

The Molecular Orbitals of Water

I.1 Introduction

At the beginning of Szabo and Ostlund's chapter on the Hartree-Fock approximation, the authors write, "The Hartree-Fock approximation is important not only for its own sake but as a starting point for more accurate approximations" (Szabo & Ostlund 1982). Despite the fact that most computational chemists today have moved far beyond the primitive versions of Hartree-Fock theory, Szabo and Ostlund still recognize the importance of Hartree-Fock as the foundation underlying more sophisticated contemporary electronic structure theory. In this project, I attempt to apply basic Hartree-Fock theory to the molecular orbitals of water, in which a computer program takes LCAO guess coefficients, solves for new LCAO coefficients, and repeats this loop until the coefficients no longer change. This is an extremely crude description of the Hartree-Fock SCF (self-consistent field) method, yet it is the method that people have used to calculate the molecular orbitals of water as early as 1968 with the advent of computers (Aung 1968), and it is the method that the English mathematician Hartree derived in 1928, a mere two years after the Austrian physicist Schrödinger formulated his famous wave equation (Gavroglu 2012).

Although my project is far behind the "cutting edge" of contemporary electronic structure theory, the water molecule is nonetheless one of the most important molecules on earth. And despite the fact that the MOs of water have already been calculated for almost half a century, people still debate the electronic structure of water today. In an article titled "No Rabbit Ears on Water: The Structure of the Water Molecule: What Should We Tell the Students?", Michael Laing parodies VSEPR theory and the sp^3 hybridized version of water taught in intro-chemistry courses (Laing 1987), only to be opposed a year later by a professor who still defended the two equivalent "squirrel ears" lone pairs on water (Martin 1988). Between Lewis-structure diagrams and Hartree-Fock approximations, what is the structure of water and how does MO theory change our understanding of it?

I.2 Hartree-Fock

The molecular orbitals of minimal-basis water are characterized by a linear combination of STO-3G basis atomic orbitals. By using the STO-3G basis set, I am calculating the molecular orbitals of water using the minimal number of atomic wavefunctions (one wavefunction per atomic orbital, so seven).

$$\Psi_{H_2O} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 + c_7\phi_7$$

Atomic Orbitals: O_{1s} O_{2s} O_{2p_x} O_{2p_y} O_{2p_z} H_{1s} H_{2s}

I use the Hartree-Fock SCF method to solve for approximate energies and wavefunctions of water's molecular orbitals. Normally, it is impossible to analytically solve the eigenvalue equation $\hat{H}|\Psi_{H_2O}\rangle = E_n|\Psi_{H_2O}\rangle$ because the Hamiltonian includes electron-electron repulsion

components that are too complicated to evaluate. However, the Hartree-Fock approximation conveniently approximates the electron-electron repulsion term to be the potential of a spherically symmetric charge distribution field. Instead of each electron experiencing repulsions from the other nine moving electrons in the water molecule, Hartree-Fock approximates this term as each independent electron experiencing repulsion energy from the sum of the other nine electrons' average charge distributions (which evaluates to a constant).

From here, I can calculate the energies and coefficients of the LCAO using the variational principle. From our work in PS10, we know that by expanding the variational principle and solving for the minimum energy with respect to each coefficient, we end up with a matrix equation $(H - E_n S)(c) = 0$, where $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$ and $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$.

$$\langle E \rangle = \frac{\int d\vec{r}^3 \Psi_{H_2O}^* \hat{H} \Psi_{H_2O}}{\int d\vec{r}^3 \Psi_{H_2O}^* \Psi_{H_2O}} \quad \begin{pmatrix} H_{11} - E_n S_{11} & H_{12} - E_n S_{12} & \cdots & H_{17} - E_n S_{17} \\ H_{21} - E_n S_{21} & H_{22} - E_n S_{22} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ H_{71} - E_n S_{71} & \cdots & \cdots & H_{77} - E_n S_{77} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_7 \end{pmatrix} = 0$$

I constructed the matrices $H \equiv F$ and S by taking pre-calculated one-electron integrals, two-electron integrals and overlap integrals from PSI3, an open source *ab initio* electronic structure package (Crawford, et al. 2007). It is important to note here that these open-source packages and my calculations were all in atomic units, where $\hbar = 1, m_e = 1, e = 1, k_e = 1$. All other units are derived from these constants. For example, 1 a.u. of length is 1 bohr, or 1 radius of a H atom, and 1 a.u. of energy is 1 hartree. Below are expressions for constructing the two-electron matrix.

