CHEM 8950
ADVANCE QUANTUM CHEMISTRY

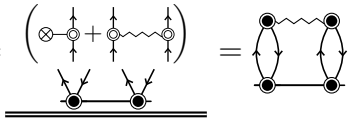
This assignment is due Friday, April 24 at 5PM by email.

Coupled Electron Pair Approximation

CEPA$_0$ energy equation:

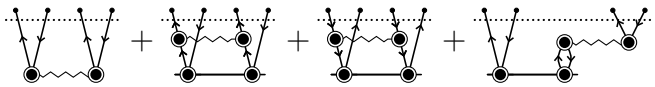
$$E_{\mathrm{c}} = \langle \Phi | H_c (1 + T_2) | \Phi \rangle \tag{0.1}$$

$$= \quad = \tag{0.2}$$



CEPA$_0$ amplitude equation:

$$t_{ab}^{ij} = \frac{\langle \Phi_{ij}^{ab} | V(1 + T_2) | \Phi \rangle_{\mathrm{L}}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = \tag{0.3}$$



Determine the programmable equations from the diagrams above. For any terms that have $\hat{P}_{(\ldots)}^{(\ldots)}$ they 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_{ij}^{ab}.
- Iterations:
  1. Solve for the new t_{ij}^{ab} using the old amplitudes.
  2. Print the CEPA$_0$ correlation energy using the new t_{ij}^{ab}.
  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 CEPA$_0$ correlation energy in addition to the total energy.

There is one additional input keyword for this program:

```
Settings["cc_max_iter"] = 75
```

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 CEPA$_0$

```
Psi4 Hartree-Fock Energy: -75.6335074773


  Spin-Orbital CEPA0


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  0.1633 seconds.
Forming denominator (oovv) ... done in  0.0005 seconds.
Antisymmetrizing <pq||rs> = (pr|qs) - (ps|qr) ... done in  0.0155 seconds.
Performing integral transformations:
     <oo||vv> ... done in  0.0190 seconds.
     <oo||oo> ... done in  0.0156 seconds.
     <vo||ov> ... done in  0.0498 seconds.
     <vv||vv> ... done in  0.1568 seconds.

Beginning CEPA0 iterations ...
    Iteration   1: energy  -0.1591601529 dE -1.59160E-01 |dT| +3.82786E-01
    Iteration   2: energy  -0.1726231052 dE -1.34630E-02 |dT| +5.74981E-02
    Iteration   3: energy  -0.1758466040 dE -3.22350E-03 |dT| +2.29994E-02
    Iteration   4: energy  -0.1768857365 dE -1.03913E-03 |dT| +1.20234E-02
    Iteration   5: energy  -0.1773020912 dE -4.16355E-04 |dT| +7.33581E-03
    Iteration   6: energy  -0.1774943706 dE -1.92279E-04 |dT| +4.85164E-03
    Iteration   7: energy  -0.1775937496 dE -9.93790E-05 |dT| +3.33440E-03
    .
    .
    .
    Iteration  54: energy  -0.1777487753 dE -6.26466E-12 |dT| +6.11786E-10
    Iteration  55: energy  -0.1777487753 dE -4.51228E-12 |dT| +4.41413E-10
    Iteration  56: energy  -0.1777487753 dE -3.25043E-12 |dT| +3.18486E-10
    Iteration  57: energy  -0.1777487753 dE -2.34165E-12 |dT| +2.29792E-10
    Iteration  58: energy  -0.1777487753 dE -1.68709E-12 |dT| +1.65798E-10
    Iteration  59: energy  -0.1777487753 dE -1.21578E-12 |dT| +1.19625E-10
    Iteration  60: energy  -0.1777487753 dE -8.76077E-13 |dT| +8.63104E-11

CEPA0 correlation energy:  -0.1777487753
Total CEPA0 energy:       -75.8112562526 (HF + CEPA0)
CEPA0 total time:  7.8996 seconds.
```

Extra Credit (20 points)

Apply density-fitting to the $\langle ab||cd\rangle$ term. To receive credit for this you must not store any version of the full $\langle ab||cd\rangle$ or $(ab|cd)$ type pf two-electron integral in memory.

For density-fitting, simply use the `df_basis` keyword from before and re-perform the CEPA0 computation. No sample output or assistance will be provided.