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

In words, the **Fock matrix elements between AOs χ_μ and χ_ν** 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 ½ 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 attactions (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 StateChemistry 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(O-H)=0.95 Å) and bond angle (∠H-O-H= 104.5°)**.

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.

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

```
%chk=C:\564-17\Jean-h20.chk
# hf/sto-3g pop=full

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

0 1
8  0.000000   0.000000    0.116321
1 0 .000000   0.751155    -0.465285
1  0.000000   -0.751155    -0.465285
```

Route card; tells what to do

Blank line

Comments

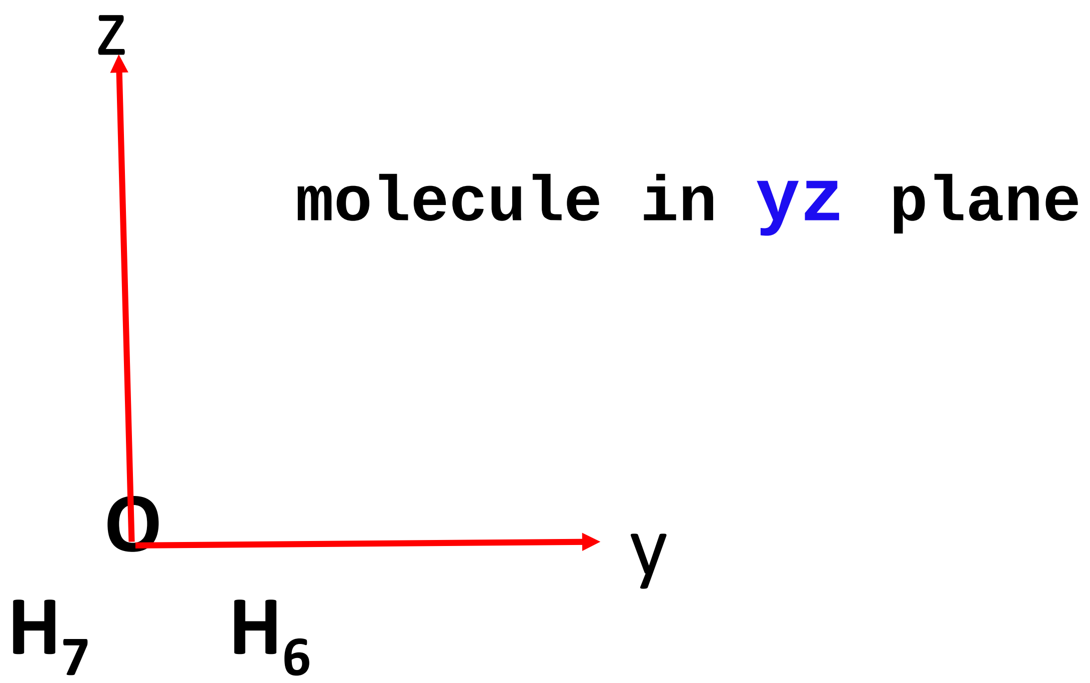
Blank line

charge

2S +1 = spin multiplicity

Atomic No, Cartesian coords.

