

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

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In words, the **Fock matrix elements between AOs  $\chi_\mu$  and  $\chi_\nu$**  are:

- 1) The kinetic energy matrix elements: (in  $h_{\mu\nu}$  )
- 2) The integral over nuclear attraction (also in  $h_{\mu\nu}$ )
- 3) Electrostatic repulsion between all AO products pairs ( $\chi_\lambda\chi_\sigma$ ), minus  $\frac{1}{2}$  the repulsion of the exchanged pairs weighted by  $D_{\lambda\sigma}$  .

**It is crucial that (except for the kinetic energy), that you translate and visualize the above equation as a statement of simple electrostatic attractions (negative) and repulsions (positive) involving charge clouds of AOs squared on the diagonal, and involving charge-like clouds of AO products off the diagonal.**

Examine actual HF-SCF output from a computation for water using Gaussian 09.

(pdf from Jean Standard course website, Illinois State Chemistry 460 Spring 2015 Dr. Jean M. Standard April 22, 2015)

## A Hartree-Fock Calculation of the Water Molecule

### Introduction

An example Hartree-Fock calculation of the water molecule will be presented. In this case, the water molecule will have its geometry **fixed at the experimental values of bond lengths ( $R(\text{O-H})=0.95 \text{ \AA}$ ) and bond angle ( $\angle\text{H-O-H}= 104.5^\circ$ ).**

Thus, the electronic energy and wavefunction will be computed for fixed nuclear positions; this is known as a **single-point energy calculation**.

**A minimal basis set of atomic orbital functions** will be employed.

Gaussian input file text file  
typed by Callis and named  
jean-h2o.gjf (job input file)

All input files must have .gjf  
extension.

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Location of checkpoint file; necessary  
to plot MOs, vibrations, etc.

%chk=C:\564-17\Jean-h20.chk

# hf/sto-3g pop=full

Route card; tells what to do

Blank line

water from Jean Standard pdf, ordered to  
match output by callis molecule in yz plane

Comments

charge  
0 1  $2S + 1 = \text{spin multiplicity}$

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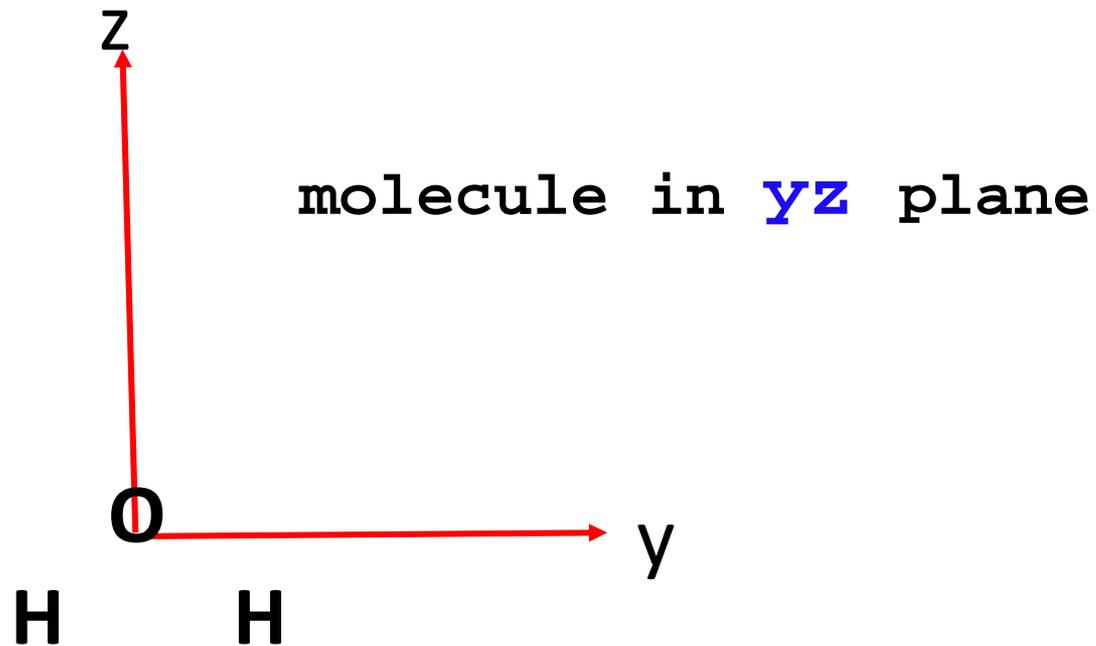
8 0.000000 0.000000 0.116321

1 0 .000000 0.751155 -0.465285

Atomic No, Cartesian  
coords.

