(B)

Problem set on CC and EOMCC (for you to practice and digest).

1. Coupled Cluster singles for one-electron Hamiltonian.

Use
$$\hat{H} = \hat{h} = \sum_{p,q} h_{pq}\, p^+ q$$
$$H_N = h_0 + \sum_{p,q} h_{pq} \{p^+ q\}$$
$$h_0 = \sum_i h_{ii}$$
$$\hat{T} = \hat{T}_1 = \sum_{i,a} t_i^a \{a^+ i\}$$

Usual index conventions.

a. show that now
$$\bar{H} = e^{-T_1} \hat{h} e^{T_1}$$
$$= \hat{h} + [\hat{h}, T_1] + \frac{1}{2} [[\hat{h}, T_1], T_1]$$

b) We will use $\bar{H} = (\hat{H} e^{T_1})_{\text{connected}}$

Evaluate algebraically (crossing rule
$$R_i^a = \langle HF | i^+ a \; (\hat{h} + \hat{h}\hat{T} + \tfrac{1}{2}\hat{h}\hat{T}\hat{T}) | HF \rangle$$
Identity, and keep only connected terms (each $\hat{T}$ connected to $\hat{h}$).

c. Evaluate diagrammatically $(He^T)_{\text{conn},\, i}^{\;a} \{a^+ i\}$ and compare algebraic formula to result in b)

d. Evaluate $(He^T)_0 = E$ for CCS.

2. Diagrammatic derivation of CCD equations

Use the full $\hat{H}_N$ and $\hat{T} = \hat{T}_2 = \sum_{\substack{k,l \\ c,d}} t_{kl}^{cd} \{c^+ k d^+ l\}$

Draw the diagrams for
$\left(H_N + H_N T + \frac{1}{2} H_N TT\right)_{conn.\ ij}^{ab} \{a^+ i b^+ j\}$

Proceed systematically as for CISD in previous problem set.

a.) skeletons (no arrows)
b.) diagrams (add arrows)
c) Add signs, factors
d.) Add labels.
e.) Evaluate algebraic expression

The linear term $\hat{H}_N \hat{T}$ is similar to CID (identical)

There will be permutations
$(1 - P_{i \leftrightarrow j} - P_{a \leftrightarrow b} + P_{i \leftrightarrow j, a \leftrightarrow b})$
(same as in CISD)

Pay careful attention to terms in $\frac{1}{2} H_N TT$. They are different from CID and replace $-E_c T_2$.

3.) Evaluate other $\bar{H}$ elements, which all involve only linear T_2

$$\bar{H} = H + (HT)_{conn.}$$

Draw the diagrams, including labels / factors

Indicate which labels are equivalent, and indicate the permutation you would apply for each matrix elements
(Consult my notes, which are a bit brief perhaps)

4) For 2-electron systems both CISD and CCSD are exact. Also CID and CCD yield identical results.
Use $T_2 = \sum_{a,b} t_{ij}^{ab}$ (no summation over i,j), It must be true that

$$\frac{1}{2}(H\,T_2\,T_2)_{conn} = -E_c\,T$$

$$E_c = \frac{1}{2}\sum_{c,d} \langle ij||cd\rangle\, t_{ij}^{cd}$$

See if you can derive this result! This leads to the important notion of exclusion principle violating terms (EPV).