

Lecture 29, April 7, 2006**Solved Homework**

Water, H₂O, involves 2 hydrogen atoms and an oxygen atom. To minimally represent hydrogen is simple—one needs only a 1s function. As there are two H atoms, we will need two such functions, one centered on each atom. Oxygen has electrons in the second principal quantum level, so we will need one 1s, one 2s, and three 2p functions (one each of p_x, p_y, and p_z). So, that's five functions total on O, plus one each on the H atoms which is then 7 total.

The total number of one-electron integrals we need to solve is determined by considering that we need kinetic-energy integrals

$$T_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle$$

and potential energy integrals

$$V_{\mu\nu} = \left\langle \mu \left| - \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right| \nu \right\rangle$$

Since both μ and ν can be any one of the 7 basis functions, there are 7 x 7 possible kinetic energy integrals (49) and the same number of potential energy integrals *for each nucleus*. As there are 3 nuclei, that is 7 x 7 x 3 = 147 integrals. The grand total of one-electron integrals is thus 196.

The two-electron integrals are

$$(\mu\nu|\lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

where now μ , ν , λ , and σ can be any one of the seven basis functions (note that letting them be *any* function covers both all Coulomb and all exchange integrals). There are thus 7 x 7 x 7 x 7 = 2401 two-electron integrals.

The numbers computed above involve the contracted basis functions, each of which, since the basis is STO-3G, is composed of 3 primitive functions. Thus, for any individual one-electron integral, there will be 3 x 3 = 9 separate integrals involving the primitives. There are thus 9 x 196 = 1764 individual primitive one-electron integrals.

As for the two-electron integrals, again, every individual integral will require considering every possible combination of constituent primitives which is $3 \times 3 \times 3 \times 3 = 81$. Thus, the total number of primitive two-electron integrals is $81 \times 2401 = 194,481$ (gulp!) Notice that even for this small molecule the number of two-electron integrals totally dominates the number of one-electron integrals. The disparity only increases with molecular size.

All this to find 5 occupied molecular orbitals from which to form a final Slater determinant (10 electrons, two to an orbital, so 5 orbitals).

The situation sounds horrible, but it should be recognized that by using gaussians, the solutions to *all* of the integrals are known to be analytic formulae involving only interatomic distances, cartesian exponents, and α values in the gaussians. So, the total number of floating-point operations to solve the almost 200,000 grand-total integrals may be about 1,000,000. In computer speak that's one megaflop (megaflop = million FLoating-point OPerations). A modern digital computer processor can achieve *giga*flop per second performance, so the computer can accomplish all these calculations in under one second. In fact, modern computers are *so* fast at calculations that it can be faster to recompute the integral values than to take the time to write them onto a storage device to retrieve the number later!

The second way in which things can be improved is to recognize that there are symmetries of which advantage can be taken. From the turnover rule, it must be true that

$$T_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle = \left\langle \nu \left| -\frac{1}{2} \nabla^2 \right| \mu \right\rangle = T_{\nu\mu}$$

and the same is true for the nuclear attraction integrals. This reduces the total number of contracted integrals to $N(N+1)/2$ where N is the number of contracted basis functions. For water this will be 28, then, instead of 49. When basis functions μ and ν are the same (but possibly on different atoms) there will be additional savings from symmetry since they will be composed of the same primitives. A similar analysis for the two-electron integrals leads to a final number of $N(N+1)(N^2+N+2)/8$. For water, with $N = 7$, that is 406 contracted two-electron integrals—a substantial improvement over 2401. Writing computer code to take advantage of these symmetries is an important component of creating a useful quantum chemistry computational program.