1 0.000000 -0.751155 -0.465285

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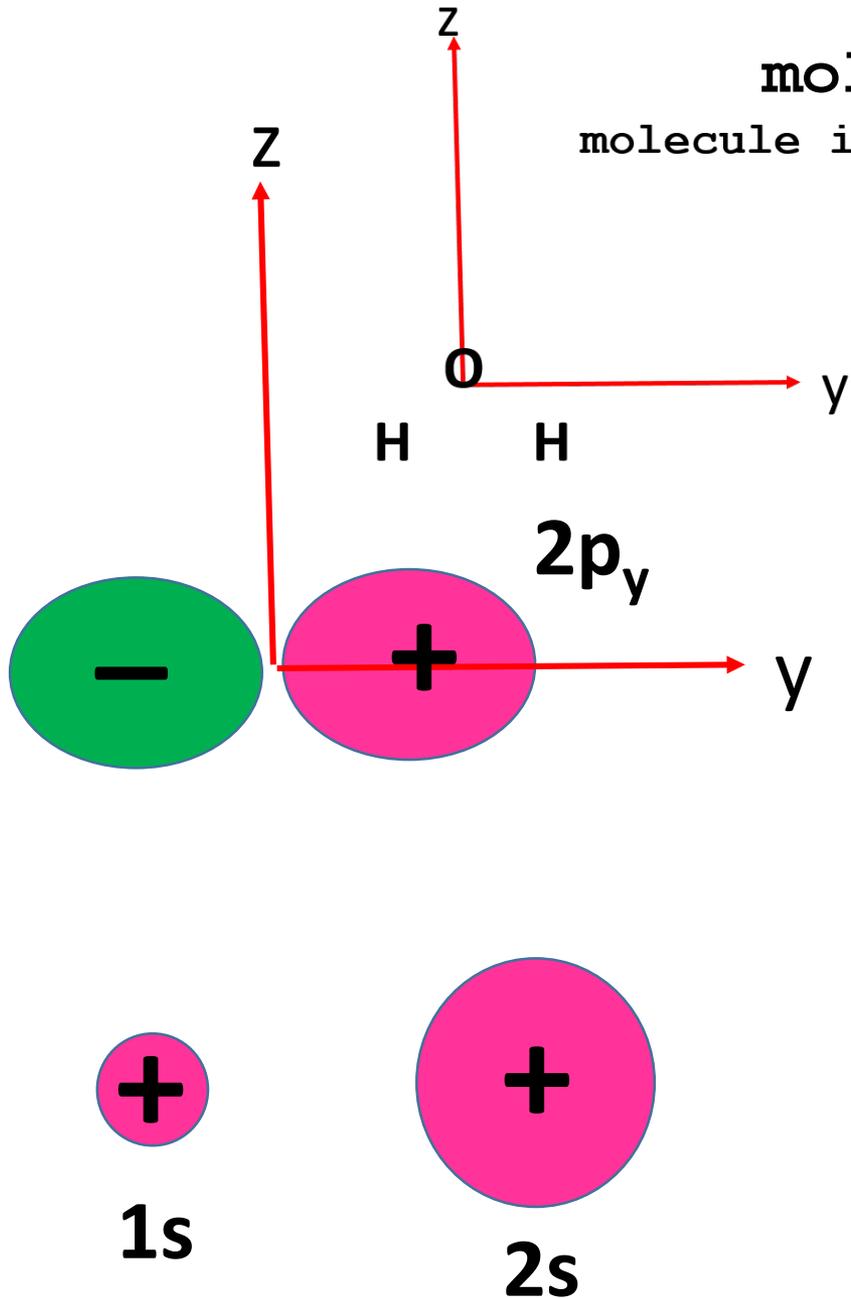