Blank line



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

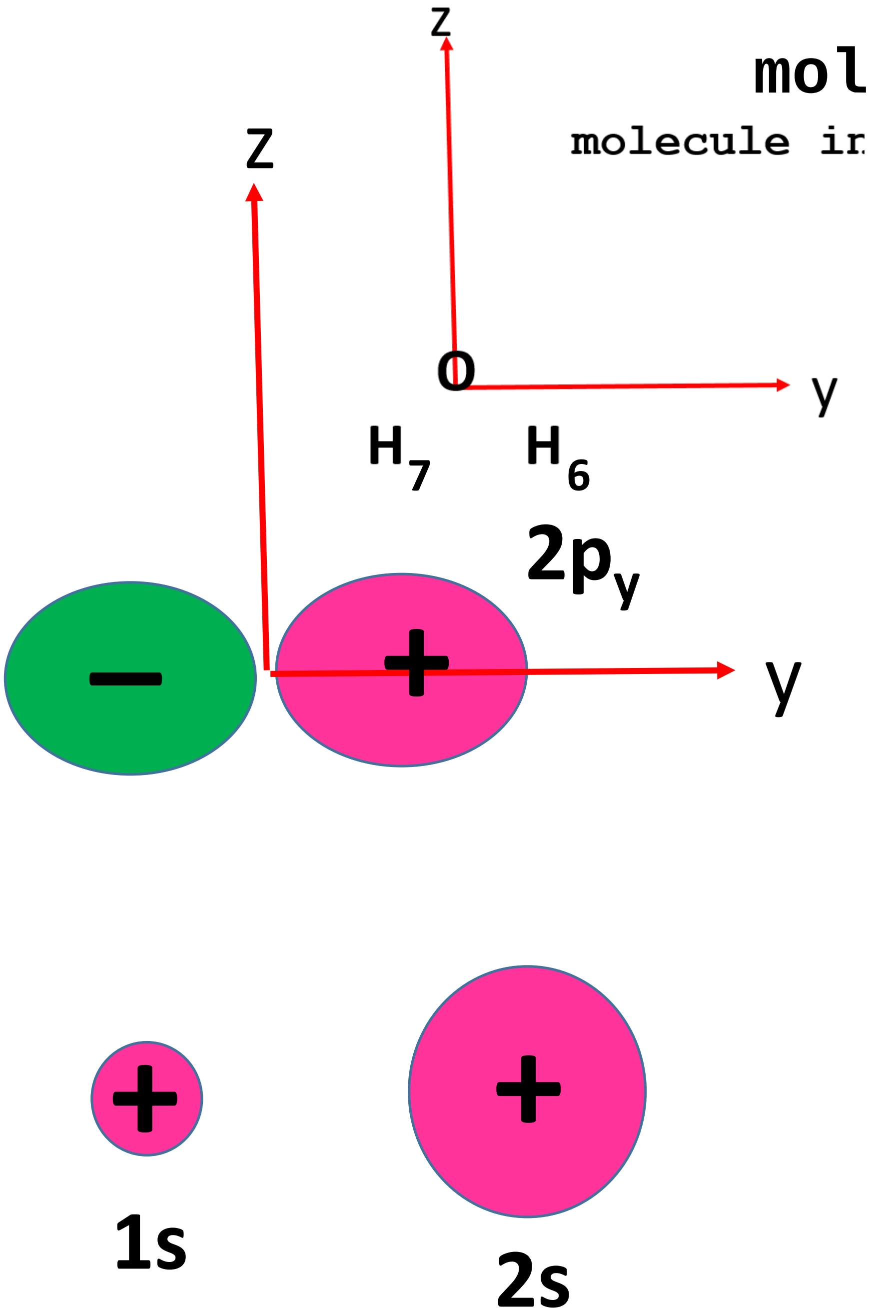
Look at the .out file or .log file

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

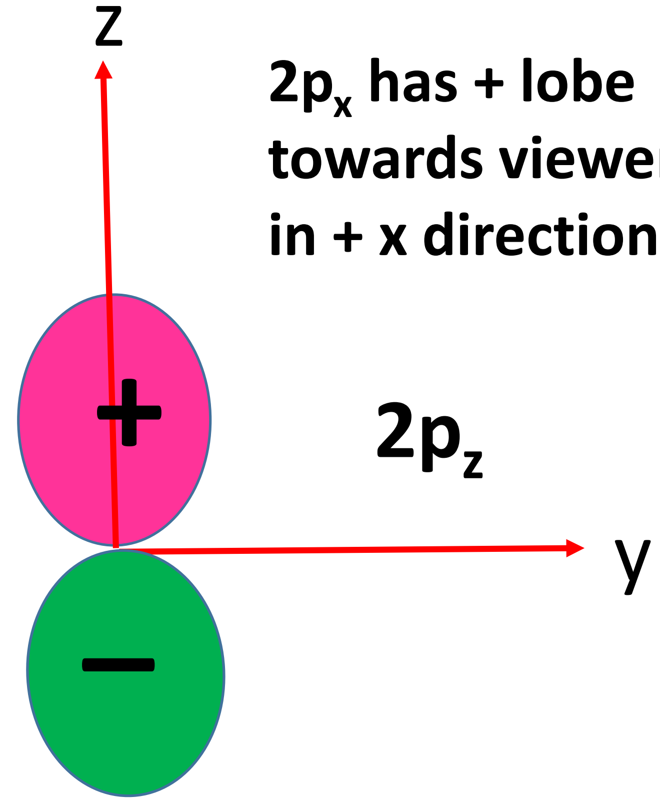
Basis function #	Basis function type
1	1s O
2	2s O
3	$2p_x$ O
4	$2p_y$ O
5	$2p_z$ O
6	1s H_a
7	1s H_b

Next get oriented with the orbital PHASES relative to molecule orientation

molecule in yz plane



2p$_x$ has + lobe towards viewer in + x direction



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

$$\Psi_{H_2O} = \frac{1}{\sqrt{10!}} \left| \phi_1\bar{\phi}_1 \ \ \phi_2\bar{\phi}_2 \ \ \phi_3\bar{\phi}_3 \ \ \phi_4\bar{\phi}_4 \ \ \phi_5\bar{\phi}_5 \right| .$$

The functions ϕ_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 $S_{\mu\nu} = S_{\nu\mu}$.

$$<\mu|\nu> = S_{\mu\nu} = S_{\nu\mu}$$

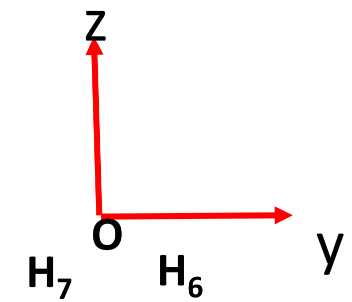
Try to understand EVERYTHING about this matrix

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

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 $S_{\mu\nu} = S_{\nu\mu}$.

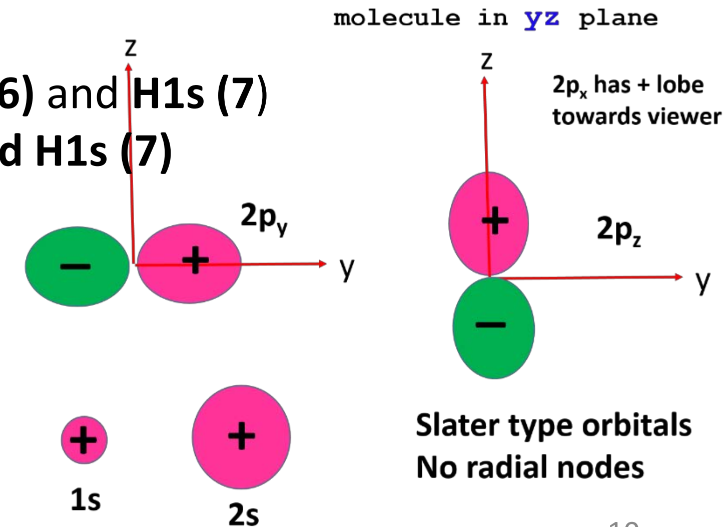
S =

	O1s	O2s	2px	2py	2pz	H_a 1s	H_b 1s
O1s	1.000						
O2s	0.237	1.000					
2px	0.000	0.000	1.000				
2py	0.000	0.000	0.000	1.000			
2pz	0.000	0.000	0.000	0.000	1.000		
H_a1s	0.055	0.479	0.000	0.313	−0.242	1.000	
H_b 1s	0.055	0.479	0.000	−0.313	−0.242	0.256	1.000



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)**
why H1s (6) and H1s (7) have large + overlap



The Kinetic Energy Matrix

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

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

Why so large?

