

# CHEM 8950

## ADVANCE QUANTUM CHEMISTRY

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

### Spin-Orbital Formulism

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

$$\begin{pmatrix} C^\alpha & 0 \\ 0 & C^\beta \end{pmatrix} \quad (0.1)$$

Similarly concatenate the orbital energies:

$$\begin{pmatrix} \epsilon^\alpha & \epsilon^\beta \end{pmatrix} \quad (0.2)$$

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  $\alpha$  and  $\beta$  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:

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

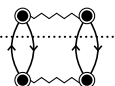
Convert the ERIs from chemist to physicist notation and antisymmetrize them:

$$\langle 1\ 2\ ||\ 3\ 4 \rangle = (1\ 3\ |\ 2\ 4) - (1\ 4\ |\ 2\ 3) \quad (0.4)$$

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:

$$\langle p\ q\ ||\ r\ s \rangle = C_P^p C_Q^q C_R^r C_S^s \langle P\ Q\ ||\ R\ S \rangle \quad (0.5)$$

## MP2

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


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"] = """
O 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)
```