Lecture 30, April 10, 2006

Solved Homework

The guess MO occupied coefficients were

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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
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To evaluate a density matrix element we use

$$P_{\lambda\sigma} = 2 \sum_{i}^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

where in this case we are asked to solve for $\lambda = 2$ and $\sigma = 1$. As there are 5 occupied MOs, we will sum over all 5 the product of a_{2i} with a_{1i}. So, for MO 1 we have 0.025513 times 0.994311. For MO 2, 0.833593 times –0.232461. For MO 3, 0 times 0. For MO 4, 0.556639 times –0.107426. And, for MO 5, 0 times 0 again. If we sum the three non-zero products, and multiply by two, we obtain –0.456 (to 3 digits). This verifies the density matrix element.

Hartree-Fock MOs for Water

Our basis MOs were provided as a figure in the preceding lecture and that figure is not reproduced here. In a nutshell, however, basis function #1 was an oxygen 1s orbital, #2 was an oxygen 2s orbital, #3 was an oxygen $2p_x$ orbital, #4 was an oxygen $2p_y$ orbital, #5 was an oxygen $2p_z$ orbital, #6 was one hydrogen 1s orbital, and #7 was the other hydrogen 1s orbital.

Recall that the final optimized MOs for water were

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Final MOs:
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	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

So, we see that the lowest energy orbital (by a lot!) is a nearly pure oxygen 1s orbital since the coefficient of the oxygen 1s basis function is very nearly 1 and all other coefficients are rather close to 0. Note, however, that the coefficient is not really a percentage measure. That's because the basis functions are not necessarily orthogonal to one another (remember the overlap matrix?). Let's consider the next molecular orbital up, number 2. It has a dominant contribution from the oxygen 2s basis function, but non-trivial contributions from many other basis functions too.

Let's verify that this MO is truly normalized. That is, we will evaluate $|\psi|^2$ for the particular set of coefficients and basis functions. This gives

$$
|\psi_2|^2 = \left\langle \begin{array}{l} -0.23251(O1s) + 0.83085(O2s) \\ -0.13216(O2p_z) + 0.15919(H_a1s) \\ +0.15919(H_a1s) \end{array} \middle| \begin{array}{l} -0.23251(O1s) + 0.83085(O2s) \\ -0.13216(O2p_z) + 0.15919(H_a1s) \\ +0.15919(H_a1s) \end{array} \right\rangle
$$

$$
\begin{aligned}
= &(-0.23251)^2 S_{11} + 2(-0.23251 \times 0.83085)S_{12} + 2(-0.23251 \times -0.13216)S_{15} \\
&+2(-0.23251 \times 0.15919)S_{16} + 2(-0.23251 \times 0.15919)S_{17} + (0.83085)^2 S_{22} \\
&+2(0.83085 \times -0.13216)S_{25} + 2(0.83085 \times 0.15919)S_{26} \\
&+2(0.83085 \times 0.15919)S_{27} + (-0.13216)^2 S_{55} + 2(-0.13216 \times 0.15919)S_{56} \\
&+2(-0.13216 \times 0.15919)S_{57} + (0.15919)^2 S_{66} + 2(0.15919 \times 0.15919)S_{67} \\
&+(0.15919)^2 S_{77}
\end{aligned}
\tag{30-1}
$$

Note that the zero coefficients for two basis functions (the oxygen $2p_x$ and $2p_y$ orbitals) means that there are only five terms in the linear expansion for MO 2. Note also that the factors of two in front of cross terms in the product come from the symmetry of the cross terms: they are the same whether we multiply the mth term in the linear expansion by the nth term or vice versa. Finally, note that we have represented the various overlap integrals < basis function m | basis function n > with their shorthand notation.

