LTs1: Molecular Distortions
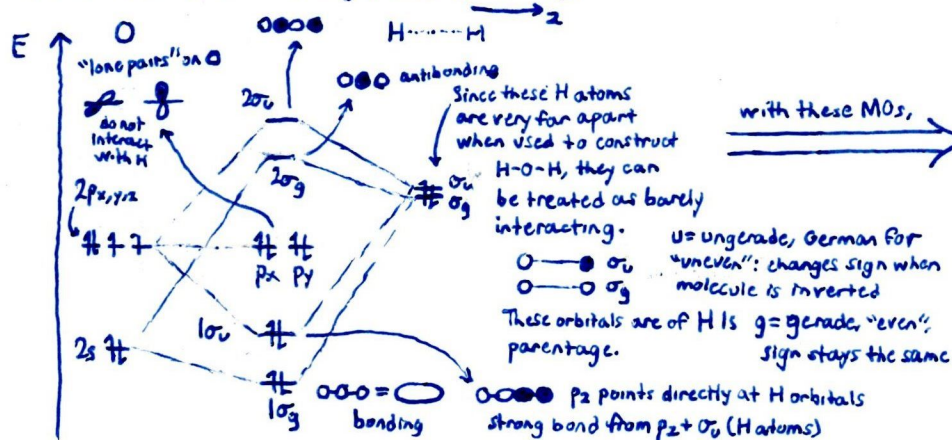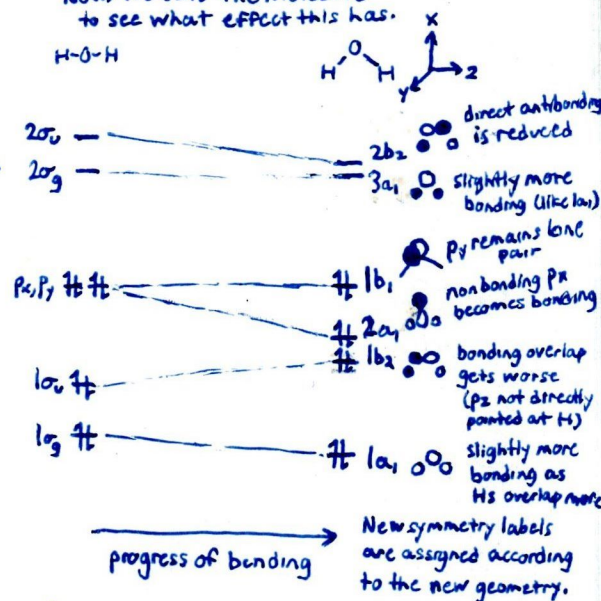
What other kinds of questions can we apply MO theory to?

Suppose for a moment that you didn't know water was bent $\left(\text{H}^{\nearrow \text{O} \searrow}\text{H}\right)$ and assumed it to be a straight line (H–O–H).

Now, we bend the molecule to see what effect this has.

H–O–H

For real calculations, the intrinsic energies of atomic orbitals (which key us in on the relative energies of H and orbitals) come from "valence orbital ionization energy" tables describing how tightly bound various e^- are. These can be found in textbooks and online.

Key takeaway: MO theory can select the appropriate molecular geometry from plausible alternatives; valence-shell electron pair repulsion theory (VSEPR) is also used to predict geometries, but is based on handwavey electron-counting rules/guessing the lone pair count from valency, meaning it lacks the power to describe all molecules.

New symmetry labels are assigned according to the new geometry.

A similar distortion diagram or "Walsh diagram" can be used to show that NH_3 $\left(\text{H}^{\nearrow \text{N} \searrow}\text{H}\right)$ is more stable as a pyramid than a flat shape. The expected "lone pair" pops out as the highest-energy MO.

Since bending H_2O leads the highest occupied molecular orbital (HOMO) to become bonding, the molecule prefers this nuclear geometry. A good rule of thumb for stabilizing molecules is to lower the highest occupied orbital in energy.

(Note that s-p mixing, e.g. between $2a_1$ and $1a_1$, has not been worked out for this example. It will move some energy levels somewhat, e.g. by lowering $1a_1$ through $\circ^{\circ}_{\circ} + \circ^{\bullet}_{\circ} \rightarrow \circ^{\bullet}_{\circ}$ but will not alter the primary conclusion that bending is stabilizing.)