Problem set 2: Szabo and Ostlund: Chapter II (up to page 89, sections 2.1 - 2.3); Lecture notes.

We will put electronic structure theory into perspective and define the general problem that has to be solved. We discuss antisymmetry of the wave function in some detail and introduce a basis of Slater determinants, which are the antisymmetrized equivalent of the pure Hartree products of one-electron orbitals. This allows us to formulate the linear variation problem in the space of all determinants that can be formed from a finite set of spin-orbitals. The solution to the secular problem, or more conveniently the diagonalization of the Hamiltonian matrix, defines the full configuration interaction or Full CI solution. It gives the best possible result, given the initial set of 1-electron basis functions. In practice this solution is only feasible for rather small basis sets, but it defines the theoretical framework of quantum chemistry.
We will develop the rules to evaluate the Hamiltonian matrix elements over the Slater determinants, making use of the antisymmetrization operator.

Exercises:

1. Szabo and Ostlund: 2.1, 2.2, 2.4, 2.5, 2.7

2. S&O: 2.9, 2.12, 2.13, 2.14

3. S&O: 2.17, 2.18, 2.21

4. Using the terminology of Szabo and Ostlund, paragraph 2.3.7, evaluate the expectation values of the Hamiltonian for the following determinants: $|\psi_1\psi_2|, |\psi_1\bar{\psi}_2|, |\psi_1\bar{\psi}_1|, |\psi_1\bar{\psi}_1\psi_2|, |\psi_1\psi_2\psi_3|, |\psi_1\bar{\psi}_2\psi_3|, |\psi_1\bar{\psi}_1\bar{\psi}_2\psi_3|$. First draw an occupation diagram as is done in S&O, and from this write down the energy expression. See also exercise 2.23 in S&O.

5. The N-particle antisymmetrization operator can be given in the following form $\hat{A} = \sum_{i=1}^{N!} (-)^{p_i} \hat{P}_i$, where the sum runs over all N! permutations of N coordinates, and p_i is the parity of the permutation that indicates if it consists of an even or odd number of transpositions or interchanges. Show that $\hat{A}\hat{A} = N!\hat{A}$. Further information: the antisymmetrizer is sometimes normalized differently as $\hat{A}' = \frac{1}{N!}\sum_{i=1}^{N!} (-)^{p_i} \hat{P}_i$. In this case applying the antisymmetrization operator twice yields the same result, which one might expect. It then acts as a projection operator on the antisymmetric subspace.

6. Every permutation can be written as a product of transpositions $\hat{P}_i = \hat{T}_1\hat{T}_2....\hat{T}_k$. Show that every transposition is Hermitian, and is its own inverse. Use these properties to show that the permutation operator is unitary: $\hat{P}_i^\dagger = P_i^{-1}$, and that it has the same parity as $\hat{P}_i$. Next use these results to show that the antisymmetrization operator is Hermitian.