$$\sum_{\lambda=1}^7 \sum_{\sigma=1}^7 P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma)]$$

$$\text{where } \begin{cases} P_{\lambda\sigma} = 2 \sum_{i=1}^7 c_{\lambda i}^* c_{\sigma i} \\ (\mu\nu | \lambda\sigma) = \left\langle \phi_\mu(1) \phi_\nu(2) \left| \frac{1}{r_{12}} \right| \phi_\lambda(1) \phi_\sigma(2) \right\rangle \end{cases}$$

These two-electron equations approximate electron interactions as a spherically symmetric charge field. Because I do not derive these equations, I will merely point out notable qualitative attributes. The two-electron integrals $(\mu\nu | \lambda\sigma)$ are integrals over all space, summing up the potential at every possible position multiplied by the probability distribution or overlap of every possible combination of two electrons (406 combinations in water) (Crawford, et al. 2007). The density matrix P is a function of the LCAO coefficients, which makes sense because the electron charge distribution depends heavily on the coefficients of each atomic orbital. In fact, the density matrix P is what makes the self-consistent field method work. The equations are repeated over and over again, until the input coefficients/density matrix/electronic charge

distribution are the same as, or *self-consistent* with the output coefficients/density matrix/charge distribution.

The Fock matrix F is the sum of one-electron integrals $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$ and two-electron integrals. Energies and coefficients are calculated using the variational principle/secular equations $(F - E_n S)(c) = 0$, and the total binding energy of water, or the Hartree-Fock energy is calculated using the formula $E_{tot} = \sum_{i=1}^5 (E_i + H_{ii}) + V_{nn}$ where V_{nn} is the nuclear repulsion energy. In between loops, I checked if my *new* $E_{tot} - \text{old } E_{tot} < 10^{-8}$ hartrees, which was my tolerance parameter. If not, I repeated the loop.

II.1 Results

It took me 26 iterations before my values finally converged below 10^{-8} hartrees.

Table 1: Number of Iterations vs. Hartree-Fock Energy

Iterations	1	2	3	4	5	6	7	8	9
Hartree-Fock Energy (hartrees)	-82.12641363	-74.0655038	-74.89106138	-75.42780736	-75.50319404	-75.51443639	-75.52013396	-75.5230115	-75.52440218
Iterations	10	11	12	13	14	15	16	17	18
Hartree-Fock Energy (hartrees)	-75.52508848	-75.52542822	-75.52559646	-75.52567982	-75.52572113	-75.52574161	-75.52575176	-75.52575679	-75.52575928
Iterations	19	20	21	22	23	24	25	26	
Hartree-Fock Energy (hartrees)	-75.52576051	-75.52576113	-75.52576143	-75.52576158	-75.52576166	-75.52576169	-75.52576171	-75.52576172	

My final results, which are the fruits of my project, are in the following table.

Table 2: Final Results, Molecular Orbital Energies and Coefficients

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
Energy (hartrees)	-19.64807	-0.9212478	-0.2768517	0.02433165	0.07496861	1.0432692	1.13615086
Energy (eV)	-534.6515	-25.068443	-7.5335235	0.66209827	2.04000091	28.3888155	30.9162556
O 1s	0.99961632	-0.2582905	0	0.10320274	-5.50E-16	-0.0806617	1.38E-16
O 2s	0.02627022	0.92307858	-7.65E-16	-0.5545061	2.89E-15	0.5171351	-8.24E-16
O 2px	-3.58E-18	-5.85E-15	-6.66E-16	-5.30E-15	-1	-3.38E-16	4.71E-19
O 2py	-1.96E-18	-2.86E-15	0.65525755	-1.74E-15	-2.16E-16	8.42E-15	-0.6541021
O 2pz	0.00382902	0.08114816	-3.65E-15	0.66680507	-3.47E-15	0.52856725	-3.70E-16
H1 1s	-0.0055865	0.19316697	0.53415239	0.34441483	-1.94E-15	-0.4725895	0.53486
H2 1s	-0.0055865	0.19316697	-0.5341524	0.34441483	-1.50E-15	-0.4725895	-0.53486

In the appendix, I explain why the eigenvalue energies are erroneously shifted upwards and what I do in MATLAB to artificially correct this problem.

Next, I use these coefficients and the STO-3G basis set orbitals, retrieved from an online basis set library (Feller 1996; Hehre 1969; Schuchardt, et al. 2007) to plot my molecular orbitals in MATLAB (Figure 1). All of the orbitals are viewed in the yz-plane except for MO 5, the non-bonding O_{2px} orbital, which is viewed yx-plane.

For the first five occupied MOs, the first two are mostly oxygen 1s and 2s orbitals. The next two MOs are in-phase linear combinations of an oxygen 2p_y or 2p_z orbital with hydrogen 1s orbitals, with a node bisecting the oxygen atom. The fifth MO is perpendicular to the plane of bonding, so it is the non-bonding ‘lone pair’ oxygen 2p_x orbital. As for the antibonding un-occupied orbitals, the MOs have nodes bisecting the O-H bonds because the oxygen 2p orbitals interact destructively with the out-of-phase hydrogen 1s orbitals.