T =

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	0.76

Why negative off diag?

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

The Electron-Nuclear Attraction Matrix

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

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

Why are the off diag elements mostly opposite sign of T matrix?

Figure 3. Potential energy matrix **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.

This is why one can say "The Hamiltonian is NEGATIVE"

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,

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

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.

The two-electron (+) contribution is smaller than the 1-electron contribution.
The electron repulsion is minimized: The electrons avoid each other; while maximizing proximity to the nuclei.
This is also why one can say "The Hamiltonian is NEGATIVE"

Fock integrals

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

$$F_{\mu\nu} = H^{o}_{\mu\nu} + \sum_{\lambda=1}^{K} \sum_{\sigma=1}^{K} P_{\lambda\sigma} \left[(\mu\nu \mid \lambda\sigma) - \tfrac{1}{2} (\mu\lambda \mid \nu\sigma) \right]$$

The terms $H^{o}_{\mu\nu}$ correspond to the one-electron Hamiltonian integrals,

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

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

Predict the signs of the Fock elements. F

Remember F **IS** the **Hamiltonian**

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

Figure 6. Initial Fock matrix **F** for HF/STO-3G calculation of water.

Most are negative, but SOME are positive; WHY?

$$< A >= \int \Psi^* \hat{A}\Psi d\tau = \int \hat{A}\Psi(\Psi^*)d\tau$$

where $\hat{A}$ does not operate on Ψ^*

A=H is always negative

SO, + elements means

ΨΨ* determines the

sign of the element

O2s

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

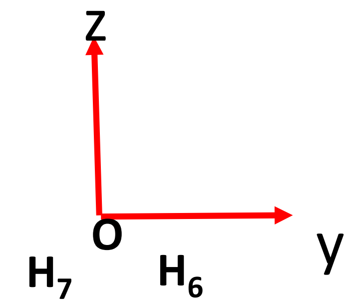
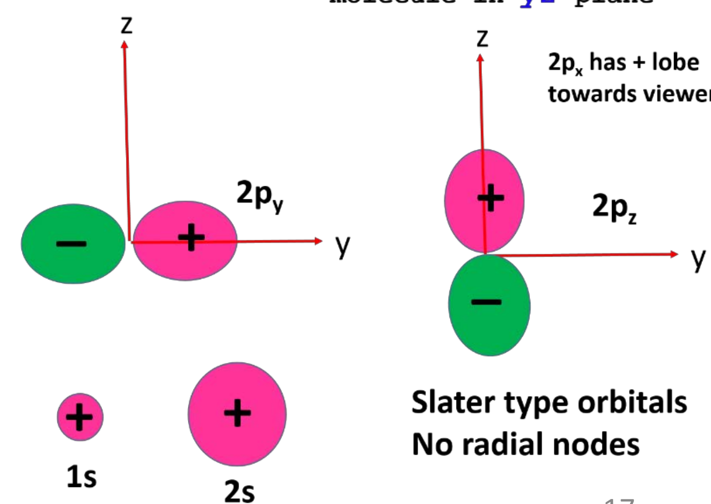


Figure 6. Initial Fock matrix **F** for HF/STO-3G calculation of water.

molecule in yz plane

Do these F integrals make sense?



Slater type orbitals
No radial nodes

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

Predict the signs of the Fock elements.

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

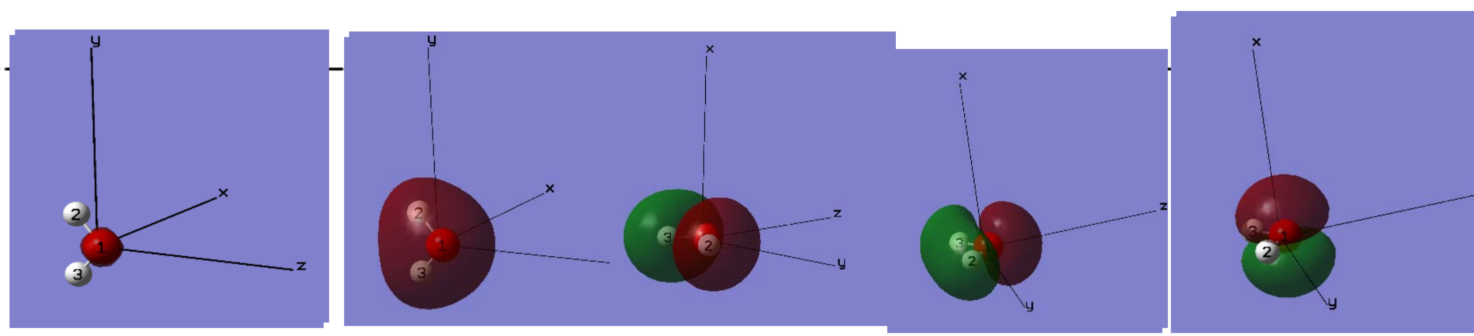
Figure 6. Initial Fock matrix **F** for HF/STO-3G calculation of water.

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.