A Hartree-Fock Calculation for Water

To find the HF MOs we need to solve the HF secular determinant

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (29-1)$$

and find its various roots. We know that we can compute overlap integrals and that Fock matrix elements are defined by

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2}\nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right] \quad (29-2)$$

Finally, the density matrix elements appearing in eq. 29-2 are defined as

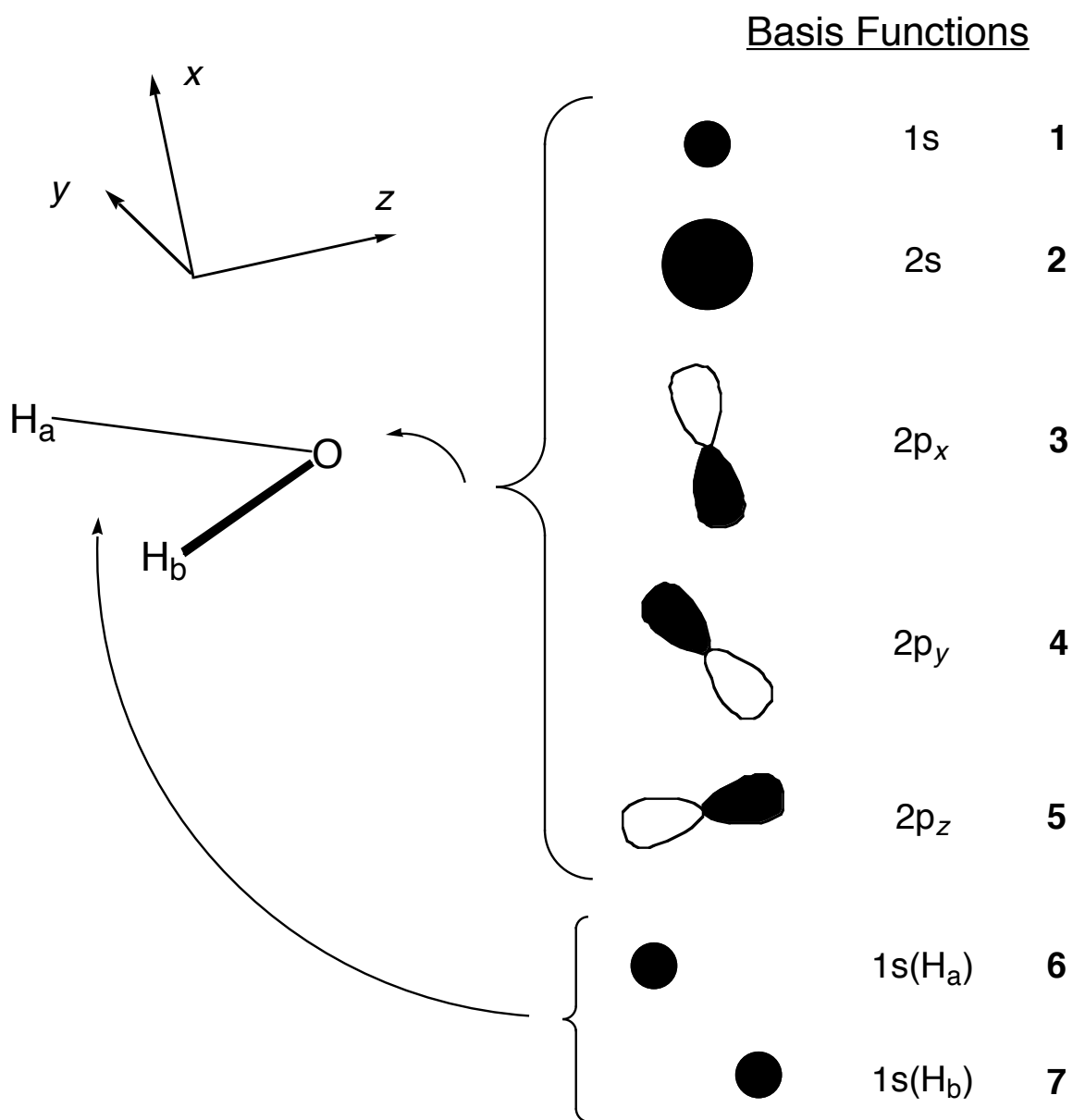
$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i} \quad (29-3)$$

where the a values are the coefficients of the basis functions in the occupied molecular orbitals. At the first step of an HF calculation, we simply guess what these are, and after that we iterate through solution of the secular determinant to derive new coefficients and we continue until we reach self-consistency.

