

# Configuration Interaction Singles

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Ground-State:    Hartree-Fock    DFT

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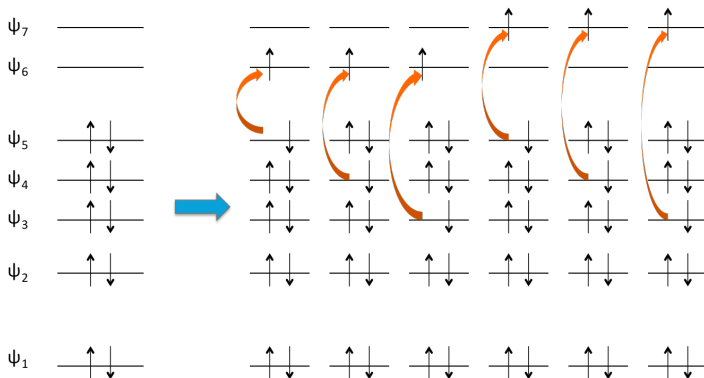


- The CIS wavefunction can be written as

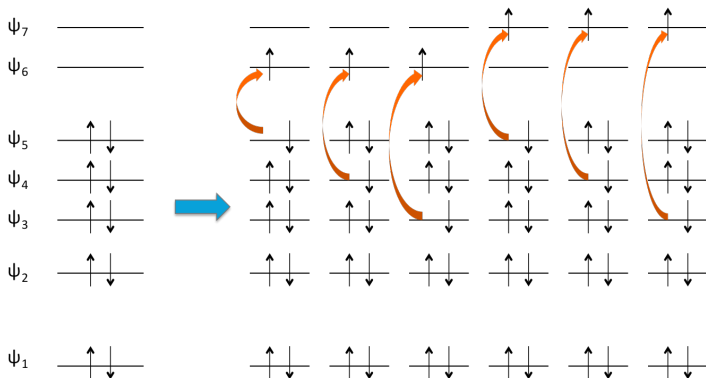
$$\Psi_{\text{CIS}} = \sum_{ai} X_{ai} \Phi_i^a$$

where  $X_{ai}$  are called excitation amplitudes.

# Configuration Interaction Singles (CIS)



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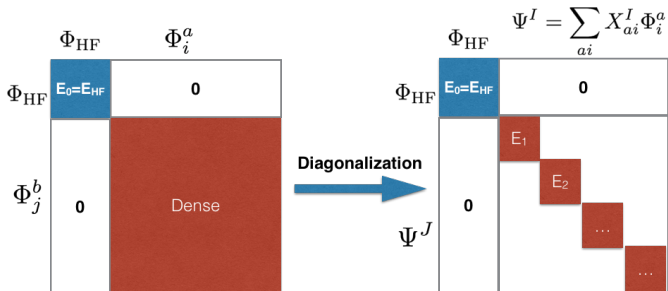


$$\Psi_{\text{CIS}}^{\text{singlet}} = \sum_{ai} X_{ai} \left[ \frac{1}{\sqrt{2}} (\Phi_i^a + \Phi_{\bar{i}}^{\bar{a}}) \right] \quad \Psi_{\text{CIS}}^{\text{triplet}} = \sum_{ai} X_{ai} \left[ \frac{1}{\sqrt{2}} (\Phi_i^a - \Phi_{\bar{i}}^{\bar{a}}) \right]$$

- The CIS wavefunction

$$\Psi_{\text{CIS}} = \sum_{ai} X_{ai} \Phi_i^a$$

are obtained by diagonalizing the Hamiltonian in the subspace spanned by all singly-excited configurations.





- Given the Hamiltonian,

$$\hat{H} = \sum_i \left( -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \right) + \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- The Hamiltonian matrix elements

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = E_0 + (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ai|bj) - (ab|ij)$$

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- For singlet configurations

$$\left\langle \frac{\Phi_i^a + \Phi_i^{\bar{a}}}{\sqrt{2}} \left| \hat{H} \right| \frac{\Phi_j^b + \Phi_j^{\bar{b}}}{\sqrt{2}} \right\rangle = E_0 + (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + 2(ai|bj) - (ab|ij)$$

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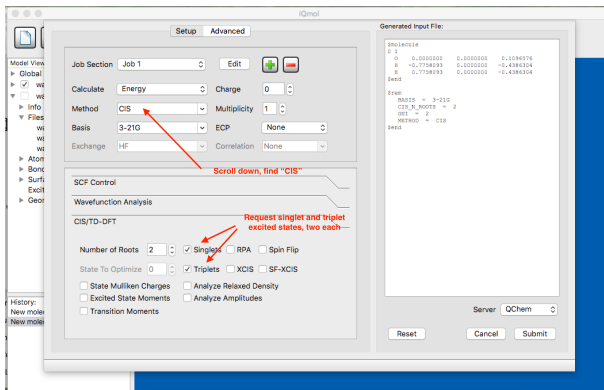
$$\left\langle \frac{\Phi_i^a + \Phi_i^{\bar{a}}}{\sqrt{2}} \middle| \hat{H} \middle| \frac{\Phi_j^b + \Phi_j^{\bar{b}}}{\sqrt{2}} \right\rangle = E_0 + (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + 2(ai|bj) - (ab|ij)$$

- For triplet configurations

$$\left\langle \frac{\Phi_i^a - \Phi_i^{\bar{a}}}{\sqrt{2}} \middle| \hat{H} \middle| \frac{\Phi_j^b - \Phi_j^{\bar{b}}}{\sqrt{2}} \right\rangle = E_0 + (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} - (ab|ij)$$

# Case Study: Water Molecule

- Use IQmol to build water molecule (O-H: 0.95 Å; H-O-H: 105°).
- Perform CIS calcn's to find two lowest singlet and triplet excited states.



