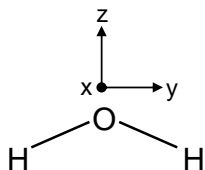


**Take-Home Quiz 3**  
**CHEM 325**  
**Spring 2009**

Name: \_\_\_\_\_

Derive a qualitative MO diagram for H<sub>2</sub>O using the molecular coordinate system defined below. Determine the SALCs and draw qualitative MO wavefunctions. Label the MOs with their symmetry designation and what type of MO each is (i. e.,  $\sigma$ ,  $\sigma^*$ , etc.) Show all work for full credit, attach extra sheets as needed. For simplicity, assume that the oxygen 2s orbital is too low in energy to have a large effect on bonding.



Water belongs to the  $C_{2v}$  point group and the O 2p orbitals transform as follows:  $2p_z$  transforms as  $a_1$ ,  $2p_x$  as  $b_1$  and  $2p_y$  and  $b_2$ . The H 1s orbitals give the following reducible representation.

	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$H_{1s}$	2	0	0	2

Use the Great Orthogonality Theorem to reduce the reducible representation to its irreducible components. Helpful hint: consider  $a_1$ ,  $b_1$  and  $b_2$  first because that is how the O atomic orbitals transform.

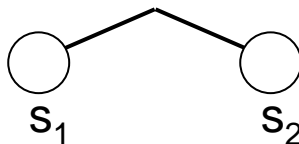
$$a_{a_1} = \frac{1}{4}((1)(2)(1) + (1)(0)(1) + (1)(0)(1) + (1)(2)(1)) = 1$$

$$a_{b_1} = \frac{1}{4}((1)(2)(1) + (1)(0)(-1) + (1)(0)(1) + (1)(2)(-1)) = 0$$

$$a_{b_2} = \frac{1}{4}((1)(2)(1) + (1)(0)(-1) + (1)(0)(-1) + (1)(2)(1)) = 1$$

So, the H 1s SALCs transform as  $a_1$  and  $b_2$ .

Label the H 1s orbitals and see how they move under each operation in the group.



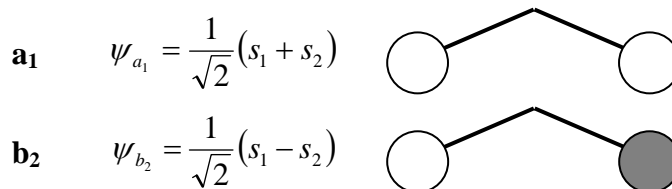
	<b>E</b>	<b>C<sub>2</sub></b>	<b>σ<sub>v</sub> (xz)</b>	<b>σ<sub>v</sub>' (yz)</b>
<b>s<sub>1</sub></b>	<b>s<sub>1</sub></b>	<b>s<sub>2</sub></b>	<b>s<sub>2</sub></b>	<b>s<sub>1</sub></b>

Using the projection operator for the two irreducible representations (a<sub>1</sub> and b<sub>2</sub>) gives

$$\hat{P}^{a_1} s_1 = ((1)(s_1) + (1)(s_2) + (1)(s_2) + (1)(s_1)) \approx s_1 + s_2$$

$$\hat{P}^{b_2} s_1 = ((1)(s_1) + (-1)(s_2) + (-1)(s_2) + (1)(s_1)) \approx s_1 - s_2$$

The normalized SALC wavefunctions, and their qualitative pictures are shown below.

