Deriving the MO diagram for water: a guided inquiry exercise for polyatomic main group MO diagrams with lone pairs and hybrid orbitals.
This exercise assumes familiarity with the graphical method for forming LGOs described elsewhere.[1-2] The first step (determining LGOs for water) is presented elsewhere but is included here for completeness.[2-3]

Water doesn't seem like it should be that difficult—2 bonds, 2 lone pairs, no problem. One possible place to start is using valence bond theory. Refresh your memory on this theory by answering these questions:

a. How many electron groups are around the oxygen in water? _____

b. What is the geometry around the oxygen? _____

c. Why hybrid orbitals would you use? _____

You should have found that there are 4 electron groups, oxygen is tetrahedral, and you would use sp^3 hybrid orbitals. Forming bonds to the two hydrogen atoms with two of the sp^3 hybrids would lead to two O-H bonds of equal energy, and we would expect the remaining two hybrids to contain lone pairs, also of equal energy. However, the photoelectron spectrum shows four energy levels instead of two, not including the oxygen 1s level.[4] Let's construct an MO diagram to understand why there are four energy levels in the valence shell of water. We will start at the beginning of the process and generate LGOs. Place your molecule in the yz plane.

Technique for constructing LGO's:
I Draw Lewis structure and assign VSEPR geometry

II Assign a point group to the *molecular geometry*

III determine the central atom's VB hybrid orbitals for the *electronic geometry*

IV use the VB hybrid orbitals as generator functions (GF)

V Generate the LGOs by taking linear combinations of the ligand σ-orbitals (lobes) to get an orbital with the same symmetry as the generator function

VI Assign proper symmetry labels from the character table

Now we can move on to form the MO diagram for water using the oxygen AOs and the hydrogen LGOs. Forming the MO diagram for water introduces the concept of orbital mixing. Orbital mixing is the general answer to the important question of what we should we do if there are more than one AO or LGO of the same symmetry on one of the two sides of the MO diagram. This mixing, in addition to allowing for better orbital overlap, also allows us to get the correct energy ordering of the two lone pairs in water. We will first derive the MO diagram without mixing using the following process:

Technique for constructing MO diagrams:
I name the MO diagram and its constituents
II place AOs and LGOs with relative energies on one sides
III place the correct number of electrons on each side
IV form MOs (bonding, antibonding and non-bonding) and give them symmetry labels
V place electrons in the MOs working from the bottom up
VI be able to sketch each MO

The instructions are on the next page; draw your MO diagram on the blank page that follows.

I name the MO diagram and its constituents
Name the central atom on one side (the left) and the LGOs on the other (right). Then in the center, place the name of the molecule. For completeness, include the point group and any geometrical information (what plane the molecule is in).

II place AOs and LGOs with relative energies on one sides
Include all valence orbitals on the central atom, and the LGOs you generated. Estimate the energy levels using principal quantum number and electronegativity. Each energy level is a short horizontal line. The LGOs can be alternatively be drawn with all having the same energy (since they are further away than bonding distance). Label each AO and LGO with a symmetry label.

III place the correct number of electrons on each side
Only include valence electrons for the central atom, and only include a single electron forming the σ-bond from the ligand. For hydrogen, it only has one electron, but if this were Cl_2O, you would still only include the single bonding electron on each chlorine.

IV form MOs (bonding, antibonding and non-bonding) and give them symmetry labels
Match symmetry labels on both sides of the MO diagram to find out which orbitals can interact. For example, an a_1 MO can interact with an a_1 LGO, but not with a b_2 LGO. Any orbitals that are not used remain as non-bonding orbitals with the same energy as the initial AO or LGO. Label each MO with σ/σ^*, π/π^*, or nb, and the symmetry label.

V place electrons in the MOs working from the bottom up

VI be able to sketch each MO

You're done! Now, evaluate your MO diagram. Does your MO diagram match your expectation in terms of number of bonds? _____yes_____
Does your MO diagram match the observed PES (4 energy levels?)__yes or no_____

If the MO diagram does not match expectations, it means it was either misinterpreted, or something went wrong. If the MO matches expectations, that is good, but move on to the next problem anyway…

When you constructed your MO diagram, you should have matched the a_1 LGO with one of two possible AOs on oxygen. What would change if you had used the other a_1 AO?

In the C_{2v} point group, it is not possible to have two degenerate energy levels, so if present, students are instructed to arbitrarily move one of the two lone pairs up or down in energy to split the degeneracy. But is there a more elegant solution? Yes.

The two a_1 symmetry orbitals on the oxygen atom can mix together to form sp hybrid orbitals. one of these orbitals points towards the hydrogen atoms and gives better overlap for bonding, while the other points away from the hydrogen atoms and would give rise to a lone pair pointing away from the molecule. Draw these two hybrid orbitals.

What would happen to on the MO diagram on the central atom side when hybrid orbitals are formed? Write a few sentences, and then draw it in a new MO diagram. Does this new MO diagram match the PES results?

Concluding remarks

How do we know when to form hybrid orbitals? Whenever there are two orbitals of the same symmetry on one side of an MO diagram, they will hybridize with each other to some extent to give better overlap with the hydrogen atoms. One of the orbitals will overlap better (spatially) with the LGOs while the other will points away. The former orbital is the one that should be used to form the bonding and antibonding MOs, while the latter comes straight over as a non-bonding orbital.

Cited References

1)   Johnson, A. R. Generating LGOs (SALCs). https://www.ionicviper.org/class-activity/generating-lgos-salcs (accessed 5/13/2020).
2)   Johnson, A. R. *J. Chem. Educ.* **2013,** *90(1)*, 56-62. (10.1021/ed300115t)
3)   Johnson, A. R. Generating LGOs and constructiong MO diagrams - pencast. https://www.ionicviper.org/classactivity/generating-lgos-and-constructing-mo-diagrams-pencast (accessed 5/13/2020).
4)   Banna, M. S.; McQuaide, B. H.; Malutzki, R.; Schmidt, V. *J. Chem. Phys.* **1986,** *84(9)*, 4739-4744. (10.1063/1.450008)