Chemistry 460
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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 ($\angle$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.

Molecular structure and coordinates

For the purposes of the example calculation, software packages such as *Gaussian 09* position the water molecule such that the atoms lie in the *yz*-plane with the center of mass at the origin; this is known as the "standard orientation". In the case of water with the specified bond lengths and angles, the cartesian coordinates of the atoms are shown in Table 1. Notice that the *y*- and *z*-coordinate values of the hydrogen atoms are symmetric or antisymmetric about the oxygen atom position, which allows for easy inclusion of the C_{2v} symmetry aspects of the water molecule in the Hartree-Fock calculations.

Table 1. Atomic coordinates (in Å) of the water molecule in its standard orientation (from *Gaussian 09* log file).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	0.000000	0.751155	-0.465285
2	8	0	0.000000	0.000000	0.116321
3	1	0	0.000000	-0.751155	-0.465285

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

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

The functions ϕ_i for water are molecular orbitals defined using the LCAO-MO approximation,

$$\phi_i(1) \;=\; \sum_{\mu=1}^{K} c_{\mu i} \, f_\mu(1) . \tag{2}$$

Here, the terms $c_{\mu i}$ correspond to linear coefficients, the functions f_μ are the atomic orbital basis functions, and K is the total number of atomic orbital basis functions used to represent the molecular orbitals. In this example calculation, a minimal basis set will be used which consists of 1s basis functions for each H atom, and the 1s, 2s, and set of 2p ($2p_x$, $2p_y$, $2p_z$) basis functions for O atom. In *Gaussian 09*, a typical basis set of this type is called STO-3G, and for water consists of 7 basis functions. The numbering of the basis functions for the rest of this example is given in Table 2.

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

Hartree-Fock-Roothan equations

Minimizing the expectation value for the energy of the Slater Determinant with the LCAO-MO approximation for the molecular orbitals yields the Hartree-Fock-Roothan (H-F-R) equations. For water with $K=7$ basis functions, the H-F-R equations are

$$\sum_{\nu=1}^{7} \left(F_{\mu\nu} - \varepsilon_i\, S_{\mu\nu} \right) c_{\nu i} = 0, \qquad \mu = 1, 2, \ldots 7. \tag{3}$$

Here, $F_{\mu\nu}$ are Fock integrals, $S_{\mu\nu}$ are overlap integrals, ε_i are the orbital energies, and the $c_{\nu i}$ are the linear coefficients.

Overlap integrals

Defining the terms in the H-F-R equations, the overlap integrals $S_{\mu\nu}$ are integrals over pairs of the atomic orbital basis functions,

$$S_{\mu\nu} = \left\langle f_\mu(1) \,\middle|\, f_\nu(1) \right\rangle. \tag{4}$$

For water, there are 7×7 = 49 overlap integrals. However, because the order of the product of functions in the integrand does not matter, we have that $S_{\mu\nu} = S_{\nu\mu}$, and therefore there are fewer unique values (28 total). The values of the overlap integrals $S_{\mu\nu}$ can be displayed in matrix form where the first index of the element (μ in this case) corresponds to the row and the second index (ν in this case) corresponds to the column in the 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 $S_{\mu\nu} = S_{\nu\mu}$.

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

Figure 1. Overlap matrix **S** for HF/STO-3G calculation of water.

In the overlap matrix, note that all the diagonal elements $S_{\mu\mu}$ equal 1 because of normalization of the basis functions. In addition, each 2p-type basis function on the oxygen atom is orthogonal ($S_{\mu\nu} = 0$) to the other 2p-type basis functions and to the 1s and 2s basis functions on the oxygen atom. Note however, that the 1s and 2s basis functions on oxygen are not orthogonal; their overlap corresponds to element S_{21}, which equals 0.237. This lack of orthogonality is a result of the choice of a gaussian form for these basis functions instead of using the eigenfunctions of a one-electron Hamiltonian operator (which would be orthogonal). This is common practice for s-type basis functions on the same nuclear center, as well as when multiple sets of p-type or higher angular momentum basis functions are employed. Finally, it should also be noted that basis functions on different nuclear centers are not in general orthogonal; thus, most of the oxygen atom basis functions overlap with those on the hydrogen atoms. The exception is the oxygen $2p_x$ basis function, which gives zero overlap with the hydrogen basis functions due to cancellation (equal but opposite overlap above and below the plane of the molecule).