Figure 1: Molecular Orbitals of Water

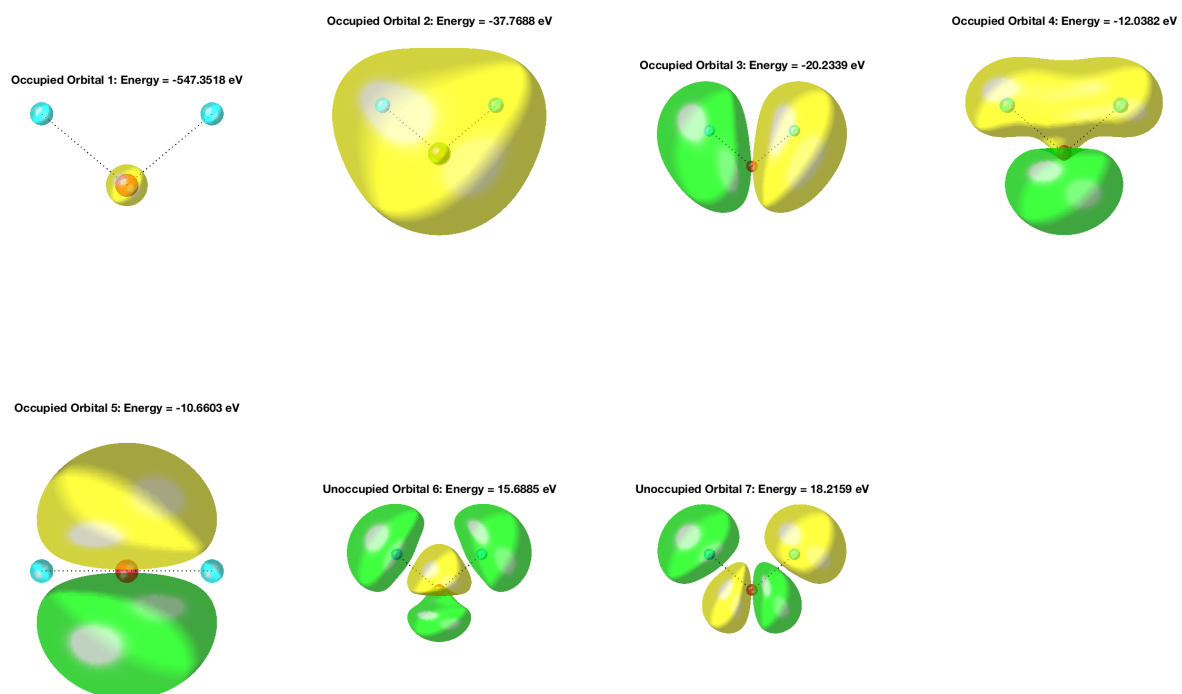
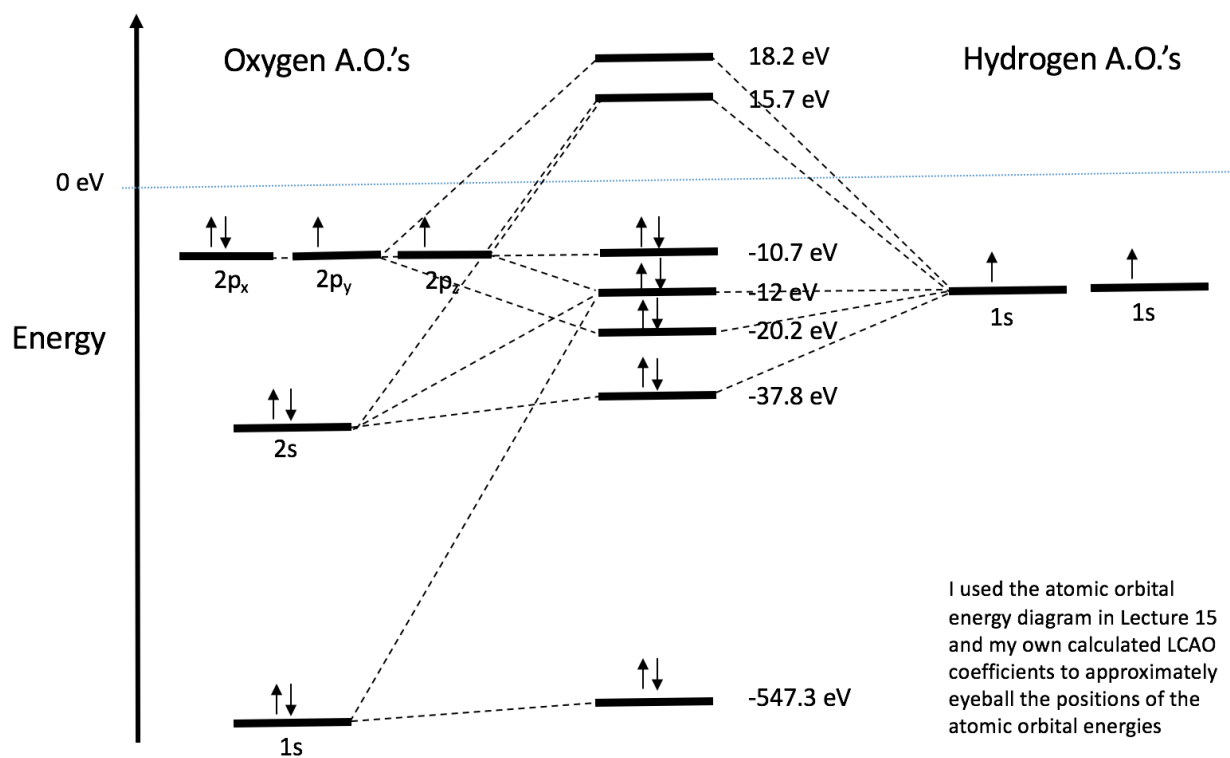