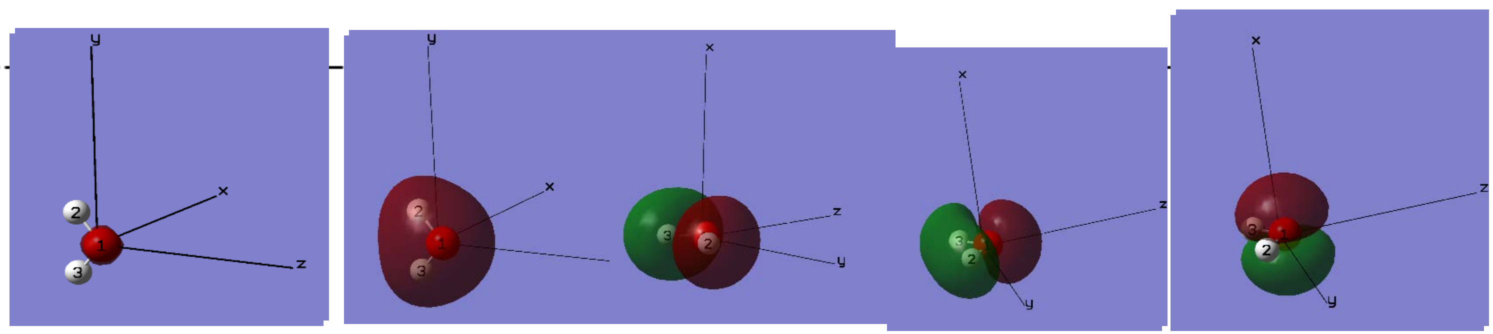
		MO:	1	2	3	4	5
		Eigenvalues --	-20.24094	-1.27218	-0.62173	-0.45392	-0.39176
1	O	1S	0.99431	-0.23246	0.00000	-0.10725	0.00000
2	O	2S	0.02551	0.83359	0.00000	0.55664	0.00000
3	O	2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	O	2PY	0.00000	0.00000	0.60718	0.00000	0.00000
5	O	2PZ	-0.00291	-0.14086	0.00000	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



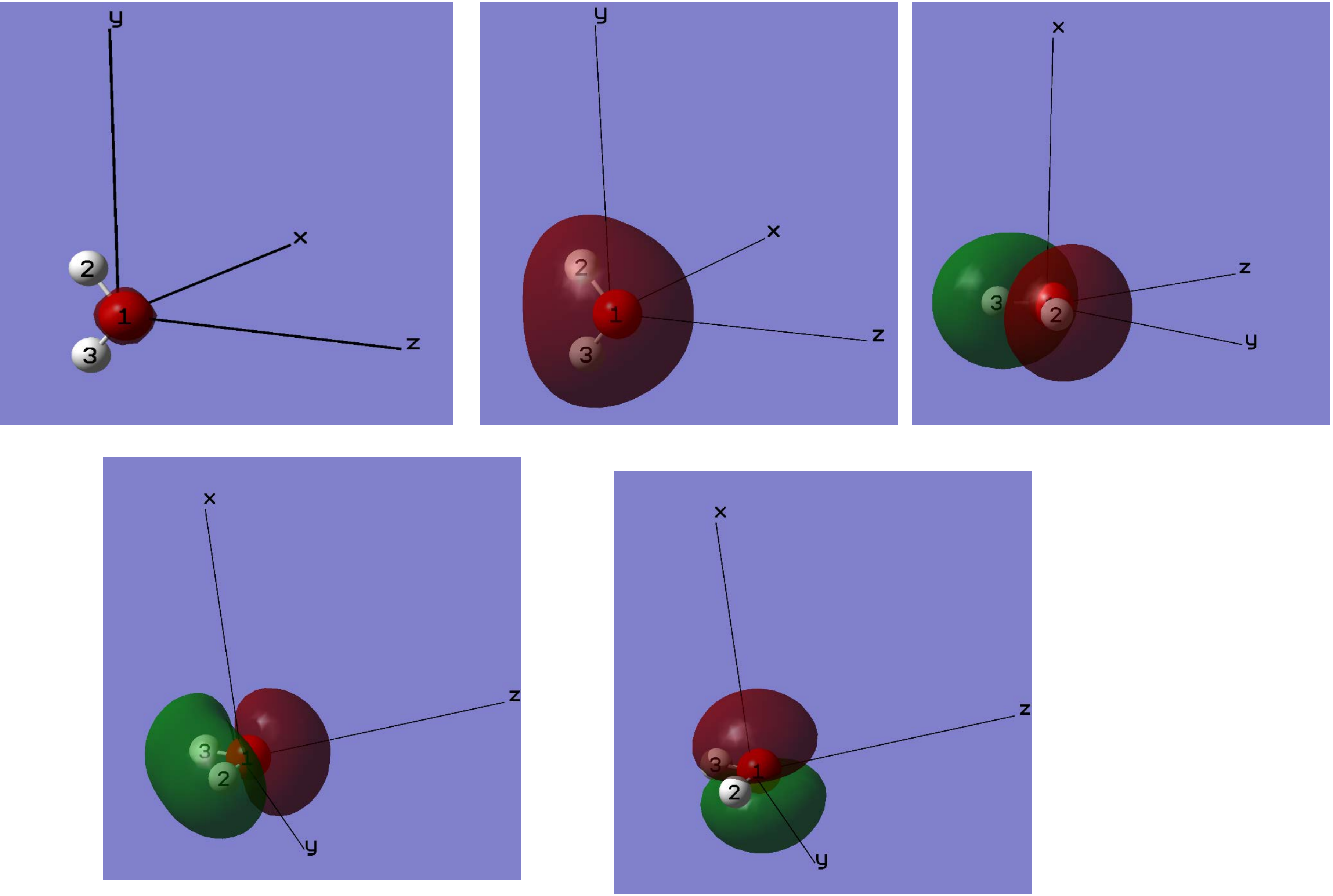
Apparently red =+ and green = negative

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

			MO:	1	2	3	4	5
			Eigenvalues --	**-20.24094**	**-1.27218**	**-0.62173**	**-0.45392**	**-0.39176**
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


