

28.2: Hartree-Fock Calculation for Water

To find the Hartree-Fock (HF) molecular orbitals (MOs) we need to solve the following secular determinant:

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{17} - ES_{17} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{27} - ES_{27} \\ \vdots & \vdots & \ddots & \vdots \\ H_{71} - ES_{71} & F_{72} - ES_{72} & \cdots & F_{77} - ES_{77} \end{vmatrix} = 0 \quad (28.2.1)$$

with S_{ij} being the overlap integrals of Equation 27.3.2, and F_{ij} the matrix elements of the Fock operator, defined using the one- and two-electron integrals in Equation 29.1.1 and Equation 29.1.2 as:

$$F_{ij} = K_{ij} + V_{ij} + \sum_{kl} P_{kl} \left[V_{ijkl} - \frac{1}{2} V_{ikjl} \right], \quad (28.2.2)$$

with the density matrix elements P_{kl} defined as:

$$P_{kl} = 2 \sum_i^{\text{occupied}} a_{ki} a_{li}, \quad (28.2.3)$$

where the a values are the coefficients of the basis functions in the occupied molecular orbitals. These values will be determined using the SCF procedure, which proceeds as follows: At the first step we simply guess what these are, then we iterate through solution of the secular determinant to derive new coefficients and we continue to do so until self-consistency is reached (i.e. the $N + 1$ step provides coefficients and energies that are equal to those in the N step).

We can try to solve the SCF procedure for water using a fixed geometry of the nuclei close to the experimental structure: O-H bond lengths of 0.95 Å and a valence bond angle at oxygen of 104.5°. To do so, we can use a minimal basis functions composed of the following seven orbitals: basis function #1 is an oxygen 1s orbital, #2 is an oxygen 2s orbital, #3 is an oxygen 2p_x orbital, #4 is an oxygen 2p_y orbital, #5 is an oxygen 2p_z orbital, #6 is one hydrogen 1s orbital, and #7 is the other hydrogen 1s orbital. The corresponding integrals introduced in the previous section can be calculated using a quantum chemistry code. The calculated overlap matrix elements are:

$$\mathbf{S} = \begin{bmatrix} \text{O } 1s & \text{O } 2s & \text{O } 2p_x & \text{O } 2p_y & \text{O } 2p_z & \text{H}_a \text{ } 1s & \text{H}_b \text{ } 1s \\ 1.000 & & & & & & \\ 0.237 & 1.000 & & & & & \\ 0.000 & 0.000 & 1.000 & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 \end{bmatrix} \quad (28.2.4)$$

There are many noteworthy features in \mathbf{S} . First, it is shown in a lower packed triangular form because every element j, i is the same as the element i, j by symmetry, and every diagonal element is 1 because the basis functions are normalized. Note that, again by symmetry, every p orbital on oxygen is orthogonal (overlap = zero) with every s orbital and with each other, but the two s orbitals do overlap (this is due to the fact that they are not pure hydrogenic orbitals—which would indeed be orthogonal—but they have been optimized, so $S_{12} = 0.237$). Note also that the oxygen 1s orbital overlaps about an order of magnitude less with any hydrogen 1s orbital than does the oxygen 2s orbital, reflecting how much more rapidly the first quantum-level orbital decays compared to the second. Note that by symmetry the oxygen p_x cannot overlap with the hydrogen 1s functions (positive overlap below the plane exactly cancels negative overlap above the plane) and that the oxygen p_y overlaps with the two hydrogen 1s orbitals equally in magnitude but with different sign because the p orbital has different phase at its different ends. Finally, the overlap of the p_z is identical with each H 1s because it is not changing which lobe it uses to interact. The kinetic energy matrix (in a.u.) is:

$$\mathbf{K} = \begin{bmatrix} 29.003 & & & & & & \\ -0.168 & 0.808 & & & & & \\ 0.000 & 0.000 & 2.529 & & & & \\ 0.000 & 0.000 & 0.000 & 2.529 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & \\ -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & \\ -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 \end{bmatrix} \quad (28.2.5)$$

Notice that every diagonal term is much larger than any off-diagonal term. Recall that each kinetic energy integral, Equation 29.1.1, involves the Laplacian operator, ∇^2 . The Laplacian reports back the sum of second derivatives in all coordinate directions. That is, it is a measure of how fast the slope of the function is changing in various directions. If we take two atomic orbitals μ and ν far apart from each other, then since gaussians go to zero at least exponentially fast with distance, ν is likely to be very flat where μ is large. The second derivative of a flat function is zero. So, every point in the integration will be roughly the amplitude of μ times zero, and not much will accumulate. For the diagonal element, on the other hand, the interesting second derivatives will occur where the function has maximum amplitude (amongst other places) so the accumulation should be much larger. Notice also that off-diagonal terms can be negative. That is because there is no real physical meaning to a kinetic energy expectation value involving two different orbitals. It is just an integral that appears in the complete secular determinant. Symmetry again keeps p orbitals from mixing with s orbitals or with each other. The nuclear attraction matrix is:

$$\mathbf{V} = \begin{bmatrix} -61.733 & & & & & & \\ -7.447 & -10.151 & & & & & \\ 0.000 & 0.000 & -9.926 & & & & \\ 0.000 & 0.000 & 0.000 & -10.152 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & -10.088 & & \\ -1.778 & -3.920 & 0.000 & -0.228 & -0.184 & -5.867 & \\ -1.778 & -3.920 & 0.000 & 0.228 & 0.184 & -1.652 & -5.867 \end{bmatrix} \quad (28.2.6)$$

