CHEM 8950

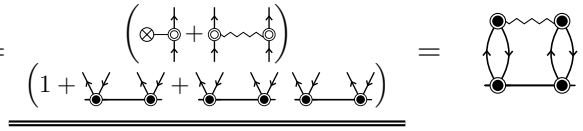
ADVANCED QUANTUM CHEMISTRY

This assignment is due May 1 at 5PM by email.

Coupled Cluster with Double Excitations (CCD)

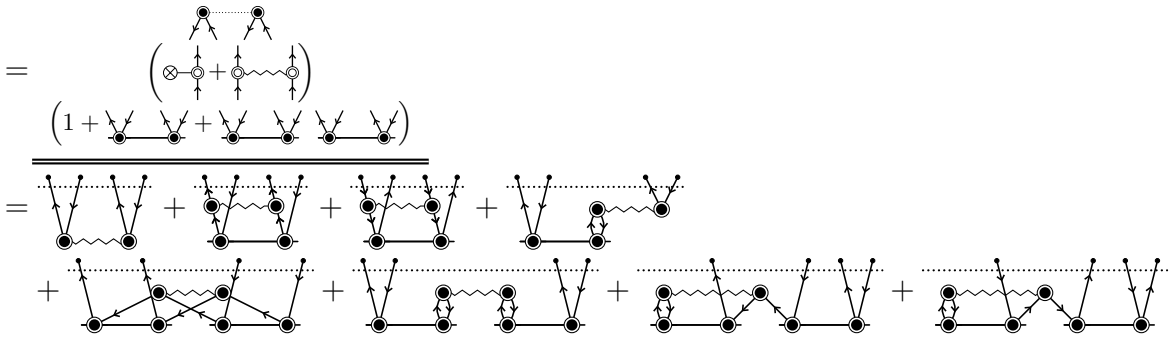
CCD energy equation:

$$E_{\mathrm{c}} = \langle \Phi | H_c (1 + T_2 + \tfrac{1}{2} T_2^2) | \Phi \rangle$$



CCD amplitude equation:

$$t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ij}^{ab} | (H_{\mathrm{c}} - f_p^p \tilde{a}_p^p) \exp(T_2) | \Phi \rangle_{\mathrm{L}} \qquad \mathcal{E}_{ab}^{ij} \equiv \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$



Determine the programmable equations from the diagrams above. For any terms that have $\hat{P}_{(\ldots)}^{(\ldots)}$ it will need to be explicitly expanded out.

Using your existing UHF code, spin-orbital setup, and integral transformation, perform the following steps:

- Use a zero-filled tensor for your initial t_{ab}^{ij} .
- Iterations:
  1. Solve for the new t_{ab}^{ij} using the old amplitudes.
  2. Print the CCD correlation energy using the new t_{ab}^{ij}.
  3. Test the convergence of the energy and t_{ij}^{ab} (using the norm of the new and old t_{ij}^{ab}), breaking the loop, if converged. Be converged to at least 10^{-6}.
- Print the final CCD correlation energy in addition to the total energy.