y
x
z
1
2
3

The Density Matrix

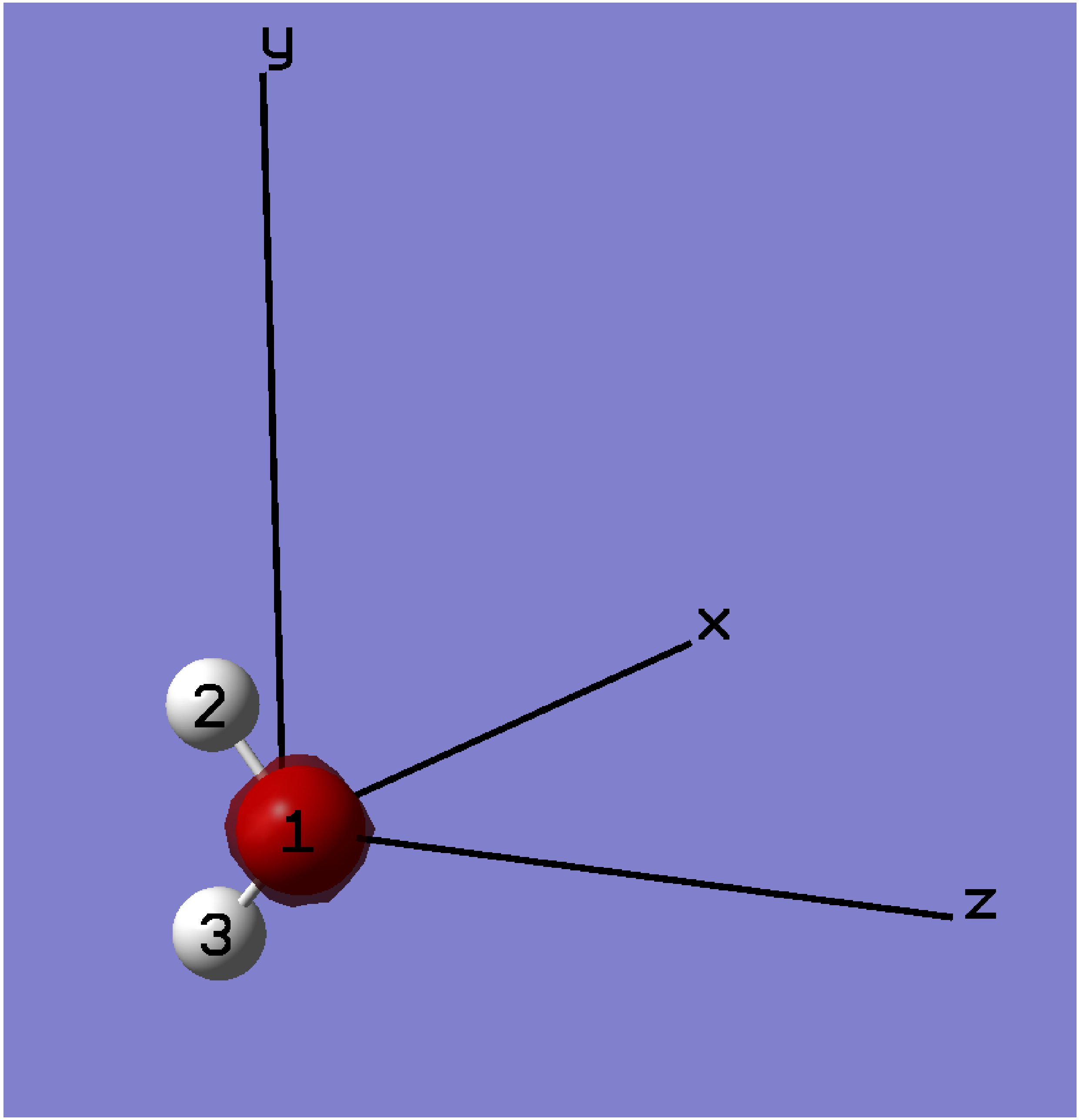
$$P_{\lambda\sigma} = 2 \sum_{i=1}^{n} c_{\lambda i}^{*} \, c_{\sigma i}$$

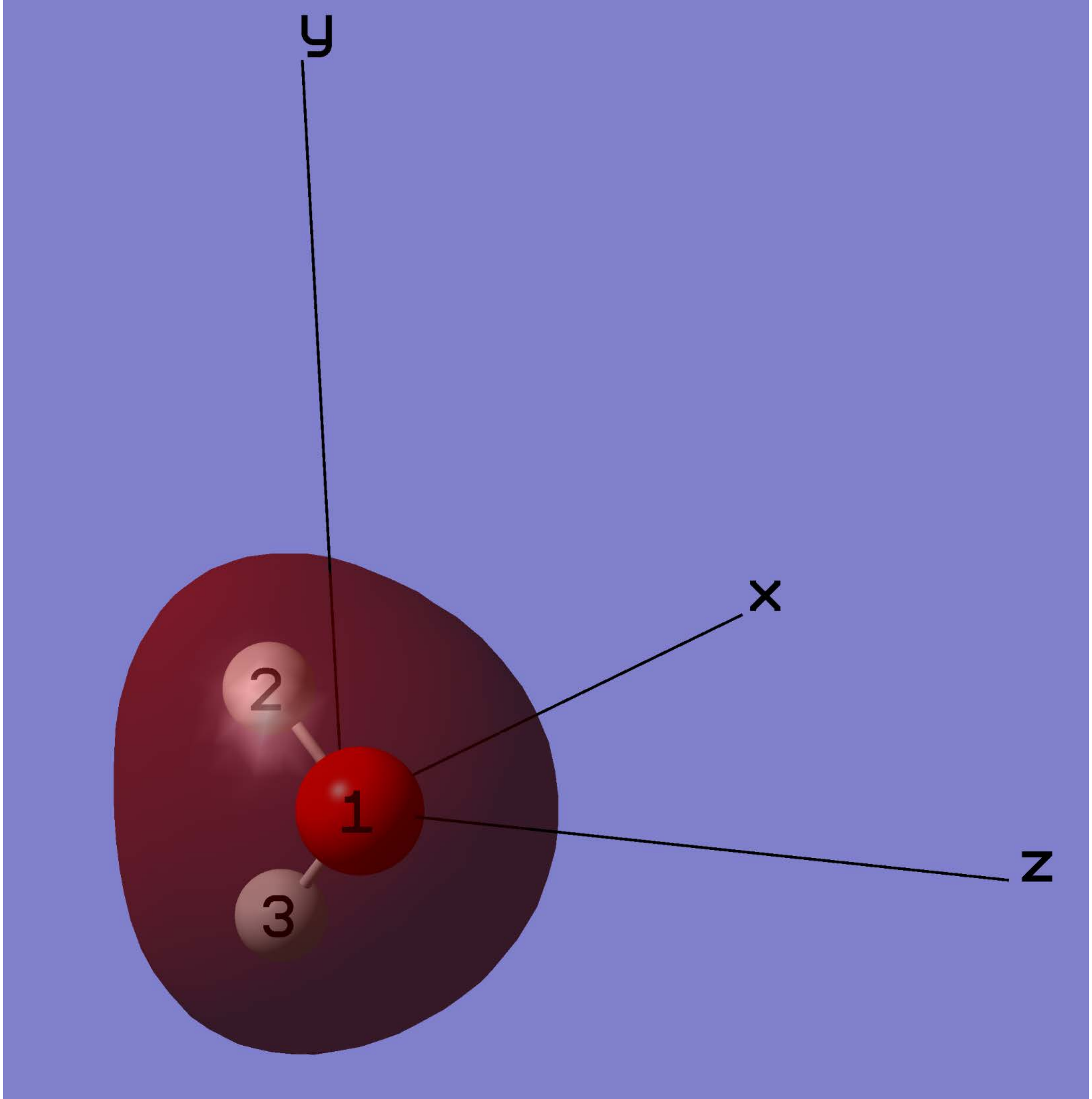
Why is the 2px diag element EXACTLY 2.000?