Figure 2: Energy Diagram of Water



II.2 Compared to Valence-Bond Theory

In valence-bond theory, the oxygen is sp^3 hybridized, with two of the orbitals sigma-bonding with hydrogen 1s orbitals, and two of the other 'lone pair' orbitals placed at tetrahedral positions.

However, the MO diagram does not depict a tetrahedral shape in water at all. Furthermore, the two equivalent 'lone pair' non-bonding orbitals are completely absent in the MO diagram of water. There is only one non-bonding oxygen $2p_x$ orbital, and one *mostly* oxygen 2s orbital that covers the entire molecule and is ~ 30 eV lower in energy than the other 'lone pair', if MO 2 can be considered a lone pair at all. Most of the bonding orbitals show that the sigma bonds formed between O and H are between O_{2p} orbitals and H_{1s} orbitals. The only possible case for hybridization would be MO 4 and MO 6, where both O_{2s} and the O_{2p} orbital contribute to the MO (sp^1 hybridized?).

Furthermore, Michael Laing in his 1987 paper uses experimental data from the photoelectron spectrum of H_2O (Figure 3) to support the MO theory of water. From Koopmans' theorem, we know that the eigenvalue of the MO is approximately its ionization energy (p. 126 Szabo & Ostlund 1982). Valence-bond theory assumes that there are only two types of orbitals in the sp^3 hybridized model, the O-H sigma bond orbital, and the oxygen's two 'lone-pair' non-bonding sp^3 orbitals. Therefore, one would only expect 2 peaks on the photoelectron spectrum. But instead, we observe 3 peaks, at MO 5, MO 4, and MO 3 (a fourth peak extrapolated at ~ 32 eV which is MO 2). Experimental data seems to support our Hartree-Fock eigenvalues with an approximate accuracy more feasible than the sp^3 hybridized model.

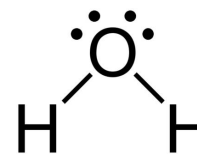


Figure 3: Photoelectron spectroscopy of H_2O

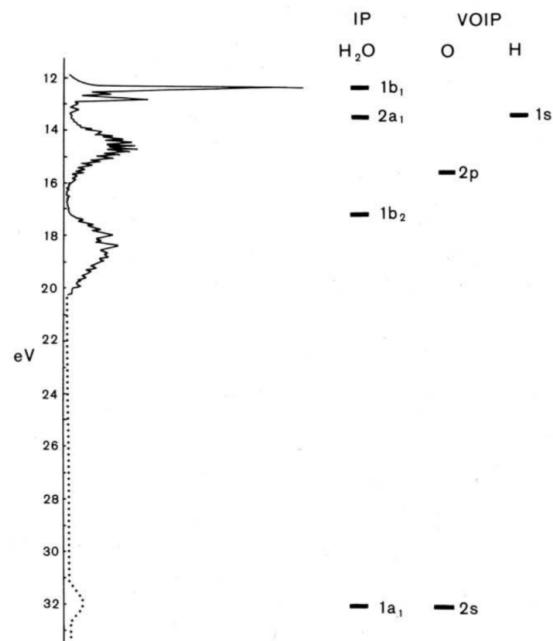


Figure 6. Photoelectron spectrum of the H_2O molecule with the ionization energies of the various molecular orbitals and atomic orbitals of the H and O atoms on the same energy scale.