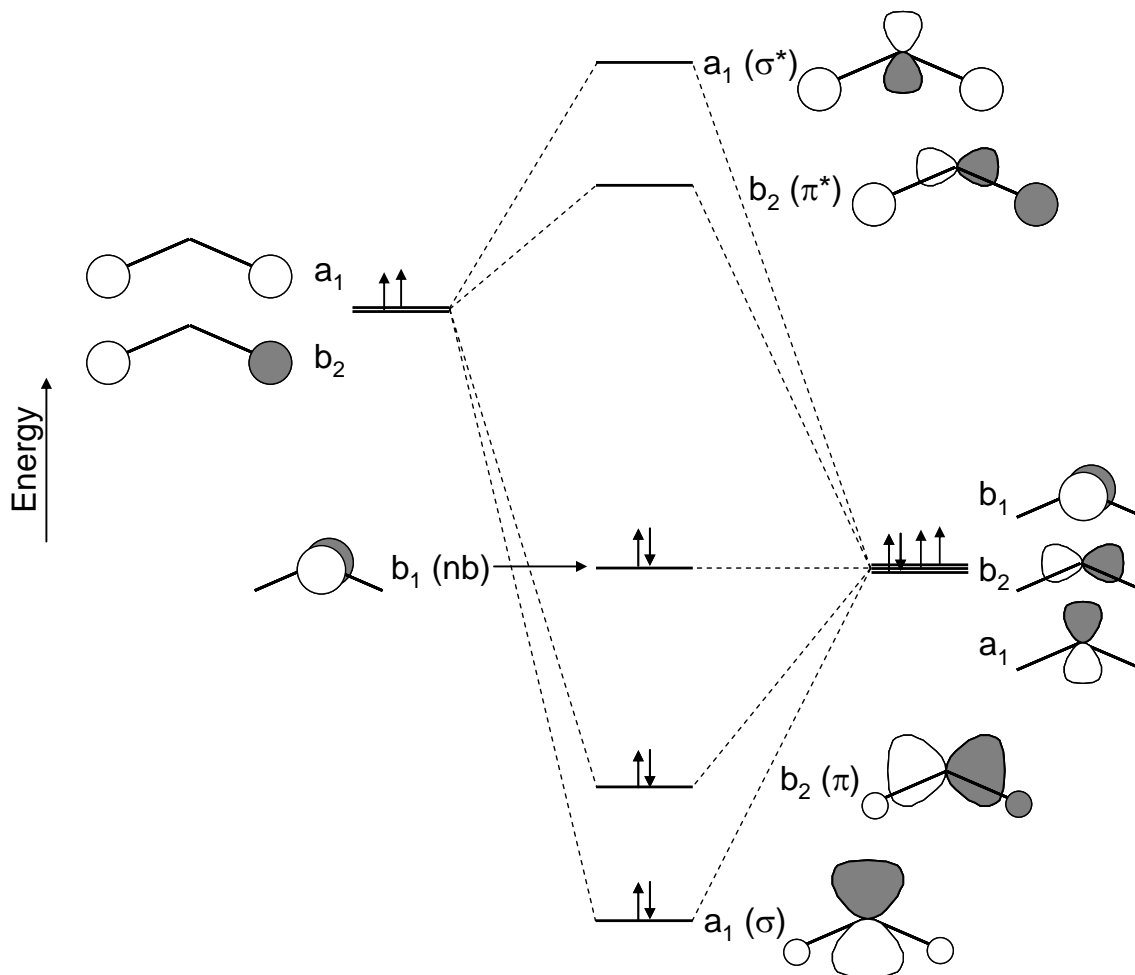


Since O is more electronegative than H, we know that the O valence orbitals must be at lower energy than the H 1s (or you could argue that since the ionization energy of O is larger than that of H the O orbitals must be more stabilized than the H 1s).

The a<sub>1</sub> SALC will overlap with the O 2p<sub>z</sub> orbital because they have the same symmetry and the b<sub>2</sub> SALC will overlap with the O 2p<sub>y</sub> orbital for the same reason. The result will be a σ bonding (and antibonding) MO with a<sub>1</sub> symmetry and a π bonding (and antibonding) MO with b<sub>2</sub> symmetry. The O 2p<sub>x</sub> will not interact with either SALC because it does not have the proper symmetry to do so.

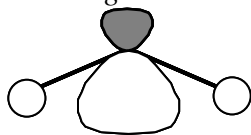
Determining whether the a<sub>1</sub> σ bonding MO is lower in energy than the b<sub>2</sub> π bonding MO (and the corresponding order for the antibonding MOs) is perhaps a little tricky. However, the O 2p<sub>z</sub> orbital is directed between the two H 1s orbitals, but there is a fair amount of electron density along the H–O interatomic vector and there is no node in the wavefunction. The overlap between the O 2p<sub>y</sub> and the H 1s is maybe not as good as in the case of the O 2p<sub>z</sub> (because it is more side-on) and there is a node in this wavefunction that affects (albeit to a small extent) the H–O. Therefore, we would place the a<sub>1</sub> σ bonding MO lower in energy than the b<sub>2</sub> π

**bonding MO (and the  $a_1 \sigma^*$  antibonding MO higher in energy than the  $b_2 \pi^*$  antibonding MO), as shown below.**



We would describe the bonding in water as consisting of two bonds, one  $\sigma$  and one  $\pi$ , both of which are dominated by the O  $2p$  atomic orbitals. There is also a nonbonding MO that is comprised solely of an O  $2p_x$  atomic orbital. The Lewis dot structure would have two bonds and two lone pairs, which VSEPR Theory would then predict as having a bent structure. In valence bond theory, we would describe the O as being  $sp^3$  hybridized with two  $\sigma$  bonds formed by the overlap of the O  $sp^3$  hybrid orbitals with the H  $1s$  orbitals, and the two lone pairs occupying two of the  $sp^3$  hybrid orbitals. Note the contrasts and similarities between the MO and valence bond approaches. Whereas valence bond theory describes the two bonds as being localized between the O and H (one  $\sigma$  bond between O and one H and one  $\sigma$  bond between O and the other H), MO theory has bonding delocalized between the three atoms and designates them  $\sigma$  and  $\pi$ . The Lewis dot structure has two lone pairs on the O, which are described in valence bond theory as occupying  $sp^3$  orbitals on the O, while in MO theory these lone pairs are the nonbonding  $b_1$  (O  $2p_x$ ) and the O  $2s$ , which is left virtually unchanged by bond formation since it is so low in energy. Note that there may be an effect on the  $a_1 \sigma$  bonding MO due to interaction with the  $a_1$  O  $2s$  orbital, which is dependent on the energy difference between these orbitals. This will lead to a destabilization of the  $a_1 \sigma$  bonding MO and a stabilization of the  $a_1$  O  $2s$  orbital. There will

also be a change in the  $a_1$   $\sigma$  bonding MO with the admixture of some O 2s character, which we



could draw qualitatively as . Although this looks like a valence bond hybrid orbital, the degree of mixing is not what is predicted by valence bond theory and is likely to be much less (dictated by the energy difference between the O 2s and the  $a_1$   $\sigma$  bonding MO).