Again, diagonal elements are bigger than off-diagonal elements because the $1/r$ operator acting on a basis function ν will ensure that the largest contribution to the overall integral will come from the nucleus k on which basis function ν resides. Unless μ also has significant amplitude around that nucleus, it will multiply the result by roughly zero and the whole integral will be small. Again, positive values can arise when two different functions are involved even though electrons in a single orbital must always be attracted to nuclei and thus diagonal elements must always be negative. Note that the p orbitals all have different nuclear attractions. That is because, although they all have the same attraction to the O nucleus, they have different amplitudes at the H nuclei. The p_x orbital has the smallest amplitude at the H nuclei (zero, since they are in its nodal plane), so it has the smallest nuclear attraction integral. The p_z orbital has somewhat smaller amplitude at the H nuclei than the p_y orbital because the bond angle is greater than 90° (it is 104.5° ; if it were 90° the O-H bonds would bisect the p_y and p_z orbitals and their amplitudes at the H nuclei would necessarily be the same). Thus, the nuclear attraction integral for the latter orbital is slightly smaller than for the former.

The sum of the kinetic and nuclear attraction integrals is usually called the one- electron or core part of the Fock matrix and abbreviated \mathbf{h} (i.e., $\mathbf{h} = \mathbf{K} + \mathbf{V}$). One then writes $\mathbf{F} = \mathbf{h} + \mathbf{G}$ where \mathbf{F} is the Fock matrix, \mathbf{h} is the one-electron matrix, and \mathbf{G} is the remaining part of the Fock matrix coming from the two-electron four-index integrals (cf Equation 28.2.2). To compute those two-electron integrals, however, we need the density matrix, which itself comes from the occupied MO coefficients. So, we need an initial guess at those coefficients. We can get such a guess many ways, but ultimately any guess is as good as any other. With these coefficients we can compute the density matrix using Equation 28.2.3

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & \\ -0.456 & 2.010 & & & & & \\ 0.000 & 0.000 & 2.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 \end{bmatrix} \quad (28.2.7)$$

With \mathbf{P} , we can compute the remaining contribution of \mathbf{G} to the Fock matrix. We will not list all 406 two-electron integrals here. Instead, we will simply write the total Fock matrix:

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & \\ -5.163 & -2.453 & & & & & \\ 0.000 & 0.000 & -0.395 & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 \end{bmatrix} \quad (28.2.8)$$

So, we're finally ready to solve the secular determinant, since we have \mathbf{F} and \mathbf{S} fully formed. When we do that, and then solve for the MO coefficients for each root E , we get new occupied MOs. Then, we iterate again, and again, and again, until we are satisfied that further iterations will not change either our (i) energy, (ii) density matrix, or (iii) MO coefficients (it's up to the quantum chemist to decide what is considered satisfactory).

In our water calculation, if we monitor the energy at each step we find:

$$\begin{aligned} E(RHF) &= -74.893\,002\,803 && \text{a.u. after 1 cycles} \\ E(RHF) &= -74.961\,289\,145 && \text{a.u. after 2 cycles} \\ E(RHF) &= -74.961\,707\,247 && \text{a.u. after 3 cycles} \\ E(RHF) &= -74.961\,751\,946 && \text{a.u. after 4 cycles} \\ E(RHF) &= -74.961\,753\,962 && \text{a.u. after 5 cycles} \\ E(RHF) &= -74.961\,754\,063 && \text{a.u. after 6 cycles} \\ E(RHF) &= -74.961\,754\,063 && \text{a.u. after 7 cycles} \end{aligned} \quad (28.2.9)$$

Which means that our original guess was really not too bad—off by a bit less than 0.1 a.u. or roughly 60 kcal mol⁻¹. Our guess energy is too high, as the variational principle guarantees that it must be. Our first iteration through the secular determinant picks up nearly 0.07 a.u., our next iteration an additional 0.000 42 or so, and by the end we are converged to within 1 nanohartree (0.000 0006 kcal mol⁻¹).

The final optimized MOs for water are:

	1	2	3	4	5	6	7
E	-20.24094	-1.27218	-0.62173	-0.45392	-0.39176	.61293	.75095
1	.99411	-.23251	.00000	-.10356	.00000	-.13340	.00000
2	.02672	.83085	.00000	.53920	.00000	.89746	.00000
3	.00000	.00000	.00000	.00000	1.0000	.00000	.00000
4	.00000	.00000	.60677	.00000	.00000	.00000	.99474
5	-.00442	-.13216	.00000	.77828	.00000	-.74288	.00000
6	-.00605	.15919	.44453	-.27494	.00000	-.80246	-.84542
7	-.00605	.15919	-.44453	-.27494	.00000	-.80246	.84542

where the first row reports the eigenvalues of each MO, in E_h (i.e., the energy of one electron in the MO). The sum of all of the occupied MO energies should be an underestimation of the total electronic energy because electron-electron repulsion will have been double counted. So, if we sum the occupied orbital energies (times two, since there are two electrons in each orbital), we get $2(-20.24094 - 1.27218 - 0.62173 - 0.45392 - 0.39176) = -45.961\,060$ we now subtract the electron-electron repulsion energy 38.265 406 we get $-84.226\,466$ If we add the nuclear repulsion energy 9.264 701 to this we get a total energy $-74.961\,765$ The difference between this and the converged result above ($-74.961\,754$) can be attributed to rounding in the MO energies, which are truncated after 5 places. Notice that the five occupied MOs all have negative energies. So, their electrons are bound within the molecule. The unoccupied MOs (called “virtual” MOs) all have positive energies, meaning that the molecule will not spontaneously accept an electron from another source.

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