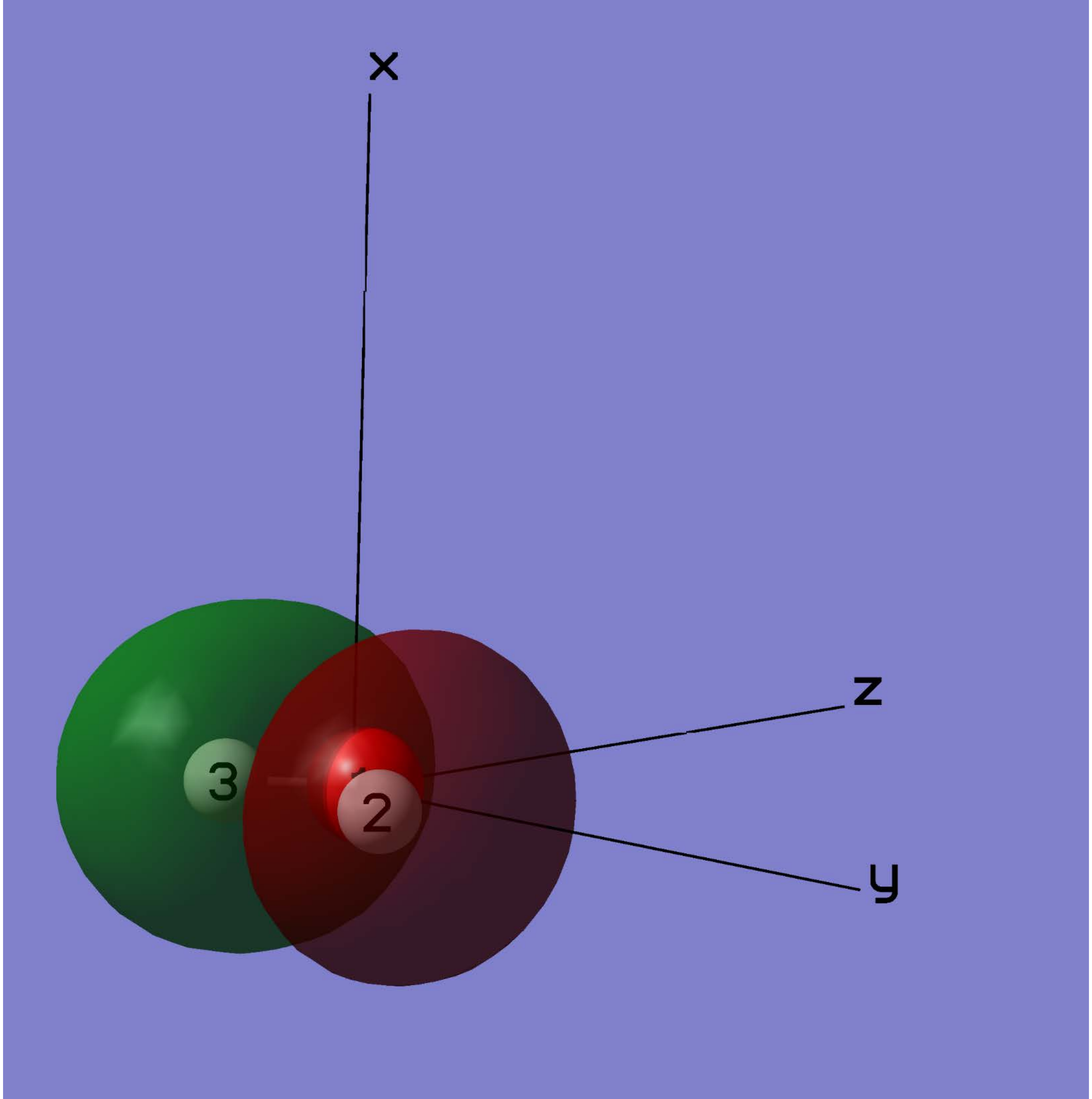
$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & \\ -0.456 & 2.010 & & & & & \\ 0.000 & 0.000 & 2.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183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