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

$$F_{\mu\nu} = H^{\circ}_{\mu\nu} + \sum_{\lambda=1}^{K} \sum_{\sigma=1}^{K} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \tfrac{1}{2}(\mu\lambda | \nu\sigma) \right]. \qquad (5)$$

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

$$H^{\circ}_{\mu\nu} = \left\langle f_{\mu}(1) \left| -\frac{1}{2} \hat{\nabla}_1^2 - \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_{\alpha 1}} \right| f_{\nu}(1) \right\rangle. \qquad (6)$$

Here, the term $-\dfrac{1}{2}\hat{\nabla}_1^2$ corresponds to the kinetic energy operator for electron 1, while the term $-\displaystyle\sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_{\alpha 1}}$ corresponds to the potential energy operator for the electron-nuclear attractions, where Z_{α} is the atomic number of nucleus α and $r_{\alpha 1}$ is the distance between nucleus α and electron 1. The one-electron intergrals are usually evaluated in two parts, the kinetic energy integrals $T_{\mu\nu}$ and the potential energy integrals $V_{\mu\nu}$.

Kinetic energy integrals
As might be expected, the kinetic energy integrals $T_{\mu\nu}$ are defined as

$$T_{\mu\nu} = \left\langle f_{\mu}(1) \left| -\frac{1}{2}\hat{\nabla}_1^2 \right| f_{\nu}(1) \right\rangle. \qquad (7)$$

For a calculation of water with the STO-3G basis set as specified in Table 2, the kinetic energy matrix **T** is shown in Figure 2. Again, only the lower portion is shown because the upper portion is related by symmetry since $T_{\mu\nu} = T_{\nu\mu}$.

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

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

For the kinetic energy elements $T_{\mu\nu}$, note that the diagonal elements are in general much larger in magnitude than the off-diagonal elements, and the diagonal elements are always positive. The off-diagonal elements are generally small in magnitude and may be either positive or negative.

Potential energy integrals

The potential energy integrals $V_{\mu\nu}$ are defined as

$$V_{\mu\nu} \;=\; \left\langle f_\mu(1) \left| \; -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_{\alpha 1}} \; \right| f_\nu(1) \right\rangle . \tag{8}$$

For our water calculation at the HF/STO-3G level, the kinetic energy matrix **T** is shown in Figure 3. Again, only the lower portion is shown because the upper portion is related by symmetry since $V_{\mu\nu} = V_{\nu\mu}$.

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

Figure 3. Potential energy matrix **V** for HF/STO-3G calculation of water.

Here we see that the potential energy diagonal elements $V_{\mu\mu}$ are in general much larger in magnitude than the off-diagonal elements. The diagonal elements are always negative; this is because the electron-nuclear interaction for electrons in the same orbital is always attractive (i.e., negative). The off-diagonal elements are again small in magnitude and may be either positive or negative.

One-electron Hamiltonian integrals

The one-electron kinetic energy and potential energy integrals may be combined to form the one-electron Hamiltonian integrals, $H_{\mu\nu}^{\circ}$, using the relation

$$H_{\mu\nu}^{\circ} \;=\; T_{\mu\nu} \;+\; V_{\mu\nu} , \tag{9}$$

or $\mathbf{H}^{\circ} \;=\; \mathbf{T} \;+\; \mathbf{V}$ in matrix form. The one-electron integrals $H_{\mu\nu}^{\circ}$ are shown in matrix format in Figure 4.

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

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

Two-electron integrals

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

$$(\mu v | \lambda \sigma) = \left\langle f_\mu(1) f_\lambda(2) \left| \frac{1}{r_{12}} \right| f_v(1) f_\sigma(2) \right\rangle$$

(10)

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

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.

Density matrix elements and initial guess

Finally, the terms $P_{\lambda\sigma}$ in the H-F-R equations are density matrix elements,

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

(11)

where the c's are the linear coefficients of the LCAO-MO expansion. Because of the dependence of the density matrix elements on the linear coefficients of the LCAO-MO expansion, we have to make a guess at these values in order to construct the Fock integrals and begin the calculation. *Gaussian 09* uses as its default for most systems a guess for the coefficients from a fairly simple model known as extended Hückel theory.