We may refer back to the last lecture for the overlap matrix (which is a constant once the molecular geometry is set). It was

$$
\mathbf{S} = \begin{bmatrix}
1.000 & & & & & & \\
0.237 & 1.000 & & & & & \\
0.000 & 0.000 & 1.000 & & & & \\
0.000 & 0.000 & 0.000 & 1.000 & & & \\
0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & \\
0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & \\
0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000
\end{bmatrix}
\tag{30-2}
$$

Solving eq. 30-1 we have

$$
\begin{aligned}
|\psi_2|^2 &= 0.05406 \bullet 1 - 0.38636 \bullet 0.237 + 0.06146 \bullet 0 \\
&\quad -0.07403 \bullet 0.055 - 0.07403 \bullet 0.055 + 0.69031 \bullet 1 \\
&\quad -0.21961 \bullet 0 + 0.26453 \bullet 0.479 \\
&\quad +0.26453 \bullet 0.479 + 0.01747 \bullet 1 - 0.04208 \bullet -0.242 \\
&\quad -0.04208 \bullet -0.242 + 0.02534 \bullet 1 + 0.05068 \bullet 0.256 \\
&\quad +0.02534 \bullet 1 \\
&= 0.05406 - 0.09157 + 0.0 - 0.00407 - 0.00407 + 0.69031 \\
&\quad -0.0 + 0.12671 + 0.12671 + 0.01747 + 0.01018 + 0.01018 \\
&\quad +0.02534 + 0.01297 + 0.02534 \\
&= 0.99956 \\
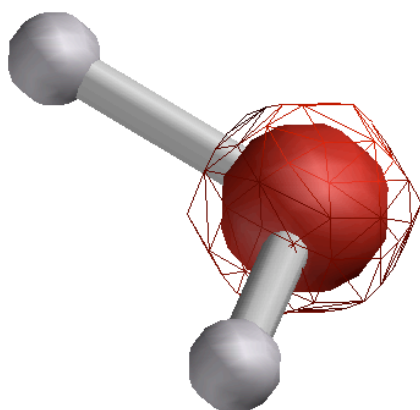&\approx 1
\end{aligned}
\tag{30-3}
$$

where the deviation from 1 is associated with rounding the overlap matrix to 3 digits. So, what is the nature of this orbital? Well, the final numbers in the last sum *do* add to 1, so we may consider them to represent percentages. Thus, the sixth term, which involves the coefficient of the oxygen 2s orbital squared is somewhat like saying that the orbital has 69% 2s character. An additional 2 x 12.7% derives from terms involving the overlap of the oxygen 2s orbital and the different hydrogen 1s orbitals. There is evidently 5.4% 1s character, about 3% deriving from the oxygen p_z orbital, and the remaining 6% or so comes from the hydrogen 1s orbitals either unmixed or mixing only with each other.

Such an analysis is good to do once, to see what is going on, but what is much nicer, usually, is to *visualize* the molecular orbital. Remember that ψ^2 at a particular point in space represents a probability density. So, we can map a grid in 3-dimensional space with values of ψ^2 and we can analyze the pattern just as we once did for rather simple hydrogenic orbitals. Typically, we pick a particular level of probability density, say 0.04 bohr^{-3}, and treat that as a contour surface. That surface is called an "isodensity" surface. Having identified that surface, we can then look not at the value of ψ^2 but rather at the sign of ψ to recover phase information. We color positive regions blue and negative regions red (one can also simply plot ψ at some isoamplitude contour without squaring it, but isodensity surfaces tend to be good representations of van der Waals surfaces, so this is more typical). Remember, of course, that computation of amplitude or probability density comes from the basis functions being used in the linear expansion—that's in part why we like working with guassians, because evaluating the relevant integrals at any position in space can be done analytically.

On the next few pages are depictions of the 5 occupied and 2 unoccupied MOs mapped from their one-electron wave functions. The depictions use a wire mesh for an isodensity surface of 0.1 a.u. Blue mesh corresponds to one phase (let's arbitrarily call it negative) and red to the other (positive).

