(A)

problemset 6: Second quantization, Wick's theorem and diagrams.

This problemset builds on the written lecture notes. We use the notation

a, b, c, d : virtual orbitals
i, j, k, l : occupied orbitals
p, q, r, s : general orbitals

non-zero contractions

$$\overbrace{i^+ j} = \delta_{ij} \qquad \overbrace{a b^+} = \delta_{ab}.$$

1. Use Wick's theorem to write the second quantized Hamiltonian in normal order w.r.t. HF reference state:

$$\hat{H}_N = E_{HF} + \sum_{pq} f_{pq} \{p^+ q\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{p^+ r^+ s q\}$$

2. Using the normal ordered form of the Hamiltonian evaluate

a. $\langle HF | a \hat{H}_N b^+ | HF \rangle$

b. $\langle HF | i^+ a \hat{H}_N b^+ j | HF \rangle$

3. Use the technique of diagrams to evaluate

a. $(\hat{H}_N \hat{C})_a \{a^+\}$ $\quad \hat{C} = \sum_b C_b \{b^+\}$

b. $(\hat{H}_N \hat{C})_i^a \{a^+ i\}$ $\quad \hat{C} = \sum_{j,b} C_j^b \{b^+ j\}$

c. Indicate how these equations are equivalent to what you derived in problem 2.
(Hint: evaluate $H\hat{C}$ using the matrix from problem 2)

4. Draw the diagrams for the C.I.S.D. method and evaluate results. (Follow my notes).

a. draw skeletons, then diagrams,
b. include signs, factors
c. include labels.
d. Algebraic formulas.

Evaluate

$(H_N C)_i^a \{a^+ i\}$ $\quad (\hat{H}_N \hat{C})_{ij}^{ab} \{a^+ i\, b^+ j\}$

$\hat{C} = \hat{C}_1 + \hat{C}_2 = \sum_{i,a} C_i^a \{a^+ i\}$

$+ \frac{1}{4} \sum_{i,j,a,b} C_{ij}^{ab} \{a^+ i\, b^+ j\}$