

## 28.3: Shapes and Energies of Molecular Orbitals

If we analyze the optimized coefficients of the occupied MOs reported in [Equation 29.2.10](#), we observe 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. 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 as well. In order to understand which kind of orbital it is, it is useful to try to visualize some of its properties. For example, recall that the square of the orbital at a particular point in space represents a probability density. As such, we can map values of the square of each orbital on a grid in 3-dimensional space, and then pick a value of probability density, say  $0.04 a_0^{-3}$ , and plot that as a contour surface (remember that a probability density is a 4-dimensional quantity, so we need to take a slice at some constant density to be able to plot it in 3-D). That surface is called an "isodensity" surface. In addition to the square of the function, we can also regions where the wave function is positive blue and regions where it's negative red. The five occupied and two unoccupied MOs mapped from their one-electron wave functions are plotted in figure 28.3.1.

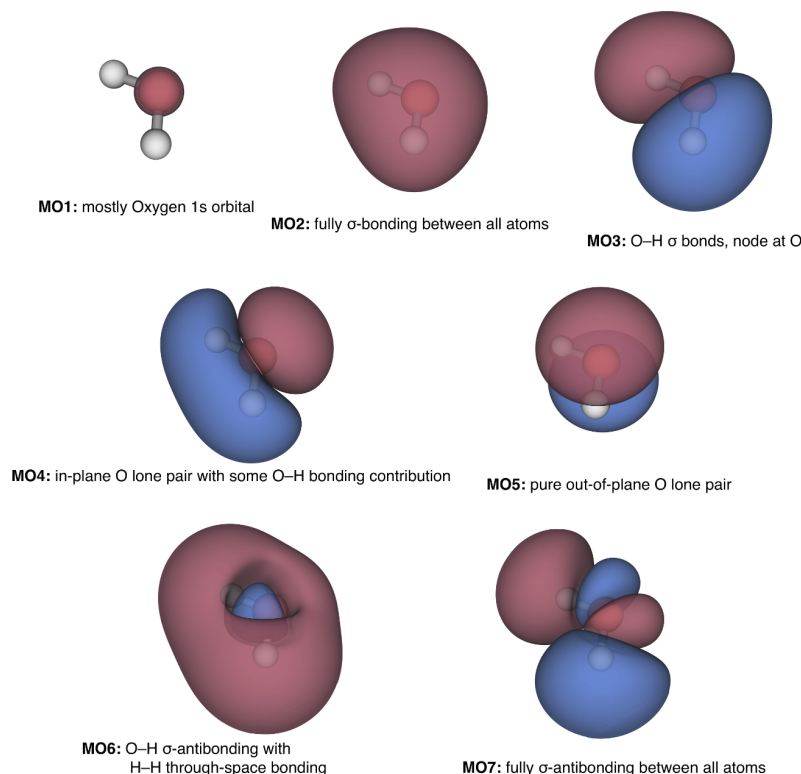


Figure 28.3.1: Isodensity maps of the Molecular Orbitals (MOs) of water.

Going back to the Lewis structure of water as taught in general chemistry courses, it says that there is one pair of electrons in one O-H  $\sigma$  bond, one pair in another identical such  $\sigma$  bond, and two equivalent pairs that constitute the lone pairs on oxygen. The two lone pairs and the O-H bonds should be pointing towards the apices of a tetrahedron because they are all considered to be  $sp^3$  hybridized.

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  $\sigma$  bonds are present, but another that has an odd "bonding-all-over" character to it.

Is it really possible that for something as simple as water all the things you've ever been told about the Lewis structure are wrong? Water must have two equivalent lone pairs, right?

It turns out that the molecular orbital results can be tested with spectroscopic experiments, and suffice to say, they agree perfectly.

But the  $sp^3$ -hybridized picture of water works well, for example, to explain its hydrogen-bonding behavior: 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? 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**. To explain the tetrahedral H-bond lattice we can plot some constant level of electron density (i.e. 0.02) and map onto this isodensity surface the values of the electrostatic potential. We can find these values by bringing a positive test charge onto that surface and recording how much would it find itself attracted (because of a net negative electrostatic potential) or repelled (because of a net positive electrostatic potential). This is done in figure 28.3.2 Notice how the negative potential is entirely on the oxygen side and the positive potential entirely on the hydrogens side. Moreover, the negative potential splays out to the tetrahedral points and the positive potential does too (those points for the purple region being roughly where the H atoms are).

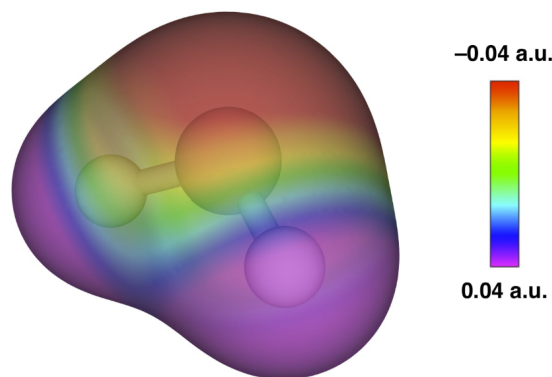


Figure 28.3.2: Molecular electrostatic potential of water plotted on a 0.02 a.u. isodensity surface.

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