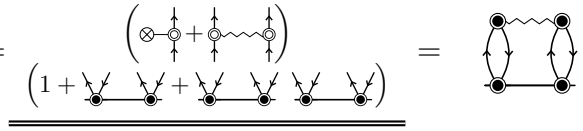
CHEM 8950
Advanced Quantum Chemistry

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

Coupled Cluster with Double Excitations (CCD)

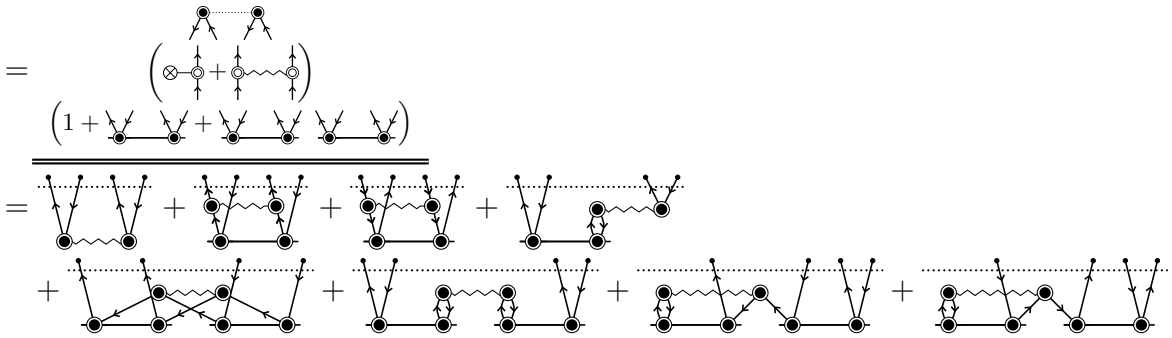
CCD energy equation:

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



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.

Sample Input

```
Settings = dict()
Settings["basis"] = "cc-pvdz"
Settings["df_basis"] = "cc-pvdz-ri"
Settings["molecule"] = """
  1 2
  O
  H 1 R
  H 1 R 2 A
  R = 1.0
  A = 104.5
  symmetry c1
"""
Settings["nalpha"] = 5
Settings["nbeta"] = 4
Settings["scf_max_iter"] = 50
Settings["cc_max_iter"] = 75
```

Truncated output for CCD

```
Psi4 Hartree-Fock Energy: -75.6335074773


  Spin-Orbital CCD


Number of basis functions:            25
Number of molecular orbitals:         25
Number of spin orbitals:              50
    Number of occupied spin orbitals: 9
    Number of virtual spin orbitals:  41

Computing AO integrals (pq|rs) ... done in  0.1792 seconds.
Forming denominator (oovv) ... done in  0.0014 seconds.
Antisymmetrizing <pq||rs> = (pr|qs) - (ps|qr) ... done in  0.0159 seconds.
Performing integral transformations:
     <oo||vv> ... done in  0.0194 seconds.
     <oo||oo> ... done in  0.0156 seconds.
     <vo||ov> ... done in  0.0542 seconds.
     <vv||vv> ... done in  0.1747 seconds.

Beginning CCD iterations ...
    Iteration   1: energy  -0.1591601529 dE -1.59160E-01 |dT| +3.82786E-01
    Iteration   2: energy  -0.1708162298 dE -1.16561E-02 |dT| +5.29557E-02
    Iteration   3: energy  -0.1733637529 dE -2.54752E-03 |dT| +1.97685E-02
    .
    .
    .
    Iteration  44: energy  -0.1747055094 dE -7.68463E-12 |dT| +6.89962E-10
    Iteration  45: energy  -0.1747055094 dE -5.13106E-12 |dT| +4.61747E-10
    Iteration  46: energy  -0.1747055094 dE -3.42662E-12 |dT| +3.09017E-10
    Iteration  47: energy  -0.1747055094 dE -2.28867E-12 |dT| +2.06805E-10
    Iteration  48: energy  -0.1747055094 dE -1.52886E-12 |dT| +1.38400E-10
    Iteration  49: energy  -0.1747055094 dE -1.02143E-12 |dT| +9.26217E-11

CCD correlation energy:  -0.1747055094
Total CCD energy:       -75.8082129867 (HF + CCD)
CCD total time:  2.0414 seconds.
```