III. Conclusion and Outlook

The molecular orbital energies and wavefunctions of water were thus approximated using Hartree-Fock. The resulting coefficients and MO diagram showed us a structure of H_2O entirely different from sp^3 hybridized water. In addition, data from photoelectron spectroscopy (Laing 1987) qualitatively corroborated MO theory over valence-bond theory.

Further studies on the characteristics of water as a hydrogen-bonded system take into account the MO nature of the single water molecule. A 2005 study on hydrogen-bonding, for example, concluded from its x-ray absorption spectroscopy, that in a hydrogen-bond, electrons from the non-bonding MO 5 on one water molecule are donated to the two anti-bonding orbitals MO 6 & 7 on another molecule (Nilsson, et al. 2005). Knowledge of MOs on the single water molecule could potentially elucidate the geometry of hydrogen-bonding in more exciting and complex systems like protein folding and metal ion hydration.

References

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APPENDIX A: Error

Even though my given integrals were imported from PSI3 (Crawford, et al. 2007), I followed the steps delineated in Dr. Jean Standard's document (2015) to calculate the MOs of water. This was a significant source of error in my final results. Even though both sources used the STO-3G basis set to calculate their integrals, there was a noticeable difference in their one-electron potential energy matrices.

Potential

	1	2	3	4	5	6	7
1	-61.6882822	-7.4363118	0.0000000	0.0000000	-0.0186797	-1.6150635	-1.6150635
2	-7.4363118	-10.1101908	0.0000000	0.0000000	-0.2221598	-3.6569582	-3.6569582
3	0.0000000	0.0000000	-9.9595668	0.0000000	0.0000000	0.0000000	0.0000000
4	0.0000000	0.0000000	0.0000000	-10.0957534	0.0000000	-2.0901916	2.0901916
5	-0.0186797	-0.2221598	0.0000000	0.0000000	-10.0553869	-1.8259929	-1.8259929
6	-1.6150635	-3.6569582	0.0000000	-2.0901916	-1.8259929	-5.7165220	-1.5685885
7	-1.6150635	-3.6569582	0.0000000	2.0901916	-1.8259929	-1.5685885	-5.7165220

(Crawford, et al. 2007)

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

(Standard 2015)

Some elements in the potential matrix, like $\langle \phi_7 | PE | \phi_2 \rangle$ differ by 0.263 hartrees, or 7.16 eV, and others $\langle \phi_6 | PE | \phi_4 \rangle$ differ by 1.862 hartrees, or 50.67 eV. It's differences like these in the potential energy matrix that would shift my eigenvalues up by a value of ~ 0.4 hartrees or ~ 11 eV above Dr. Jean M. Standard's values.

Table 3: Molecular Orbital Energies, Margins of Error

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
My Energies (hartrees)	-19.64807041	-0.9212478	-0.2768517	0.02433165	0.07496861	1.0432692	1.13615086
Theoretical E (hartrees)	-20.24094	-1.27218	-0.62173	-0.45392	-0.39176	0.61293	0.75095
Difference (hartrees)	0.592869589	0.35093219	0.34487826	0.47825165	0.46672861	0.4303392	0.38520086
Difference (eV)	16.13281154	9.54935631	9.38462026	13.013897	12.700339	11.7101321	10.4818548

Theoretical energies calculated by Dr. Jean M. Standard (2015)

Normally, I would calculate a percent error and move on, but this error is not insignificant. Even though the first 5 MOs of water should be occupied (10 electrons, 2 electrons per orbital), my energies for MO 4 and MO 5 are positive (0.024 and 0.07 hartrees), which shouldn't be the case for molecular orbitals that are naturally occupied. I decided to artificially correct my error in the MATLAB code, so that it would generate Figure 1 with energies that would at least make sense.

Table 4: Corrected Molecular Orbital Energies, correction term = -12.7 eV

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
Old Energies (eV)	-534.6515032	-25.068443	-7.5335235	0.66209827	2.04000091	28.3888155	30.9162556
Corrected Energies (eV)	-547.3518421	-37.768782	-20.233862	-12.038241	-10.660338	15.6884765	18.2159167
Theoretical Energies (eV)	-550.7843147	-34.617799	-16.918144	-12.351799	-10.660338	16.6786834	20.4344008
Difference (eV)	3.43247257	-3.1509827	-3.3157187	0.31355799	0	-0.9902069	-2.2184842

Theoretical energies calculated by Dr. Jean M. Standard (2015)

I chose to align my MO 5 energy with Dr. Standard's MO 5 energy, because that MO is the non-binding O 2p_x orbital, whose value should agree (and be less than 0) because the energy of an oxygen p orbital by itself is a constant no matter what context it's in.