8	0.000000	0.000000	0.116321
1	0.000000	0.751155	-0.465285
1	0.000000	-0.751155	-0.465285

**Table 2.** Basis functions for the HF/STO-3G calculation of the water molecule.

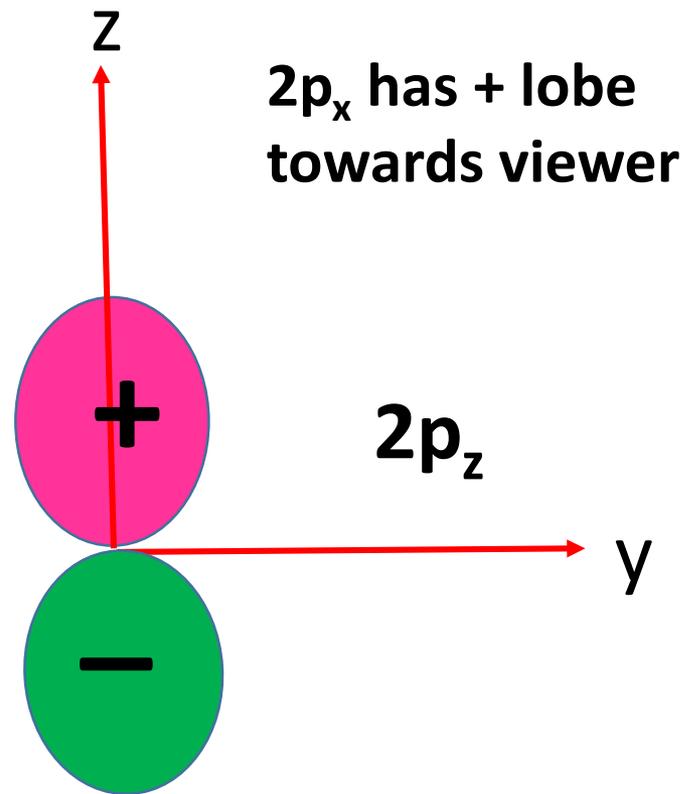
Basis function #	Basis function type
1	1s O
2	2s O
3	2p <sub>x</sub> O
4	2p <sub>y</sub> O
5	2p <sub>z</sub> O
6	1s H <sub>a</sub>
7	1s H <sub>b</sub>

Next get oriented with the orbital PHASES relative to molecule orientation



molecule in  $yz$  plane

molecule in



Slater type orbitals  
No radial nodes

### Atomic orbital basis functions

The water molecule has a total of 10 electrons, eight from the oxygen atom and one each from the hydrogen atoms. Therefore, for a closed shell molecular system like water in its ground state with 10 total electrons, the wavefunction in the form of a Slater Determinant is

$$\Psi_{\text{H}_2\text{O}} = \frac{1}{\sqrt{10!}} \left| \begin{array}{ccccc} \phi_1 \bar{\phi}_1 & \phi_2 \bar{\phi}_2 & \phi_3 \bar{\phi}_3 & \phi_4 \bar{\phi}_4 & \phi_5 \bar{\phi}_5 \end{array} \right|.$$

The functions  $\phi_i$  for water are molecular orbitals defined using the LCAO-MO approximation,