Before you look at the MOs, you might want to think about the tenets of bonding that you learned in freshman chemistry and in organic chemistry. In particular, what does a Lewis structure for water look like? Once you've done that, see if you can match up the valence electrons in your Lewis structure with particular MO pictures for the occupied valence MOs 2-5 (i.e., all of the occupied orbitals but the oxygen 1s core).
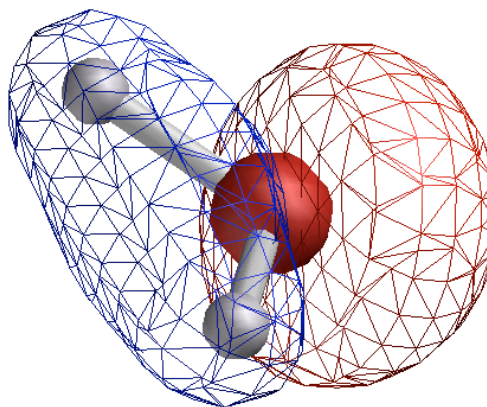
MO 1 (mostly Oxygen 1s orbital)   MO 2 (fully σ-bonding between all atoms)
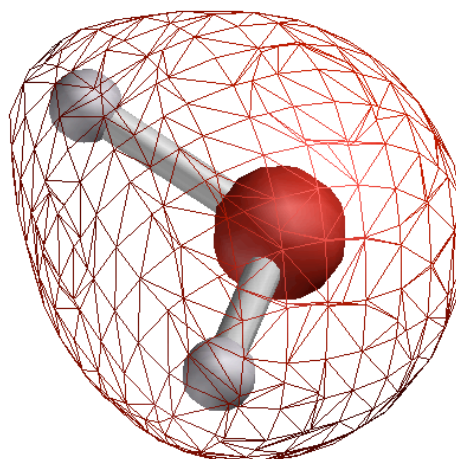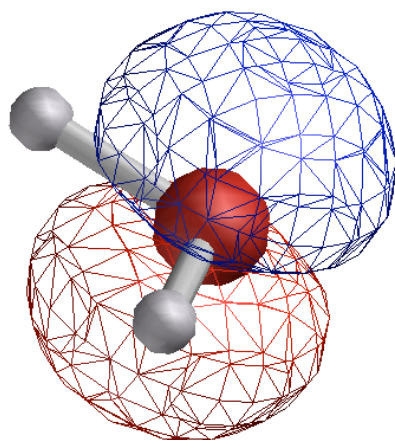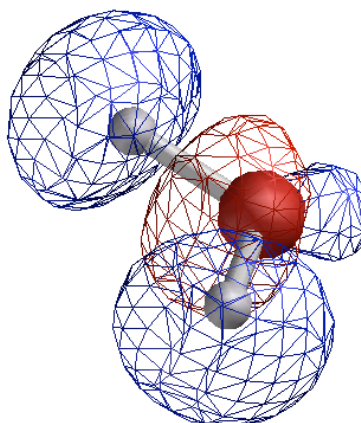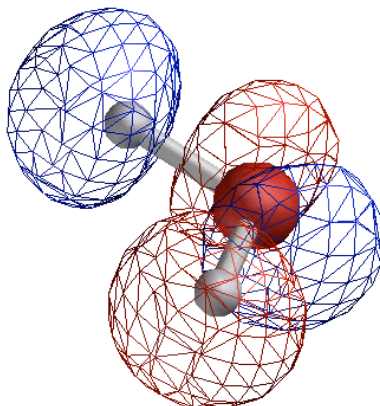
MO 3 (O–H σ bonds, node at O)
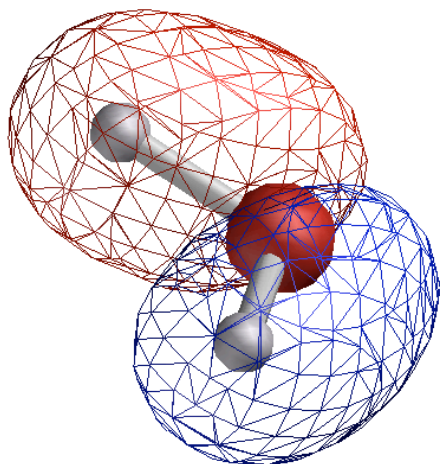
MO 4 (in-plane O lone pair with some O–H bonding contribution)