Further speculation on why using Crawford's data but following Standard's method for Hartree-Fock would produce error leads me to also speculate that Crawford's and Standard's methods for calculating eigenvalues were probably different. While using Standard's method had me solve the secular determinant using brute force symbolic MATLAB, Crawford probably used a version of Hartree-Fock that constructed a transformation matrix X, which would have diagonalized the overlap and Fock matrix, S and F, and turned the secular equations into an eigenvalue equation that could be solved using the 'eigs' function in MATLAB (p. 146 Szabo & Ostlund 1982). By following Standard's method, I had to use 'vpasolve(det(F - E*overlap)==0,E)' instead, which was rather imprecise, since my overlap integral was not diagonalized. Plugging back in my first eigenvalue into the equation gave me 2.6996e-08, not 0 like expected, which is significant because my tolerance parameter was 1e-08.

APPENDIX B: MATLAB

```
%% Import data from online text files
clear
% Data can be found on http://vergil.chemistry.gatech.edu/h2oints.txt
% (Crawford, et al. 2007)
% 1) Geometric coordinates of the 3 nuclei in H2O
% 2) Overlap integrals
% 3) 1-electron integrals
% 4) 2-electron integrals
fileID = fopen('water_minimal_basis_data.txt');
geometry = cell2mat(textscan(fileID, '%s %f %f %f', 'HeaderLines',23));
geometry = geometry/0.529177249; % convert from Angstroms to Bohrs
fileID = fopen('water_minimal_basis_data.txt');
overlap = cell2mat(textscan(fileID, '%d %f %f %f %f %f %f', 'HeaderLines',40));
fileID = fopen('water_minimal_basis_data.txt');
one_electron = cell2mat(textscan(fileID, '%d %f %f %f %f %f %f %f',
'HeaderLines',82));
fileID = fopen('water_minimal_basis_data.txt');
two_electron = cell2mat(textscan(fileID, '%s %f %f %s %f %f) %s %f',
'HeaderLines',95));
two_electron(:,1:4) = two_electron(:,1:4) + 1; % to correct AO number

% Data can be found on
http://chemistry.illinoisstate.edu/standard/che460/handouts/460water.pdf
% (Standard 2015)
% 5) Initial guess coefficients for LCAO
fileID = fopen('water_matrix_data.txt');
c = cell2mat(textscan(fileID, '%d %s %s %f %f %f %f %f', 'HeaderLines',6));

fclose('all');

% NOTE: The potential energy matrix and overlap matrix in the Georgia Tech document is
% slightly different than the potential energy matrix and overlap matrix in the
% Illinois State document.
% As a result, the one_electron matrix = kinetic + potential is slightly
% different in both documents, which may have resulted in a small percent
% error in my results

%% Beginning the SCF iterations

HFE = zeros(1,31);
HFE(1) = 0; % setting Hartree-Fock Energy to 0 at the beginning for arbitrary
comparison
for k=1:30 % max number of iterations

%% Density matrix P

c = c(:,1:5); % to cut off unoccupied orbitals

P = zeros(7,7);
for i=1:7
    for j=1:7
        P(i,j) = 2*sum(conj(c(i,:)).*c(j,:));
    end
end

%% Fock matrix F
F = zeros(7,7); % Fock matrix
f = zeros(7,7); % Two electron integral component of Fock matrix
```

```

for i=1:7
    for j=1:7
        for l=1:7
            for s=1:7
                % The two electron integral data was given in a certain
                % order where for any [pq|rs] p > q > r > s
                % The following code sorts the variables provided in the
                % conditions of the for loop. I use this to search the
                % imported data two_electron for the two-electron integral
                % values
                te_one = zeros(1,4);
                if i >= j
                    te_one(1) = i;
                    te_one(2) = j;
                else
                    te_one(1) = j;
                    te_one(2) = i;
                end
                if l >= s
                    te_one(3) = l;
                    te_one(4) = s;
                else
                    te_one(3) = s;
                    te_one(4) = l;
                end
                if te_one(3) > te_one(1)
                    te_one = te_one([3 4 1 2]);
                elseif te_one(3) == te_one(1)
                    if te_one(4) > te_one(2)
                        te_one = te_one([3 4 1 2]);
                    end
                end
                coulomb = 0;
                for row = 1:length(two_electron)
                    if(two_electron(row,1:4) == te_one)
                        coulomb = two_electron(row,5);
                        break
                    end
                end
                te_two = zeros(1,4);
                if i >= l
                    te_two(1) = i;
                    te_two(2) = l;
                else
                    te_two(1) = l;
                    te_two(2) = i;
                end
                if j >= s
                    te_two(3) = j;
                    te_two(4) = s;
                else
                    te_two(3) = s;
                    te_two(4) = j;
                end
                if te_two(3) > te_two(1)
                    te_two = te_two([3 4 1 2]);
                elseif te_two(3) == te_two(1)
                    if te_two(4) > te_two(2)
                        te_two = te_two([3 4 1 2]);
                    end
                end
                exchange = 0;
            end
        end
    end
end

