

1. Explain why the maximum excitation level of the wavefunction increases by +2 with each order in perturbation theory.
2. Prove that the leading contribution to the  $k$ -tuples CI operator has order  $\lceil k/2 \rceil$  in perturbation theory.
3. Write down the CISD energy and singles and doubles equations in terms of  $C_k$  operators. Identify the leading order of each term in perturbation theory with and without Brillouin's theorem.
4. Prove that CIS $\cdots m$  is correct to order  $\lfloor m/2 \rfloor$  in the wavefunction and  $2\lfloor m/2 \rfloor + 1$  in the energy.
5. Write down the CCSD energy and singles and doubles equations in terms of  $T_k$  operators. Identify the leading order of each term in perturbation theory with and without Brillouin's theorem.
6. Explain why the leading contribution to the  $k$ -tuples cluster operator has order  $k - 1$ .
7. Prove that CCS $\cdots m$  is correct to order  $m - 1$  in the wavefunction and  $m + \lfloor m/2 \rfloor$  in the energy.
8. "Derive" the [T] correction and evaluate it, showing both the diagrams and their algebraic interpretation.<sup>1 2</sup> You may write your answer in terms of  $^{[2]}t_{abc}^{ijk}$  amplitudes and evaluate those separately.

$$E_{[T]} = \langle \Phi | T_2^\dagger V_c T_3^{[2]} | \Phi \rangle \quad T_3^{[2]} = \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc \\ ijk}} \tilde{a}_{ijk}^{abc} \langle \Phi_{ijk}^{abc} | R_0 V_c T_2 | \Phi \rangle \quad (1)$$

9. Prove that the left and right EOM-CC wave operators are given by

$$^k R = \exp(-T)(^k C_0 + ^k C) \quad ^k L = (^k C_0 + ^k C)^\dagger \exp(T) \quad (2)$$

where  $^k C_0 + ^k C$  is the CI wave operator for the  $k^{\text{th}}$  state. Use this to show that we can determine excited state expectation values and transition matrix elements for an observable  $W$  as  $\langle \Psi_k | W | \Psi_k \rangle = \langle \Phi | ^k L \bar{W} ^k R | \Phi \rangle$  and  $\langle \Psi_k | W | \Psi_l \rangle = \langle \Phi | ^k L \bar{W} ^l R | \Phi \rangle$  where  $\bar{W} \equiv \exp(-T)W\exp(T)$ .

10. Evaluate the CCD lambda equations, showing both the diagrams and their interpretation.
13. Derive the  $(m + 1)_\Lambda$  correction from the coupled-cluster Löwdin functional.
14. "Derive" the (T) correction as an approximation to  $(T)_\Lambda$  correction and evaluate it.

$$E_{(T)} = E_{[T]} + \langle \Phi | T_1^\dagger V_c T_3^{[2]} | \Phi \rangle \quad (3)$$

<sup>1</sup>"Derive" here means "give detailed motivation for".

<sup>2</sup>The operator  $Q_3$  here simply projects onto the space of triply substituted determinants.