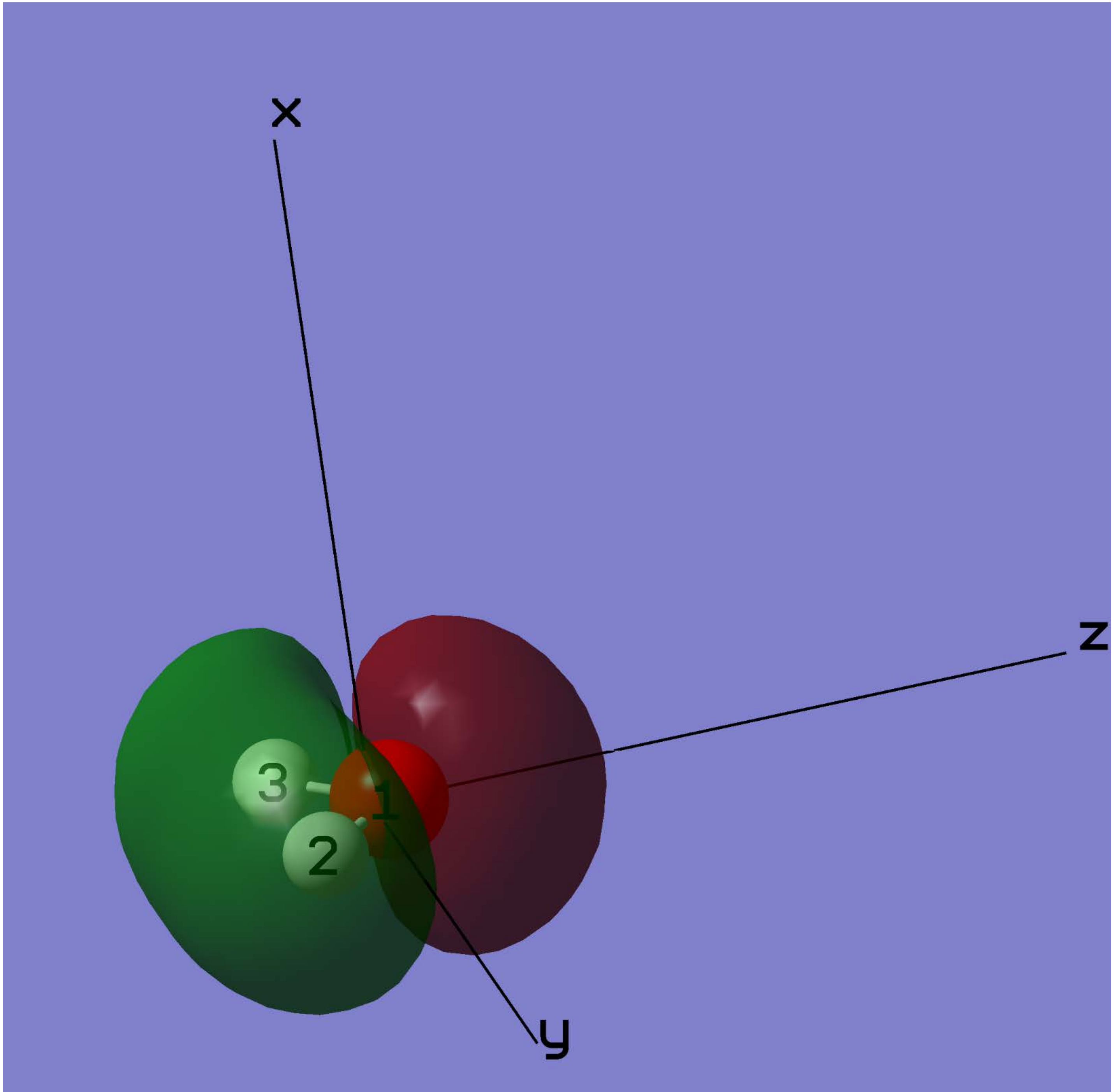
Correlate the size and signs of off diags with bonding