# Q-Chem Output File

```
-----  
CIS Excitation Energies  
-----  
  
Excited state 1: excitation energy (eV) = 8.6220  
Total energy for state 1: -75.26854889 au  
Multiplicity: Triplet  
Trans. Mom.: 0.0000 X 0.0000 Y 0.0000 Z  
Strength : 0.0000000000  
D( 5) --> V( 1) amplitude = 0.9925  
  
Excited state 2: excitation energy (eV) = 9.7113  
Total energy for state 2: -75.22851575 au  
Multiplicity: Singlet  
Trans. Mom.: 0.0000 X 0.1673 Y 0.0000 Z  
Strength : 0.0066622120  
D( 5) --> V( 1) amplitude = 0.9957  
  
Excited state 3: excitation energy (eV) = 10.3138  
Total energy for state 3: -75.20637513 au  
Multiplicity: Triplet  
Trans. Mom.: 0.0000 X 0.0000 Y 0.0000 Z  
Strength : 0.0000000000  
D( 4) --> V( 1) amplitude = 0.9808  
  
Excited state 4: excitation energy (eV) = 12.0281  
Total energy for state 4: -75.14337509 au  
Multiplicity: Singlet  
Trans. Mom.: -0.0000 X 0.0000 Y 0.5514 Z  
Strength : 0.0895913457  
D( 4) --> V( 1) amplitude = 0.9882
```

For this (HOMO->LUMO) transition,  
the triplet state has a lower  
energy than the singlet one

# Singlet and Triplet Excitation Energies

- Copy over
  - /home/yihan/qm\_tutorial/qchem\_files/FCIDump
  - /home/yihan/qm\_tutorial/python\_files/read\_fcidump.py
- Follow the Hartree-Fock energy code, compute
  - singlet/triplet excitation energies for the HOMO  $\rightarrow$  LUMO transition
  - singlet/triplet excitation energies for the HOMO-1  $\rightarrow$  LUMO transition

```
# HOMO-1 -> LUMO or HOMO -> LUMO excitation
for i in [Nocc-1, Nocc-2]: # HOMO and HOMO-1
    for a in range(5,6): # LUMO
        dE1 = E0rb[a] - E0rb[i]
        dE2J = 2*integrals.two_e_integrals[a,i,a,i]
        dE2K = integrals.two_e_integrals[i,i,a,a]
        dE_singlet = 27.211 * (dE1 + dE2J - dE2K)
        dE_triplet = 27.211 * (dE1 - dE2K)
        write("i: %3d a: %3d dE = %7.4f (singlet) %7.4f (triplet)\n"
```

- Redo the calculation using actual amplitudes, after copying over
  - /home/yihan/qm\_tutorial/water.cis.amplitudes
  - /home/yihan/qm\_tutorial/python\_files/matrix\_print.py
  - /home/yihan/qm\_tutorial/python\_files/read\_amplitudes.py

```

NVir, NOV = NOrb - NOcc, NOcc * NVir
amp = np.zeros(4*NOV)
read_amplitudes(amp, NOcc, NVir, NOV, "water.cis.amplitudes")
for istrate in range(0, 4):
    matrix_print_1d(amp[istrate*NOV:(istrate+1)*NOV], NVir, NOcc, 6, "X")
    dE1, dE2J, dE2K = 0.0, 0.0, 0.0
    for i in range(0, NOcc):
        for a in range(NOcc, NOrb):
            Xai = amp[a-NOcc + i*NVir + istrate * NOV]
            dE1 += 2 * Xai * Xai * (EOrb[a] - EOrb[i])
            for j in range(0, NOcc):
                for b in range(NOcc, NOrb):
                    Xbj = amp[b-NOcc + j*NVir + istrate * NOV]
                    dE2J += 4.0 * integrals.two_e_integrals[a, i, b, j] * Xai * Xbj
                    dE2K += 2.0 * integrals.two_e_integrals[a, b, i, j] * Xai * Xbj
dE_singlet = 27.211 * (dE1 + dE2J - dE2K)
dE_triplet = 27.211 * (dE1 - dE2K)
write("istrate: %3d dE = %7.4f (singlet) %7.4f (triplet)\n\n" % (istrate+1, dE_singlet, dE_triplet))

```

- For a triplet state involving HOMO and LUMO, there are three components:
  - $S_z=0$ , slide 8
  - $S_z=1, -1$ . Now let us compute the energy of the  $S_z=1$  component.

```
#finally check triplet (Sz=1) state with `HOMO` and `LUMO` singly occupied
E1, E2J, E2K = 0.0, 0.0, 0.0
for i in range(0, NOcc+1):
    if i <= NOcc-2: E1 += 2.0 * integrals.one_e_integrals[i,i] #doubly-occupied
    else: E1 += integrals.one_e_integrals[i,i] #singly-occupied
    for j in range(0, NOcc+1):
        if i <= NOcc-2 and j <= NOcc-2: #both doubly-occupied
            E2J += 2.0 * integrals.two_e_integrals[i,i,j,j]
            E2K += 1.0 * integrals.two_e_integrals[i,j,i,j]
        elif i <= NOcc-2 or j <= NOcc-2: # one singly-occupied, one doubly-occupied
            E2J += 1.0 * integrals.two_e_integrals[i,i,j,j]
            E2K += 0.5 * integrals.two_e_integrals[i,j,i,j]
        elif i >= NOcc-1 and j >= NOcc-1: #both alpha singly-occupied
            E2J += 0.5 * integrals.two_e_integrals[i,i,j,j]
            E2K += 0.5 * integrals.two_e_integrals[i,j,i,j]
ETot = ENuc + E1 + E2J - E2K
print("ETot:", ETot, "E1:", E1, "E2J=", E2J, "E2K=", E2K)
```