Only the coefficients for the occupied MOs are required to form the density matrix; note that the sum in Equation (11) goes up to n rather than K. Thus, for the five occupied MOs of water, the initial guess for the coefficients from extended Hückel theory is given in Table 3.

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

		MO:	1	2	3	4	5
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

To begin the first cycle of solving the H-F-R equations, the coefficients of the initial guess are used to form the density matrix elements, $P_{\lambda\sigma}$, using Equation (11). For water, the initial density matrix **P** is given in Figure 5.

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

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

Fock matrix elements from initial guess

Finally, the Fock matrix elements $F_{\mu\nu}$ may be formed from the one-electron Hamiltonian integrals $H_{\mu\nu}^{\circ}$, the density matrix elements $P_{\lambda\sigma}$, and the two-electron integrals. Combining these yields the initial Fock matrix, **F**, given in Figure 6.

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

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

Solving the secular determinant

At this point, the secular determinant, which is $K \times K$ in size, may be set equal to zero and solved,

$$\det \left| \mathbf{F} - \varepsilon\, \mathbf{S} \right| \; = \; 0, \tag{12}$$

where each element of the determinant corresponds to the factor $F_{\mu\nu} - \varepsilon S_{\mu\nu}$. Solution of the secular determinant yields K molecular orbital energies, ε_i, $i = 1, 2, \ldots K$. The first n of these MO energies correspond to occupied MOs, while the remaining higher MO energies correspond to the virtual MOs. For water, as stated previously, the first five MOs are occupied and the remaining two are virtual.

Obtaining the new coefficients

To obtain the coefficients $c_{\mu i}$ for each MO, the molecular orbital energies ε_i are substituted one-at-a-time into the H-F-R equations, Equation (3), and a system of K linear equations is solved. When this is carried out using the Fock matrix constructed from the initial guess, new coefficients are obtained; these are referred to as the coefficients for cycle 2, since cycle 1 refers to the initial coefficients. The coefficients of the occupied MOs for cycle 2 are given in Table 4; note that coefficients for the virtual orbitals also may be obtained but are not shown here.

Table 4. Coefficients $c_{\mu i}$ for the occupied molecular orbitals of water at cycle 2 of the iterative solution of the H-F-R equations.

		MO:	1	2	3	4	5
1	O	1S	0.99412	-0.23304	0.00000	-0.10353	0.00000
2	O	2S	0.02667	0.83417	0.00000	0.54133	0.00000
3	O	2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	O	2PY	0.00000	0.00000	0.60840	0.00000	0.00000
5	O	2PZ	-0.00440	-0.13111	0.00000	0.77477	0.00000
6	Ha	1S	-0.00604	0.15685	0.44314	-0.27966	0.00000
7	Hb	1S	-0.00604	0.15685	-0.44314	-0.27966	0.00000

When comparing the coefficients from cycle 1 to those from cycle 2, it can be seen that there are numerous quantitative changes to the coefficients, but qualitatively there is not much difference. This suggests that the initial guess was pretty good.

Hartree-Fock energy

The iterative solution process for the H-F-R equation continues for several more cycles. The solution is considered to be converged when the changes in the coefficients, density matrix, MO energies, and total energy (or some combination thereof) from one cycle to the next drop below specified numerical threshholds.

The Hartree-Fock energy (i.e., the expectation value $\langle E \rangle$ of the Slater determinant wavefunction) may be calculated using the following equation,

$$\langle E \rangle = \sum_{i=1}^{n} \left\{ 2\varepsilon_i - \sum_{j=1}^{n} \left(2J_{ij} - K_{ij} \right) \right\}. \tag{13}$$

Alternately, using the definition of the orbital energy ε_i as the expectation value of the Fock operator, we have

$$\varepsilon_i = \left\langle \phi_i \left| \hat{F} \right| \phi_i \right\rangle$$

$$= \left\langle \phi_i \left| -\frac{1}{2}\hat{\nabla}_1^2 - \sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_{\alpha 1}} \right| \phi_i \right\rangle + \sum_{j=1}^{n} \left\langle \phi_i \left| 2\hat{J}_j - \hat{K}_j \right| \phi_i \right\rangle \tag{14}$$

$$\varepsilon_i = H_{ii}^{\circ} + \sum_{j=1}^{n} \left(2J_{ij} - K_{ij} \right).$$