$$\phi_i(1) = \sum_{\mu=1}^K c_{\mu i} f_{\mu}(1) .$$

# The Overlap Matrix

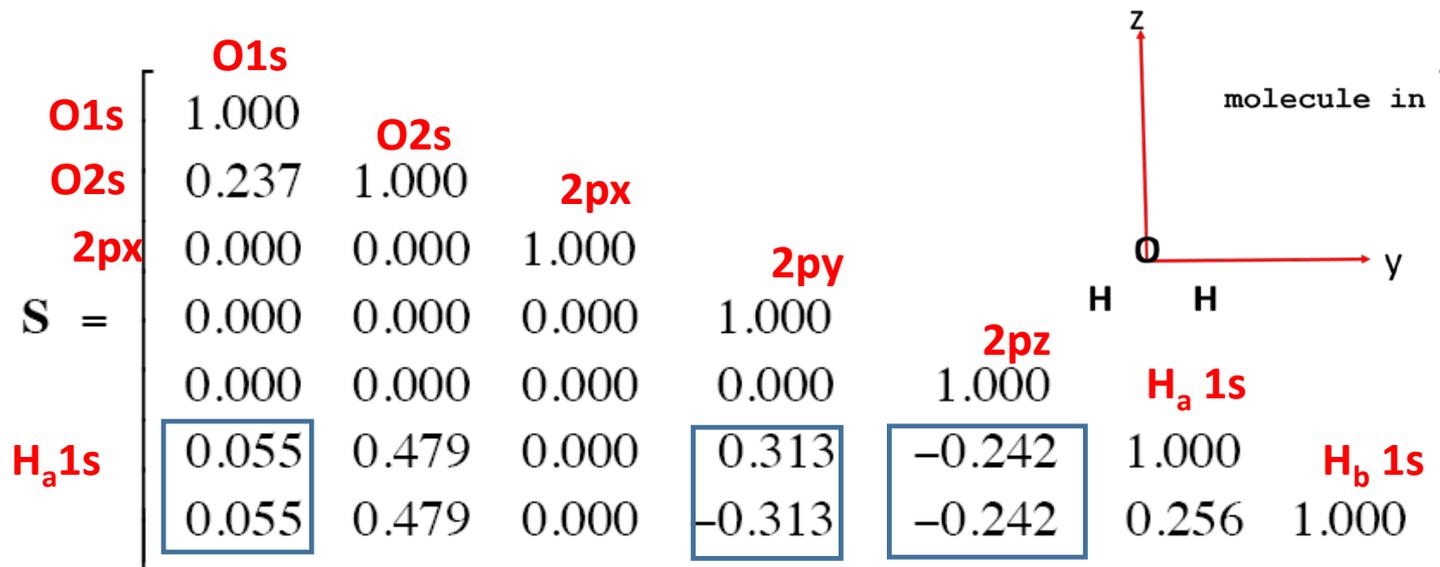
For the STO-3G basis set with the basis functions specified in the order given in Table 2, the overlap matrix **S** is shown in Figure 1. Note that only the lower portion is shown because the upper portion is related by symmetry since  $S_{\mu\nu} = S_{\nu\mu}$ .

$$\langle \mu | \nu \rangle = S_{\mu\nu} = S_{\nu\mu}$$

**Try to understand EVERYTHING about this matrix**

$$\mathbf{S} = \begin{bmatrix} 1.000 & & & & & & & & \\ 0.237 & 1.000 & & & & & & & \\ 0.000 & 0.000 & 1.000 & & & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & & & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 & & \end{bmatrix}$$

For the STO-3G basis set with the basis functions specified in the order given in Table 2, the overlap matrix  $S$  is shown in Figure 1. Note that only the lower portion is shown because the upper portion is related by symmetry since  $S_{\mu\nu} = S_{\nu\mu}$ .



## Do these overlap integrals make sense?

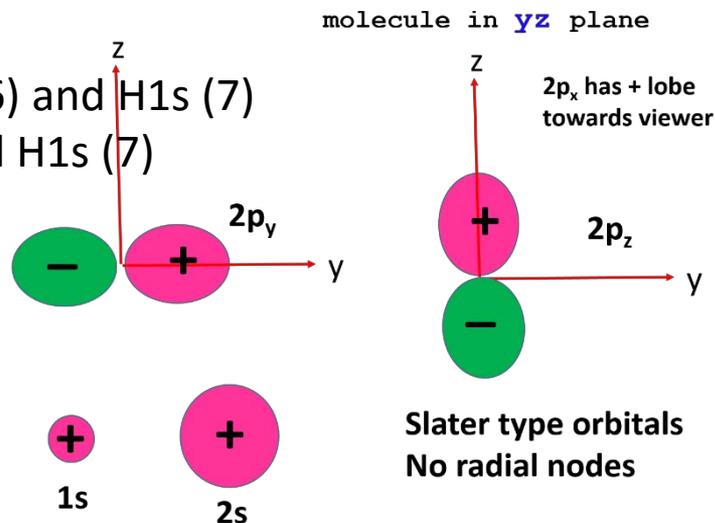
Why does AO 3 = 2px have zero for all overlap integrals

why O 1s orbital has very small overlap with both H1s (6) and H1s (7)

