Problem set 5: Second Quantization.

Due date: Thursday November 24

Reading material: Szabo & Ostlund Chapter 2, pages 89-107

Class notes on second quantization.

Lecture notes: many-Body angular momentum operators.

We will discuss when CI is very important, or when one needs to go beyond the simple MO picture, which uses only a single determinant to describe the trial wave function. This is discussed in the lecture notes. Following this we introduce the formalism of second quantization. This is an operator type of formulation, now for the electronic structure problem. It is very powerful, and it is used in almost every advanced research paper on ab initio (wave function based) quantum chemistry.

Exercises:

1. S&O: 2.24, 2.25, 2.27, 2.28

2. S&O: 2.30, 2.31, 2.32, 2.34,

3. S&O: 2.35, 2.36, 2.37, 2.38, 2.39, 2.40

See next page:

4. **Elementary exercise on second quantization:**

Consider the one-particle Hamiltonian given in second quantization

$\hat{H} = \hat{h} = \sum_{i,j} h_{ij} \hat{a}_i^\dagger \hat{a}_j \equiv \sum_{i,j} h_{ij} \hat{i}^\dagger \hat{j}$, and the Slater determinant $|\Psi_0\rangle = \hat{a}^\dagger \hat{b}^\dagger .... \hat{c}^\dagger |vac\rangle$. We will follow the notation that the orbitals *a,b* are occupied in $|\Psi_0\rangle$, $\hat{a}^\dagger |\Psi_0\rangle = 0$, while *r* and *s* indicate unoccupied orbitals: $\hat{r}|\Psi_0\rangle = 0$. The labels *i, j* are arbitrary.

Questions:

a. *Using the techniques of second quantization* without short-cuts evaluate the matrix elements over singly excited determinants $\langle \Psi_a^r | \hat{h} | \Psi_b^s \rangle$, where $|\Psi_b^s\rangle = \hat{s}^\dagger \hat{b} |\Psi_0\rangle$, in terms of the reference energy $E_0 = \langle \Psi_0 | \hat{h} | \Psi_0 \rangle$ and the one-electron matrix elements. Clearly indicate your derivation and explain your strategy. Do not use the crossing rule, argue in terms of anticommutation relations only. Explicitly list your results for the cases $i)\ a \neq b, r \neq s,\ ii)\ a = b, r \neq s,\ iii)\ a \neq b, r = s,\ iv)\ a = b, r = s$

b. Show explicitly, using the techniques of second quantization, that the reference energy is given by $E_0 = \langle \Psi_0 | \hat{h} | \Psi_0 \rangle = \sum_a h_{aa}$. You cannot use the Slater rules and simply write down this answer. Derive using the anticommutation relations.

c. Show that if $h_{ra} = h_{ar} = 0\ \forall a, r$ then $|\Psi_0\rangle$ is an eigenstate of $\hat{h}$. Show that the off-diagonal occupied matrix elements $h_{ab}, a \neq b$ do not play a role in this statement.

d. What is the most efficient way to find the eigenstates of the Hamiltonian $\hat{h} = \sum_{i,j} h_{ij} \hat{a}_i^\dagger \hat{a}_j$? Describe the strategy of your solution, and list the solutions.