in terms of spin orbitals. Identify the coulomb and exchange integrals, and explain their physical significance.

Solution:
Two-electron system is fairly easy to deal with. Since we are doing the general derivation for N-electron system in the next problem, we will omit the repeated work here. Please refer to chapter 2.3.1 in Szabo and Ostlund's *Modern Quantum Chemistry* (pages 64-66) for the detailed derivation of two-electron system.

2. Make yourself comfortable with the general derivation of this expression for N electrons.

Solution:
For N-electron system, the Hamiltonian is:

$$H = \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \tag{1}$$

Where, $h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$

In Hartree-Fock theory, we choose the form of the wave function to be that of single determinant, formed from spin orbitals:

$$|\psi_0> = |\chi_m(1)\chi_n(2)\cdots\chi_k(N)> = \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{P_n} P_n\{\chi_m(1)\chi_n(2)\cdots\chi_k(N)\} \tag{2}$$

where P_n is an operator that generates the nth permutation of the electron labels 1, 2, …N and p_n is the number of transpositions required to obtain this permutation.

The Hartree-Fock ground state energy is:

$$E_0 = <\psi_0 | H | \psi_0> = <\psi_0 | \sum_{i=1}^{N} h(i) | \psi_0> + <\psi_0 | \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} | \psi_0> \tag{3}$$

Since the electrons in a determinant are indistinguishable, matrix elements of h(1) will be identical to those h(2), h(3), etc. Then we substitute eq. (2) into eq. (3).

The first part of eq. (3) becomes:

$$<\psi_0 | \sum_{i=1}^{N} h(i) | \psi_0> = N <\psi_0 | h(1) | \psi_0>$$

$$= \frac{1}{(N-1)!}\sum_{i}^{N!}\int dx_1 dx_2 \cdots dx_N \times P_i\{\chi_m{}^*(1)\chi_n(2)^*\cdots\} h(1) P_i\{\chi_m(1)\chi_n(2)\cdots\}$$

$$= (N-1)!\frac{1}{(N-1)!}\sum_{m}^{N}\int dx_1\{\chi_m{}^*(1)\} h(1)\{\chi_m(1)\} = \sum_{m}^{N} <m | h | m> \tag{4}$$

[Note: The reason that (N-1)! factor was added in the next to the last step is that in the sum over the N! permutations, electron 1 will occupy each of the spin orbitals (N-1)! times. And the integration over the other N-1 electrons will always give a factor of 1 since the spin orbitals are normalized.]

Similarly, we can get the second part of eq. (3):

$$< \psi_0 | \sum_{i=1}^{N} \sum_{j>i}^{N} \tfrac{1}{r_{ij}} | \psi_0 >= \qquad (5)$$

$$\frac{N(N-1)}{2} \frac{1}{N!} \sum_{i}^{N!} \sum_{j}^{N!} (-1)^{P_i} (-1)^{P_j} \int dx_1 dx_2 \cdots dx_N \times P_i \{\chi_m{}^*(1)\chi_n(2)^* \cdots\} \frac{1}{r_{12}} P_j \{\chi_m(1)\chi_n(2)\cdots\}$$

Because the operator in eq. (5) involves only electrons 1 and 2, it must be that other electrons occupy the same spin orbitals in both the ith and jth permutations, or we could get zero by orthogonality upon integrating over the coordinates of these electrons. If electrons 3, 4,…,N occupy the same spin orbitals in the two permutations and electrons 1 and 2 occupy two spin orbitals, say χ_k and χ_l in the permutation P_i, then there are two possibilities for electrons 1 and 2 in the permutation P_j: They could either occupy the same spin orbitals χ_k and χ_l (same as P_i) or they could occupy χ_l and χ_k.

Therefore, we can write eq. (5) as:

$$\frac{1}{2(N-2)!} \sum_{i}^{N!} \int dx_1 dx_2 \cdots dx_N \times P_i \{\chi_m{}^*(1)\chi_n(2)^* \cdots\} \frac{1}{r_{12}} [P_i \{\chi_m(1)\chi_n(2)\cdots\} - P_{12} P_i \{\chi_m(1)\chi_n(2)\cdots\}]$$

For a reason similar to that in the first part, in the sum of N! permutations, P_i, electrons 1 and 2 can occupy any two different spin orbitals χ_m and χ_n of the set of N spin orbitals. For each choice of these two spin orbitals there are (N-2)! Ways of permuting the other N-2 electrons among the N-2 remaining spin orbitals. Therefore, eq. (5) can be written as:

$$< \psi_0 | \sum_{i=1}^{N} \sum_{j>i}^{N} \tfrac{1}{r_{ij}} | \psi_0 >$$

$$= \frac{(N-2)!}{2(N-2)!} \sum_{m}^{N} \sum_{n \neq m}^{N} \int dx_1 dx_2 \{\chi_m{}^*(1)\chi_n(2)^*\} \frac{1}{r_{12}} (1 - P_{12}) \{\chi_m(1)\chi_n(2)\}$$

$$= \frac{1}{2} \sum_{m}^{N} \sum_{n \neq m}^{N} \int dx_1 dx_2 \{\chi_m{}^*(1)\chi_n(2)^*\} \frac{1}{r_{12}} [\{\chi_m(1)\chi_n(2)\} - \{\chi_m(2)\chi_n(1)\}]$$

$$= \frac{1}{2} \sum_{m}^{N} \sum_{n \neq m}^{N} < mn | mn > - < mn | nm > \qquad (6)$$

Combine eqs. (3) (4) and (6), we get:

$$E_0 = < \psi_0 | H | \psi_0 >= \sum_{m}^{N} < m | h | m > + \frac{1}{2} \sum_{m}^{N} \sum_{n \neq m}^{N} < mn | mn > - < mn | nm >$$

$$= \sum_{m}^{N} < m | h | m > + \sum_{m}^{N} \sum_{m>n}^{N} < mn | mn > - < mn | nm > \qquad (7)$$

For two-electron system, $|\psi_0>=|\chi_1(1)\chi_2(2)>$ (m=1, n=2 here), eq. 7 becomes:

$$E_0 = \sum_m^N <m|h|m> + \sum_m^N \sum_{m>n}^N <mn|mn> - <mn|nm>$$

$$=<1|h|1> + <2|h|2> + <12|12> - <12|21> \quad (8)$$

where <12|12> is the Coulomb integral, which represents the classical Coulomb repulsion between the charge clouds $|\psi_1(x_1)|^2$ and $|\psi_2(x_2)|^2$; <12|21> is the exchange integral. The appearance of exchange integrals in the energy of a Slater determinant is a manifestation of the fact that the motion of electrons with parallel spins is also correlated.