MO 5 (pure out-of-plane O lone pair)

MO 6 (O–H σ-antibonding but some H–H through-space bonding)

MO 7 (fully σ-antibonding between all atoms)

Your Lewis structure, if you drew it correctly, says that there is one pair of electrons in one O–H σ bond, one pair in another identical such σ bond, and two pairs each of which is equivalent that constitute the lone pairs on oxygen. The two lone pairs and the O–H bonds should by pointing towards the apices of a tetrahedron because they are all considered to be sp^3 hybridized. Right?

My God, how you've been lied to before now...

As you can see, the MOs look *nothing* like the Lewis picture. Instead, amongst other details, there is one lone pair that is pure p (not sp^3), another that is, if anything, sp^2-like, but also enjoys contribution from hydrogen 1s components. There is one orbital that looks like both O–H σ bonds are present, but another that has an odd "bonding-all-over" character to it.

But, but, it's not really possible that for something as simple as water all the things you've ever been told about the Lewis structure are wrong, is it? Perhaps, you say, this MO theory is all crazy. Water *must* have two equivalent lone pairs, right?

It turns out that we can test this proposal with experiment. Shown below is the photoelectron spectrum for water (taken from http://www.wellesley.edu/Chemistry/ chem120/h2opes.html). When a photon of sufficient energy is absorbed by the water molecule, an electron is ejected and its kinetic energy counted. The difference between its kinetic energy and the photon energy is the energy by which it was bound to the molecule. In the below spectrum, the rightmost peak in each group of peaks corresponds to binding of the electron in the orbital (additional peaks come from vibrationally excited final radical cation states, about which we will not worry). We see that there are 3 major sets of peaks in the spectrum, starting at 12.61 eV, 14.1 eV, and about 17.4 eV,
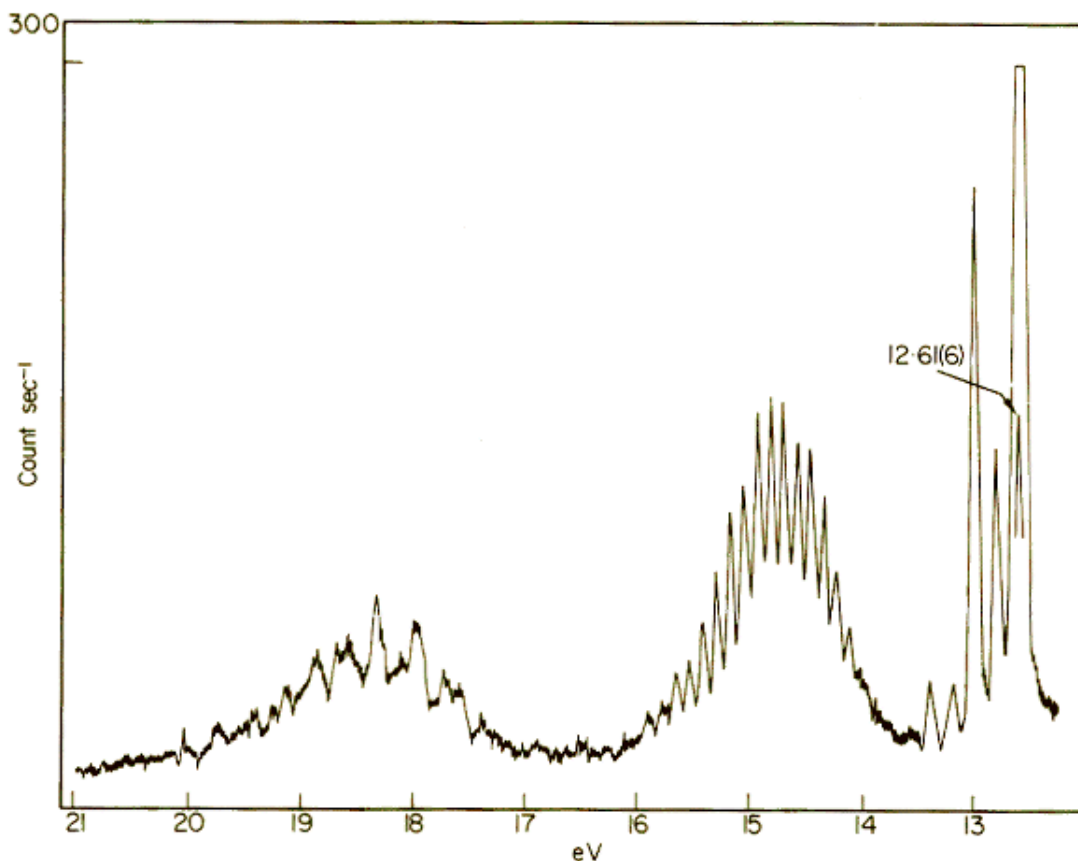
Figure 4.26   Water (full spectrum)