Note that the one-electron Hamiltonian integral H_{ii}° is the same as the one-electron eigenvalue ε_i° defined in class. Substituting Equation (14) into Equation (13) for one factor of ε_i yields an alternate form for the expectation value of the energy,

$$\langle E \rangle = \sum_{i=1}^{n} \left(\varepsilon_i + H_{ii}^{\circ} \right). \tag{15}$$

The result given in Equation (15) for $\langle E \rangle$ does not include the nuclear-nuclear repulsion energy, V_{NN} , which equals

$$V_{NN} \;\; = \;\; \sum_{\alpha=1}^{M} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \;\; , \tag{16}$$

where M corresponds to the number of nuclei, Z_α and Z_β are the atomic numbers of nuclei α and β , respectively, and $r_{\alpha\beta}$ is the distance between the two nuclei. Since the nuclei are fixed in place, this term just contributes a constant amount to the total energy. Including the nuclear-nuclear repulsion, the total Hartree-Fock energy (referred to as E_{el} in the projects and other handouts) is

$$E_{el} \;\; = \;\; \langle E \rangle \;\; + \;\; V_{NN} \;\; = \;\; \sum_{i=1}^{n} \left(\varepsilon_i + H_{ii}^\circ \right) \;\; + \;\; V_{NN} \; . \tag{17}$$

Using *Gaussian 09*, the HF/STO-3G calculation of the water molecule takes 7 cycles to reach convergence. The total Hartree-Fock energy of water at each cycle is shown in Table 5.

Table 5. Hartree-Fock energy (in hartrees) at each cycle of the HF/STO-3G calculation of water.

Cycle	E_{el} (hartrees)
1	–74.893 002 803
2	–74.961 289 145
3	–74.961 707 247
4	–74.961 751 946
5	–74.961 753 962
6	–74.961 754 063
7	–74.961 754 063

From these results, we see that the initial guess was off compared to the converged result by 0.069 hartrees, or about 43 kcal/mol. After 7 cycles, the Hartree-Fock energy is converged to 1×10^{-9} hartrees, or about 6×10^{-7} kcal/mol. Since this energy was obtained using an approximate wavefunction, the Variation Principle tells us it is too high relative to the exact energy. Use of a larger basis set and incorporation of electron correlation effects will lower the energy and bring it closer to the exact result.

Converged MO coefficients
The final MO coefficients $c_{\mu i}$ and eigenvalues ε_i for all the occupied and virtual orbitals of water are presented in Table 6.

Table 6. Converged MO eigenvalues ε_i and coefficients $c_{\mu i}$ for the occupied (1-5) and virtual (6, 7) molecular orbitals of water at the HF/STO-3G level of theory.

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MO:                        1          2          3          4          5

 Eigenvalues:         -20.24094   -1.27218   -0.62173   -0.45392   -0.39176
    (a.u.)
  1  O   1S             0.99411   -0.23251    0.00000   -0.10356    0.00000
  2  O   2S             0.02672    0.83085    0.00000    0.53920    0.00000
  3  O   2PX            0.00000    0.00000    0.00000    0.00000    1.00000
  4  O   2PY            0.00000    0.00000    0.60677    0.00000    0.00000
  5  O   2PZ           -0.00442   -0.13216    0.00000    0.77828    0.00000
  6  Ha  1S            -0.00605    0.15919    0.44453   -0.27494    0.00000
  7  Hb  1S            -0.00605    0.15919   -0.44478   -0.27494    0.00000


 MO:                        6          7

 Eigenvalues:           0.61293    0.75095
    (a.u.)
  1  O   1S            -0.13340    0.00000
  2  O   2S             0.89746    0.00000
  3  O   2PX            0.00000    0.00000
  4  O   2PY            0.00000    0.99474
  5  O   2PZ           -0.74288    0.00000
  6  Ha  1S            -0.80246   -0.84542
  7  Hb  1S            -0.80246    0.84542
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