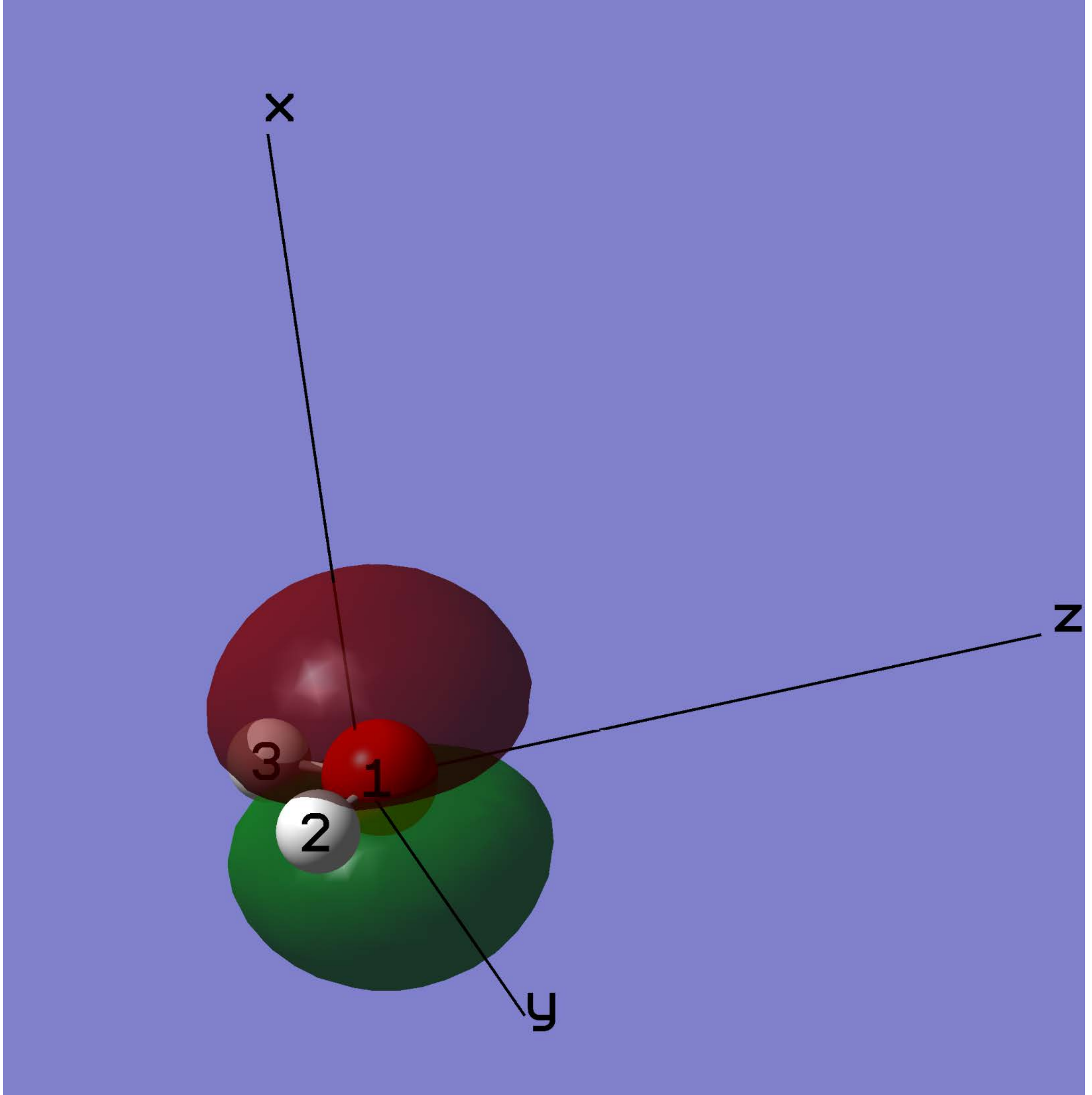
Figure 5. Initial density matrix **P** for HF/STO-3G calculation of water based on extended Hückel guess.


y
x
z
2
1
3


y
x
z
1
2
3


x
z
y
3
2


x
z
y
3
1
2


x
z
y
3
1
2

The **Fock matrix can be seen to be roughly <u>PROPORTIONAL</u> to the Density matrix.**

The reason is related to the fact that HF Energy is essentially the "product" of the density and the Fock matrices

Notice that element by element, the product $\mathbf{F}_{ij}$ x $\mathbf{P}_{ij}$ is negative, with a few exceptions. **When the product is positive, this generally indicates antibonding between the two orbitals.**

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

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

Fock matrix can be seen to roughly PROPORTIONAL to the Density matrix.

Indeed, the entire SCF-HF procedure may said to be equivalent to varying the coefficients that make up the Density Matrix until the density maximally overlaps the Fock matrix.

The reason is related to the fact that HF Energy is essentially the "product" of the density and the Fock matrices.

Notice that element by element, the product F_{rs} x P_{rs} is negative, with a few exceptions. **When the product is positive, this generally indicates antibonding between the two orbitals.**

A UNIVERSAL TRUTH:

The **Expectation Value** of ANY operator *A* is given by:

the trace of the product of the Density Matrix and the operator Matrix

If there is a density matrix, there must be a density operator.

"Density" = Probability Density = $\psi^*\psi$

We can see that in a sense, <A> is the overlap integral of the operator and the density.

$$< A > = \int \Psi^* \hat{A} \Psi d\tau = \int \hat{A} \Psi (\Psi^*) d\tau$$

where $\hat{A}$ does not operate on Ψ^*

This is better seen in bra-ket notation:

$$< A > = < \Psi^* | \hat{A} | \Psi >$$

$$= < \Psi^* | \sum_m m >< m | \hat{A} | \sum_n n >< n | \Psi >$$

$$= \sum_m \sum_n \; < \Psi_i^* | m >< m | \hat{A} | n >< n | \Psi_i >$$

$$= \sum_m \sum_n c^*_{\Psi m} A_{mn} c_{n\Psi} = \sum_m \sum_n \; c_{n\Psi} c^*_{\Psi m} A_{mn}$$

$$= \sum_m \sum_n \; P_{nm} A_{mn} = \sum_n \; \sum_m \; P_{nm} A_{mn} = \sum_n (PA)_{nn}$$

$= trace\, PA =$ sum of diagonal elements of the product of the Density matrix and matrix of operator A

Careful inspection, however, shows that the words used to state this operation *disguise* the underlying simplicity. The operation is indeed *literally* like *tracing* one matrix on the other.

(Taking the trace of the matrix product is distracting information.)

For a symmetric real matrix:

$$\sum_m \sum_n P_{nm} A_{mn} = \sum_{mn} P_{nm} A_{mn} = \sum_{mn} P_{mn} A_{mn}$$

This is simply the sum of the products of all the corresponding matrix elements, taken in any order. This is the SCALAR PRODUCT of the two matrices, i.e., completely analogous to the overlap integral of the matrices.

$$\begin{matrix} 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \end{matrix} \qquad \begin{matrix} 7 & 0 & 1 & 4 & 5 \\ 0 & 6 & 0 & 9 & 0 \\ 1 & 0 & 0 & 0 & 5 \\ 0 & 9 & 0 & 7 & 0 \\ 1 & 8 & 0 & 0 & 0 \end{matrix}$$

Once you see the pattern in the left matrix, you can quickly see that the trace of the product of these two matrices is 4 + 8 = 12 .

Next we will see how this formalism is hidden in Levine's Eq. 14.45