respectively. In a.u. those are binding energies of –0.463, –0.518, and –0.639, respectively. Referring to the orbitals above, we see that we have computed HF/STO-3G eigenvalues for the first 3 orbitals of –0.392, –0.454, and –0.622. The agreement is quantitatively only OK, but there is no doubt about the qualitative agreement that there are 3 different highest occupied MOs, two of which must then correspond to different lone pairs (note that the experimental spectrum does not have enough photon energy to eject electrons from either MOs 1 or 2, which are at 30+ eV).

As for the quantitative agreement, part of the trouble is that the HF/STO-3G level is really quite crude. If we use a basis set containing many, many more basis functions we could obtain better agreement with experiment. However, we should not expect perfect agreement in any case because the HF level of theory makes the intrinsic approximation that each electron sees a frozen field of all of the other electrons, i.e., electron correlation is not treated explicitly.

But wait, you say, still hoping to hold onto the beautiful picture of sp^3-hybridized water—what about water's well known hydrogen-bonding behavior? Everyone knows that in liquid water each water molecule makes two hydrogen bonds to other water molecules and accepts two more from different water molecules and the final structure

has a net lattice-like form that is tetrahedral at each oxygen atom. How can the above MOs explain that?

Easy.

The key point to remember is that another molecule does not see the individual orbitals of water, it just sees the final effect of all of those electrons and nuclei together. So, we can ask, if we were to bring up a positive test charge, where in space would the test charge find itself attracted (because of a net negative electrostatic potential) and where would it find itself repelled (because of a net positive electrostatic potential)? The below picture shows an isopotential surface about water with an attractive isopotential to a positive charge (e.g., the hydrogen in a hydrogen bond) being represented by a blue mesh and a repulsive isopotential being represented by a red mesh.
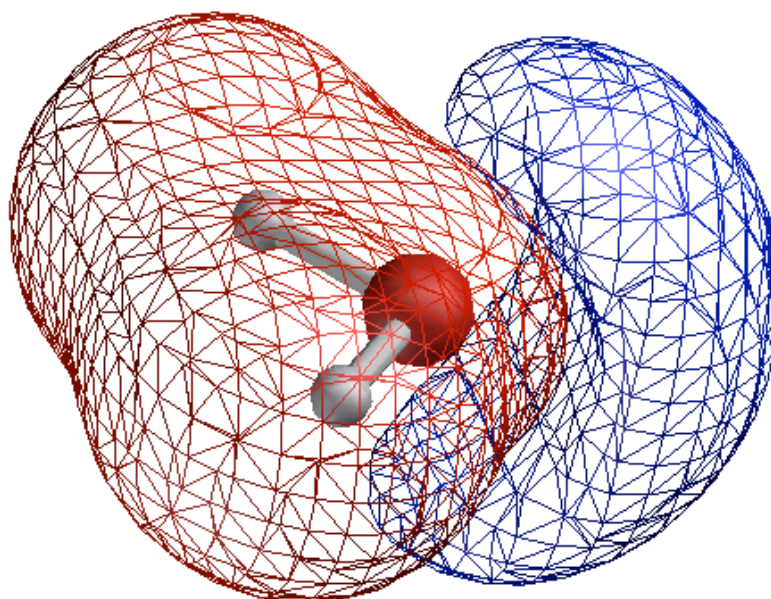
Note that the blue potential is entirely on the oxygen side and the red potential entirely on the hydrogens side. Moreover, the blue potential splays out to the tetrahedral points and the red potential does too (those points for the red potential being roughly where the H atoms are in any case). Hence it is not surprising that 4 other water molecules would organize themselves tetrahedrally about a central water molecule.

