CHEM 8950
ADVANCE QUANTUM CHEMISTRY

This assignment is due Friday, April 10 by 5PM.

Spin-Orbital Formulism

A spin-orbital code combines the α and β electrons into a single entity. So instead of separate $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ matrices, you construct a unified $\mathbf{C}$ matrix. Using your converged $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$, construct the following block diagonal matrix:

$$\begin{pmatrix} \mathbf{C}^\alpha & \mathbf{0} \\ \mathbf{0} & \mathbf{C}^\beta \end{pmatrix} \tag{0.1}$$

Similarly concatenate the orbital energies:

$$\begin{pmatrix} \epsilon^\alpha & \epsilon^\beta \end{pmatrix} \tag{0.2}$$

Sort the eigenvalues into ascending order along with the corresponding eigenvector.

```
Before sort:
 Eigenvalues:   [ 1.34883885  0.0418147  -0.6564584 ]
 Eigenvectors: [[-0.70494612 -0.73836071  0.47669838]
                [-0.68457238 -0.07927796 -0.84023093]
                [-0.1855037   0.66973014  0.25840016]]

After sort:
 Eigenvalues:   [-0.6564584   0.0418147   1.34883885]
 Eigenvectors: [[ 0.47669838 -0.73836071 -0.70494612]
                [-0.84023093 -0.07927796 -0.68457238]
                [ 0.25840016  0.66973014 -0.1855037 ]]
```

Example for H_2O^+

```
    alpha      beta      alpha     beta     alpha ...
 [-21.01861 -20.98749  -1.89821  -1.72518  -1.1685...]
[[ 0.0026   0.99475 -0.00064  0.23385  0.      ... ]
 [ 0.00007  0.02344  0.00242 -0.85992 -0.      ... ]
 [ 0.      -0.       0.      -0.      -0.      ... ]
 [ 0.      -0.      -0.       0.       0.00195 ... ]
 [ 0.00001  0.00358  0.00042 -0.16427 -0.      ... ]
 [-0.00001 -0.00501  0.00022 -0.13814 -0.00084 ... ]
 [-0.00001 -0.00501  0.00022 -0.13814  0.00084 ... ]
 [ 0.99416 -0.0026  -0.24651 -0.00061 -0.      ... ]
 [ 0.02599 -0.00006  0.92455  0.00225  0.      ... ]
 [-0.       0.      -0.      -0.      -0.      ... ]
```

```
[-0.       0.       0.      -0.       0.74493 ... ]
[ 0.00388 -0.00001  0.15883  0.00043 -0.      ... ]
[-0.00554  0.00001  0.08517  0.00036 -0.321   ... ]
[-0.00554  0.00001  0.08517  0.00036  0.321   ... ]]
```

Integral Transformation

Block the two electron integrals to prepare them for handling α and β spin cases:

```
def spin_block_tei(gao):
    I = np.eye(2)
    gao = np.kron(I, gao)
    return np.kron(I, gao.T)
```

The standard ERIs that you obtain from Psi4 are in chemist notation. The diagrams and equation you've been working with are in physicist notation:

$$\langle 1\ 2 \mid 3\ 4 \rangle_{\text{physicist}} = (1\ 3 \mid 2\ 4)_{\text{chemist}} \tag{0.3}$$

Convert the ERIs from chemist to physicist notation and antisymmetrize them:

$$\langle 1\ 2 \mid\mid 3\ 4 \rangle = (1\ 3 \mid 2\ 4) - (1\ 4 \mid 2\ 3) \tag{0.4}$$

Using your sorted-spin-blocked C and spin-blocked two electron integrals, transform your two electron integrals from the atomic orbital basis to the molecular orbital basis:

$$\langle p\ q \mid\mid r\ s \rangle = C_P^p C_Q^q C_R^r C_S^s \langle P\ Q \mid\mid R\ S \rangle \tag{0.5}$$

MP2

$$E_{\text{corr}}^{\text{MP2}} = \quad = \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{0.6}$$

Compute and print the MP2 correlation energy.
There are no new additional input keywords for this program.

input.py

```
Settings = dict()
Settings["basis"] = "STO-3G"
Settings["molecule"] = """
  0 1
  O
  H 1 R
  H 1 R 2 A
  R = 0.9
  A = 104.5
  symmetry c1
"""
Settings["nalpha"] = 5
Settings["nbeta"] = 5
Settings["scf_max_iter"] = 50
```

Output

Here is the output from my MP2 code:

```
Psi4 Hartree-Fock Energy: -74.9450210088
Psi4 MP2 Energy:          -74.9761035637


  Spin-Orbital MP2


Number of basis functions:            7
Number of molecular orbitals:         7
Number of spin orbitals:              14
    Number of occupied spin orbitals: 10
    Number of virtual spin orbitals:  4

Performing AO->MO integral transformation (ov|ov) ... done.

Anti-symmetrizing the integrals <ij||ab> = (ia|jb) - (ib|ja) ... done.

Forming denominator (oovv) ... done.

MP2 correlation energy:  -0.0310825549
Total MP2 energy:       -74.9761035637 (HF + MP2)
```