Let's now do this for water. We'll use a structure close to the experimental structure: O–H bond lengths of 0.95 Å and a valence bond angle at oxygen of 104.5 deg. In cartesian coordinates (Å), that puts oxygen at position (0.000, 0.000, 0.116), one hydrogen at (0.000, 0.751, -0.465) and the other hydrogen at (0.000, -0.751, -0.465). Thus, the origin has been taken as the molecular center of mass, the atoms lie in the yz plane (all x coordinates are zero), and the z axis is the symmetry axis of rotation present in the water molecule that makes it belong to the symmetry point group C_{2v} (don't worry if you don't know anything about symmetry point groups—it won't be important, although it does make the calculation more efficient).

The basis functions we will use are shown in the figure on the next page. Function 1 is the O 1s, function 2 the O 2s, etc.

So, with the geometry in hand, we can compute the necessary parts of the secular determinant. We begin with the overlap matrix elements. They are



$$\mathbf{S} = \begin{bmatrix} 1.000 & & & & & & \\ 0.237 & 1.000 & & & & & \\ 0.000 & 0.000 & 1.000 & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 \end{bmatrix} \quad (29-4)$$

There are many noteworthy features in \mathbf{S} . First, it is shown in a lower packed triangular form because every element m,n is the same as the element n,m 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 (because they are not hydrogenic orbitals—which would indeed be orthogonal as different eigenfunctions of a Hermitian operator—they are just different gaussians; $S_{12} = 0.237$). Note 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.

Now, the kinetic energy matrix is (in a.u.)

$$\mathbf{T} = \begin{bmatrix} 29.003 & & & & & & \\ -0.168 & 0.808 & & & & & \\ 0.000 & 0.000 & 2.529 & & & & \\ 0.000 & 0.000 & 0.000 & 2.529 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & \\ -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & \\ -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 \end{bmatrix} \quad (29-5)$$

Consistent with our analysis from last lecture's homework, every diagonal term is much larger than any off-diagonal term. Note 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

$$\mathbf{V} = \begin{bmatrix} -61.733 & & & & & & \\ -7.447 & -10.151 & & & & & \\ 0.000 & 0.000 & -9.926 & & & & \\ 0.000 & 0.000 & 0.000 & -10.152 & & & \\ 0.019 & 0.226 & 0.000 & 0.000 & -10.088 & & \\ -1.778 & -3.920 & 0.000 & -0.228 & 0.184 & -5.867 & \\ -1.778 & -3.920 & 0.000 & 0.228 & 0.184 & -1.652 & -5.867 \end{bmatrix} \quad (29-6)$$

Again, consistent with our prior analysis, diagonal elements are bigger than off-diagonal elements. 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 deg (it is 104.5 deg; if it were 90 deg 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., $\mathbf{h} = \mathbf{T} + \mathbf{V}$). 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.

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—the guess listed below is from a model like Hückel theory that goes beyond just π systems but that is not iterative. It provides:

Occupied MO coefficients at cycle 1.					
	1	2	3	4	5
1	.994311	-.232461	.000000	-.107246	.000000
2	.025513	.833593	.000000	.556639	.000000
3	.000000	.000000	.000000	.000000	1.000000
4	.000000	.000000	.607184	.000000	.000000
5	-.002910	-.140863	.000000	.766551	.000000
6	-.005147	.155621	.444175	-.285923	.000000
7	-.005147	.155621	-.444175	-.285923	.000000

So, MO 1 is very nearly a pure oxygen 1s orbital, MO 2 is mostly a pure 2s orbital with small contributions from the H 1s orbitals, MO 3 is a bonding combination of the O $2p_y$ and the H 1s orbitals (note that their coefficients change sign because the p orbital also changes sign—that's what makes the overlap bonding!) MO 4 is another bonding orbital between the 2s polarized by the $2p_z$ and the H 1s orbitals. Finally, MO 5 is the pure O $2p_x$ orbital. This is all the occupied orbital coefficients so we can compute the density matrix using eq. 29-3 and we obtain

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & & \\ -0.456 & 2.010 & & & & & & \\ 0.000 & 0.000 & 2.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 & \end{bmatrix} \quad (29-7)$$

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 present the Fock matrix as

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & & \\ -5.163 & -2.453 & & & & & & \\ 0.000 & 0.000 & -0.395 & & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 & \end{bmatrix} \quad (29-8)$$

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

Occupied MO coefficients at cycle 2.