A slightly more sophisticated analysis would moreover take account of how closely a neighbor water molecule can approach the first water molecule. What keeps molecules apart? If you say sterics (a good organic chemistry answer) you are, in some sense, avoiding the complete answer. What keeps them apart is the electrostatic repulsion

of their electron clouds, which really don't want to interpenetrate (i.e., sterics is just electronics, after all). So, a good way to think about a van der Waals surface (a steric surface) is to pick some constant level of electron density and look at that isodensity surface. That is shown below for water at the 0.01 a.u. level.
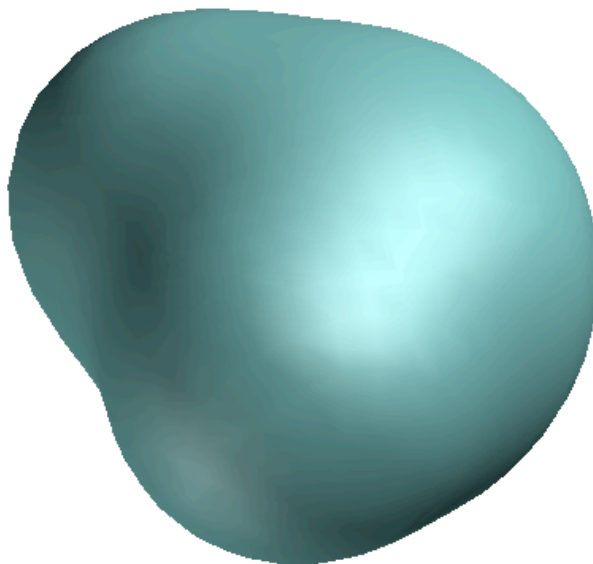

If we were to map onto this isodensity surface the values of the electrostatic potential, we would find that it is maximally negative (attractive to a positive test charge) at just the tetrahedral points we expect. We would see that it is most positive (attractive to negative lone pairs) behind each hydrogen atom, i.e., the other tetrahedral points. This is illustrated on the next page with an image taken from http://academic.reed.edu/chemistry/alan/ACS97/elpot.html and generated by the commercial program SPARTAN.

Important points to bear in mind are the differences between isoamplitude surfaces (for orbitals), isodensity surfaces (for the square moduli of orbitals or total wave functions), and isopotential surfaces (for attraction or repulsion of test charges).

So, quantum mechanics completely explains all experimental observables having to do with water. Lewis structures fail dramatically with the photoelectron spectrum.