Why 2s orbital has large + overlap with both H1s (6) and H1s (7)

why 2py has + overlap with H1s (6) and - with H1s (7)

why 2pz has - overlap with both H1s (6) and H1s (7)



# The Kinetic Energy Matrix

$$T_{\mu\nu} = \left\langle f_{\mu}(1) \left| -\frac{1}{2} \hat{\nabla}_1^2 \right| f_{\nu}(1) \right\rangle$$

Why so large? Why is this negative?  
Think about what part of the 1s orbital of O is tunneling and where the 1s and 2s overlap most.

$$\mathbf{T} = \begin{bmatrix}
 29.003 & & & & & & & \\
 -0.168 & 0.808 & & & & & & \\
 0.000 & 0.000 & 2.529 & & & & & \\
 0.000 & 0.000 & 0.000 & 2.529 & & & & \\
 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & & \\
 -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & & \\
 -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 & 
 \end{bmatrix}$$

Why negative off diag?

**Figure 2.** Kinetic energy matrix **T** for HF/STO-3G calculation of water.

# The Electron-Nuclear Attraction Matrix

$$V_{\mu\nu} = \left\langle f_{\mu}(1) \left| - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{r_{\alpha 1}} \right| f_{\nu}(1) \right\rangle$$

$$\mathbf{V} = \begin{bmatrix} -61.733 & & & & & & & & \\ -7.447 & -10.151 & & & & & & & \\ 0.000 & 0.000 & -9.926 & & & & & & \\ 0.000 & 0.000 & 0.000 & -10.152 & & & & & \\ 0.019 & 0.226 & 0.000 & 0.000 & -10.088 & & & & \\ -1.778 & -3.920 & 0.000 & -0.228 & 0.184 & -5.867 & & & \\ -1.778 & -3.920 & 0.000 & 0.228 & 0.184 & -1.652 & -5.867 & & \end{bmatrix}$$

Why are the off opposite sign of T matrix?

**Figure 3.** Potential energy matrix  $\mathbf{V}$  for HF/STO-3G calculation of water.

# The One-electron Matrix

$$H_{\mu\nu}^{\circ} = T_{\mu\nu} + V_{\mu\nu}$$

$$\mathbf{H}^{\circ} = \begin{bmatrix} -32.730 & & & & & & & & \\ -7.615 & -9.343 & & & & & & & \\ 0.000 & 0.000 & -7.397 & & & & & & \\ 0.000 & 0.000 & 0.000 & -7.623 & & & & & \\ 0.019 & 0.226 & 0.000 & 0.000 & -7.559 & & & & \\ -1.780 & -3.788 & 0.000 & 0.001 & 0.007 & -5.107 & & & \\ -1.780 & -3.788 & 0.000 & -0.001 & 0.007 & -1.643 & -5.107 & & \end{bmatrix}$$

**Figure 4.** One-electron Hamiltonian matrix  $\mathbf{H}^{\circ}$  for HF/STO-3G calculation of water.

# The Density Matrix

$$P_{\lambda\sigma} = 2 \sum_{i=1}^n c_{\lambda i}^* c_{\sigma i}$$

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & & \\ -0.456 & 2.010 & & & & & & \\ 0.000 & 0.000 & 2.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 & \end{bmatrix}$$

Why is the 2px diag element EXACTLY 2.000?

Correlate the size and signs of off diags with bonding

**Figure 5.** Initial density matrix  $\mathbf{P}$  for HF/STO-3G calculation of water based on extended Hückel guess.

## Two-electron integrals

The next step is to compute the two-electron integrals from Equation (5). The terms  $(\mu\nu|\lambda\sigma)$  and  $(\mu\lambda|\nu\sigma)$  represent two-electron repulsion integrals from the Coulomb and Exchange terms in the Fock operator,

$$\begin{aligned}(\mu\nu|\lambda\sigma) &= \left\langle f_\mu(1)f_\lambda(2) \left| \frac{1}{r_{12}} \right| f_\nu(1)f_\sigma(2) \right\rangle \\(\mu\lambda|\nu\sigma) &= \left\langle f_\mu(1)f_\nu(2) \left| \frac{1}{r_{12}} \right| f_\lambda(1)f_\sigma(2) \right\rangle.\end{aligned}\tag{10}$$

The number of two-electron integrals that must be computed is  $K^4$ , where  $K$  is the number of basis functions. For the HF/STO-3G calculation of water,  $K=7$ , so the number of two-electron integrals to be computed is 2401. Because of the symmetry of the water molecule, this number is reduced to a mere 406 integrals. Even that many would take a lot of space to list on a page, so their numerical values will not be included here.