	1	2	3	4	5
1	.994123	-.233041	.000000	-.103527	.000000
2	.026666	.834174	.000000	.541326	.000000
3	.000000	.000000	.000000	.000000	1.000000
4	.000000	.000000	.608401	.000000	.000000
5	-.004400	-.131110	.000000	.774771	.000000
6	-.006039	.156851	.443140	-.279656	.000000
7	-.006039	.156851	-.443140	-.279656	.000000

If you compare these coefficients to those above, you can see that they have not changed much in a qualitative way, but there are quantitative changes in many places. So, 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:

E(RHF) = -74.893 002 803 A.U. after 1 cycles
 E(RHF) = -74.961 289 145 A.U. after 2 cycles
 E(RHF) = -74.961 707 247 A.U. after 3 cycles
 E(RHF) = -74.961 751 946 A.U. after 4 cycles
 E(RHF) = -74.961 753 962 A.U. after 5 cycles
 E(RHF) = -74.961 754 063 A.U. after 6 cycles
 E(RHF) = -74.961 754 063 A.U. after 7 cycles

So, our original guess is 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 (0.000 000 6 kcal mol⁻¹).

We can break the energy down into its four components:

Electron kinetic energy: 74.606 167 403
 Electron-nuclear attraction energy: -197.098 028 755
 Electron-electron repulsion energy: 38.265 406 023
 Nuclear-nuclear repulsion energy: 9.264 701 265

Note that the first term is $\langle T \rangle$ and the sum of the next three terms is $\langle V \rangle$. So, we can ask whether the wave function satisfies the virial theorem $-2\langle T \rangle = \langle V \rangle$. We see that $-2\langle T \rangle = -149.212 334 806$ and $\langle V \rangle = -197.098 028 755 + 38.265 406 023 + 9.264 701 265 = -149.567 921 466$. So, the virial theorem is not satisfied exactly (as is typical for a non-exact wave function) but it is satisfied to within about 0.5%.

Having converged the SCF equations, we have final MOs from which to form our Slater-determinantal wave function. The final MO coefficients for *all* MOs (not just the occupied ones) are

Final MOs:

	1	2	3	4	5
EIGENVALUES --	-20.24094	-1.27218	-.62173	-.45392	-.39176
1	.99411	-.23251	.00000	-.10356	.00000
2	.02672	.83085	.00000	.53920	.00000
3	.00000	.00000	.00000	.00000	1.00000
4	.00000	.00000	.60677	.00000	.00000
5	-.00442	-.13216	.00000	.77828	.00000
6	-.00605	.15919	.44453	-.27494	.00000
7	-.00605	.15919	-.44453	-.27494	.00000
	6	7			
EIGENVALUES --	.61293	.75095			
1	-.13340	.00000			
2	.89746	.00000			
3	.00000	.00000			
4	.00000	.99474			
5	-.74288	.00000			
6	-.80246	-.84542			
7	-.80246	.84542			

where "eigenvalue" refers to the energy of one electron in the MO. Remember that 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 $2(-20.24094 - 1.27218 - 0.62173 - 0.45392 - 0.39176) = -45.961060$. If we now subtract the electron-electron repulsion energy 38.265406 we get -84.226466 . If we add the nuclear repulsion energy 9.264701 to this we get a total energy -74.961765 . The difference between this and the converged result above (-74.961754) can be attributed to rounding in the MO energies, which are truncated after 5 places.

Notice that the 5 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. This is certainly in keeping with our expectations. Water neither spontaneously gives up nor grabs electrons.

Next time, we will look more carefully at the orbitals themselves and at the information contained within the wave function.

Homework

To be solved in class:

Use eq. 29-3 and the initial guess MO coefficients to verify that P_{21} in eq. 29-7 is -0.456 .

To be turned in for possible grading Apr. 14:

What is the value of P_{52} for water after the first SCF step (i.e., at cycle 2)? By what percentage did it change compared to the initial guess? By what percentage did the total energy change for this same step?