```

```

        for row = 1:length(two_electron)
            if(two_electron(row,1:4) == te_two)
                exchange = two_electron(row,5);
                break
            end
        end

        % I do a double summation of the two-electron integrals
        % by constructing a matrix size l x s, and summing up the
        % entire matrix f(:)
        f(l,s) = P(l,s)*(coulomb - .5*exchange);
    end
    end
    F(i,j) = one_electron(i,j) + sum(f(:));
end
end

%% Calculate the energies of the orbitals
% because the secular determinant = 0

syms E
energies = double(vpasolve(det(F - E*overlap)==0,E));

%% Solve for coefficients
% Due to non-zero overlap, my matrix equation is not an eigenvector problem
% I use singular value decomposition to solve (F-energies*overlap)(c) = 0
c = zeros(7,7);
for i=1:7
    [U,S,V] = svd(F-energies(i)*overlap);
    c(:,i) = V(:,end);
end

%% Hartree-Fock Energy
expectation = sum(energies + diag(one_electron)); % <E>
repulsion_ab = 16/sqrt(sum((geometry(1,:)-geometry(2,:)).^2));
repulsion_bc = 1/sqrt(sum((geometry(2,:)-geometry(3,:)).^2));
repulsion_ca = 16/sqrt(sum((geometry(1,:)-geometry(2,:)).^2));
repulsion = repulsion_ab + repulsion_bc + repulsion_ca; % nuclear repulsion energy

HFE(k+1) = expectation + repulsion;

% I check to see if the change in energy between the two iterations is less
% than 1e-8 hartrees
if abs((HFE(k+1)-HFE(k))) < 1e-8
    break
end
end

disp(k) % number of iterations
format long
disp(HFE(HFE~=0)') % Hartree-Fock energies of each iteration
format short
disp(HFE(k+1)-HFE(k)) % difference in the last two Hartree-Fock energies
disp(energies); % MO energies
disp(c); % AO coefficients

%% STO-3G
% I grab my atomic orbitals from the STO-3G basis set (Feller 1996; Hehre 1969;
% Schuchardt, et al. 2007). Since I now have the coefficients to construct my LCAO
% MOs, I can plot my orbitals as pretty pictures
fileID = fopen('water_sto3g.txt');

```

```

h_1s = cell2mat(textscan(fileID, '%f %f', 'HeaderLines',16));
fileID = fopen('water_sto3g.txt');
o_1s = cell2mat(textscan(fileID, '%f %f', 'HeaderLines',22));
fileID = fopen('water_sto3g.txt');
o_2sp = cell2mat(textscan(fileID, '%f %f %f', 'HeaderLines',26));

fclose('all');

%% Coordinate System
% I use the code from pset5, orbitals_part3_redacted as a model to graph my
% molecular orbitals for water

% First, create the coordinate axes
[Y, X, Z] = meshgrid(linspace(-3.2,3.2,100), linspace(-3.2,3.2,100), linspace(-
3.2,3.2,100));

R_O = (X.^2 + Y.^2 + (Z-geometry(1,3)).^2).^5;
R_H1 = (X.^2 + (Y-geometry(2,2)).^2 + (Z-geometry(2,3)).^2).^5;
R_H2 = (X.^2 + (Y-geometry(3,2)).^2 + (Z-geometry(3,3)).^2).^5;

Rperp_O = (X.^2 + Y.^2).^5;
Rperp_H1 = (X.^2 + (Y-geometry(2,2)).^2).^5;
Rperp_H2 = (X.^2 + (Y-geometry(3,2)).^2).^5;

theta_O = atan2(Rperp_O, Z-geometry(1,3));
theta_H1 = atan2(Rperp_H1, Z-geometry(2,3));
theta_H2 = atan2(Rperp_H2, Z-geometry(3,3));

phi_O = atan2(Y, X);
phi_H1 = atan2(Y-geometry(2,2), X);
phi_H2 = atan2(Y-geometry(3,2), X);

%% STO-3G
% Second, create the atomic orbitals centered around each nucleus
% p. 181 of Szabo and Ostlund
H1_1s = zeros(size(R_H1));
for i=1:3
    H1_1s = H1_1s + h_1s(i,2)*((8*h_1s(i,1)^3/pi^3)^(1/4)*exp(-h_1s(i,1)*R_H1.^2));
end

H2_1s = zeros(size(R_H2));
for i=1:3
    H2_1s = H2_1s + h_1s(i,2)*((8*h_1s(i,1)^3/pi^3)^(1/4)*exp(-h_1s(i,1)*R_H2.^2));
end

O_1s = zeros(size(R_O));
for i=1:3
    O_1s = O_1s + o_1s(i,2)*((8*o_1s(i,1)^3/pi^3)^(1/4)*exp(-o_1s(i,1)*R_O.^2));
end

O_2s = zeros(size(R_O));
for i=1:3
    O_2s = O_2s + o_2sp(i,2)*((8*o_2sp(i,1)^3/pi^3)^(1/4)*exp(-o_2sp(i,1)*R_O.^2));
end

O_2px = zeros(size(R_O));
for i=1:3
    O_2px = O_2px +
    o_2sp(i,3)*((128*o_2sp(i,1)^5/pi^3)^(1/4)*R_O.*sin(theta_O).*cos(phi_O).*exp(-