## Fock integrals

The Fock integrals  $F_{\mu\nu}$  in Equation (3) are defined as

$$F_{\mu\nu} = H_{\mu\nu}^{\circ} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right]$$

The terms  $H_{\mu\nu}^{\circ}$  correspond to the one-electron Hamiltonian integrals,

$$H_{\mu\nu}^{\circ} = \left\langle f_{\mu}(1) \left| -\frac{1}{2} \hat{\nabla}_1^2 - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{r_{\alpha 1}} \right| f_{\nu}(1) \right\rangle .$$

$$F_{\mu\nu} = H_{\mu\nu}^0 + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right]$$

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & & & \\ -5.163 & -2.453 & & & & & & & \\ 0.000 & 0.000 & -0.395 & & & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & & & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 & & \end{bmatrix}$$

**Predict the signs of the Fock elements.**

**Figure 6.** Initial Fock matrix  $\mathbf{F}$  for HF/STO-3G calculation of water.

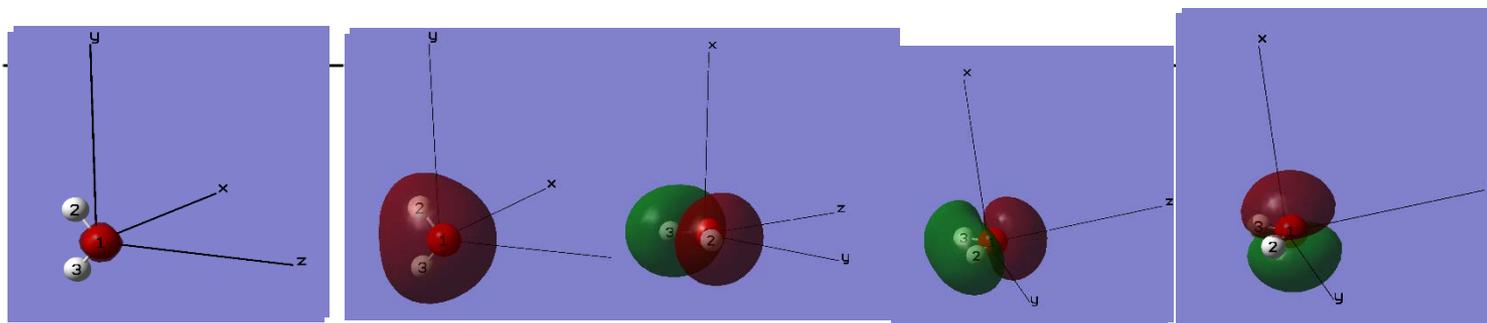
**Diagonalizing the Fock matrix gives the eigenvalues (MO energies) and eigenvectors (MOs)**

***Predict the eigenvectors qualitatively from what you know about the 2 x 2 matrix diagonalization.***

**Table 3.** Coefficients  $c_{\mu i}$  of the initial guess for the occupied molecular orbitals of water.

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MO:			1	2	3	4	5
<b>Eigenvalues --</b>			<b>-20.24094</b>	<b>-1.27218</b>	<b>-0.62173</b>	<b>-0.45392</b>	<b>-0.39176</b>
1	O	1S	0.99431	-0.23246	0.00000	-0.10725	0.00000
2	O	2S	0.02551	0.83359	0.00000	0.55664	0.00000
3	O	2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	O	2PY	0.00000	0.00000	0.60718	0.00000	0.00000
5	O	2PZ	-0.00291	-0.14086	0.00000	0.76655	0.00000
6	Ha	1S	-0.00515	0.15562	0.44418	-0.28592	0.00000
7	Hb	1S	-0.00515	0.15562	-0.44418	-0.28592	0.00000



**Apparently red =+ and green = negative**