Next time, we'll look at some other features in the wave function, and generalize a few of the concepts we've discussed more specifically above.
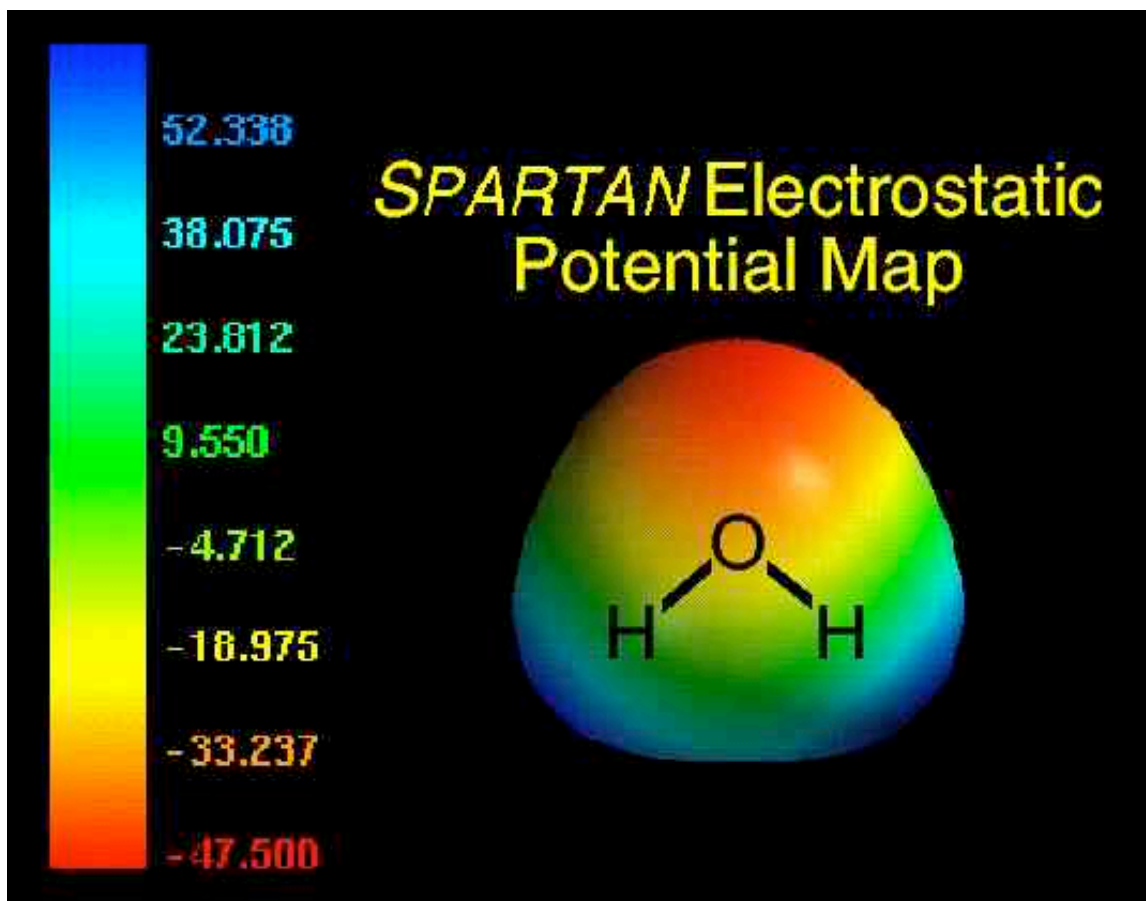
Homework

To be solved in class:

If we were to attach an extra electron to water to make the negatively charged radical anion, into which orbital would you expect that electron to go? Based on that analysis, if you were to allow the geometry to relax from that of neutral water, what would you expect to happen to the OH bond lengths? What about the internal HOH bond angle?

To be turned in for possible grading Apr. 14:

What about the radical cation generated by ionization of the least tightly held electron in water? From which orbital may it be considered to be taken? Based on that analysis, if you were to allow the geometry to relax from that of neutral water, what would you expect to happen to the OH bond lengths? What about the internal HOH bond angle?