```

```

o_2sp(i,1)*R_O.^2));
end

O_2py = zeros(size(R_O));
for i=1:3
    O_2py = O_2py +
    o_2sp(i,3)*((128*o_2sp(i,1)^5/pi^3)^(1/4)*R_O.*sin(theta_O).*sin(phi_O).*exp(-
    o_2sp(i,1)*R_O.^2));
end

O_2pz = zeros(size(R_O));
for i=1:3
    O_2pz = O_2pz + o_2sp(i,3)*((128*o_2sp(i,1)^5/pi^3)^(1/4)*R_O.*cos(theta_O).*exp(-
    o_2sp(i,1)*R_O.^2));
end

% Normalize each orbital
H1_1s = H1_1s/sqrt(sum(H1_1s(:).^2));
H2_1s = H2_1s/sqrt(sum(H2_1s(:).^2));
O_1s = O_1s/sqrt(sum(O_1s(:).^2));
O_2s = O_2s/sqrt(sum(O_2s(:).^2));
O_2px = O_2px/sqrt(sum(O_2px(:).^2));
O_2py = O_2py/sqrt(sum(O_2py(:).^2));
O_2pz = O_2pz/sqrt(sum(O_2pz(:).^2));

% In retrospect, I realize that I could have used these orbitals to
% generate my one_electron hamiltonian matrix and my overlap matrix
% instead of having to import them from online. For example, I could have
% done the following to produce my one-electron integrals (this is pseudocode):
% for i = 1:7
%     for j = 1:7
%         one_electron(i,j) = conj(AO_i(:))'*[transform matrix]*AO_j(:);
%     end
% end
% However, constructing those transform matrices (summation of laplacians
% and potential energy matrices) was something that was beyond my abilities
% Even though the overlap matrix doesn't use any transform matrix, I felt
% that it was easier to be consistent - instead of using an overlap matrix
% I generated, I just imported the data from online as well.

% Construct molecular orbitals
MOs = matlab.lang.makeUniqueStrings(repmat({'MO'}, 1, 7), 'MO');
for i=1:7
    MOs{i} =
    c(1,i)*O_1s+c(2,i)*O_2s+c(3,i)*O_2px+c(4,i)*O_2py+c(5,i)*O_2pz+c(6,i)*H1_1s+c(7,i)*H2_
    1s;
    MOs{i} = MOs{i}/sqrt(sum(MOs{i}(:).^2)); % normalize
end

%% Artificial Correction of Error

standard_MO5 = -.39176; % energy of non-bonding orbital calculated in Dr. Jean
Standard's document
correction = standard_MO5 - energies(5);
correction_eV = correction*27.2114;
corr_E = energies + correction;
corr_E_eV = corr_E*27.2114; % In my MO graphics, I use the corrected energies

%% Generate Pretty Pictures
% plotiso is a function created by Adam Cohen (2011) for pset5

```

```

figure(1)
for i=1:7
    subplot(2,4,i)
    plotiso(X, Y, Z, MOs{i}, -.1*max(MOs{i}(:)), 'green');
    plotiso(X, Y, Z, MOs{i}, .1*max(MOs{i}(:)), 'yellow');
    if i <= 5
        occ = 'Occupied ';
    else
        occ = 'Unoccupied ';
    end
    title([occ 'Orbital ' num2str(i) ': Energy = ' num2str(corr_E_eV(i)) ' eV'])
    plotiso(X,Y,Z,R_H1,.2,'cyan');
    plotiso(X,Y,Z,R_H2,.2,'cyan');
    plotiso(X,Y,Z,R_O,.2,'red');
    hold on
    plot3(geometry(1:2,1),geometry(1:2,2),geometry(1:2,3),'k:','LineWidth',1);
    plot3(geometry([1 3],1),geometry([1 3],2),geometry([1 3],3),'k:','LineWidth',1);
    if i == 5
        view([90 90])
    else
        view([90 0])
    end
end
hold off

```