Polyatomic molecules: H_2O

For polyatomic molecules appropriate atomic orbitals must be combined into symmetry adapted linear combinations (SALCs). We can identify two groups of atoms in H_2O. The central O atom (group 1) and the pair of H atoms (group 2).

H_2O belongs to the C_{2v} point group. We have already seen that group 1 consists of the valence orbitals of the O atom:

$$2\,H(1s) + O(2s) + O(2p_x) + O(2p_y) + O(2p_z)$$

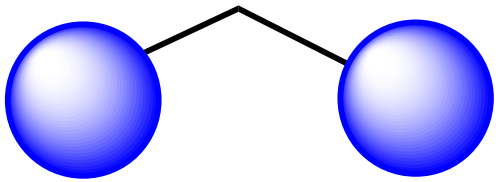
Since the oxygen is unmoved by every symmetry operation the character can be determined directly from the character table. However, the hydrogens need to be formed as SALCs first.

Reducible rep for the H atoms

To treat the H atoms we look at the set of two H atoms, each having 1s orbital. First we can consider the Reducible representation for the two 1s orbitals.

C_{2v} character table and the reducible representation for the 2H(1s) orbitals in water

C_{2v}	E	C_2	$*_v(xz)$	$*_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y
*[H(1s)]	2	0	2	0	



When we decompose this reducible representation we find:

$$\chi_{A_1} = \frac{1}{4}\big((1)(2)(1) + (1)(0)(1) + (1)(2)(1) + (1)(0)(1)\big) = 1$$

$$\chi_{A_2} = \frac{1}{4}\big((1)(2)(1) + (1)(0)(1) + (-1)(2)(1) + (1)(0)(1)\big) = 0$$

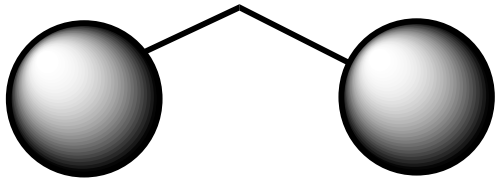
$$\chi_{B_1} = \frac{1}{4}\big((1)(2)(1) + (-1)(0)(1) + (1)(2)(1) + (-1)(0)(1)\big) = 1$$

$$\chi_{B_2} = \frac{1}{4}\big((1)(2)(1) + (-1)(0)(1) + (-1)(2)(1) + (1)(0)(1)\big) = 0$$

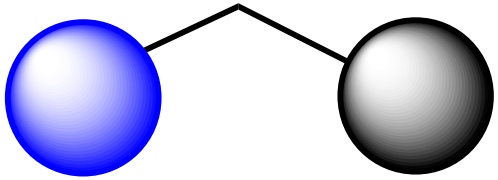
Linear combinations of H atoms

We can use a method known as projection operators to Determine what the linear combinations of H atoms Correspond to in terms of symmetry adapted atomic orbitals.

These are easily visualized in this case:



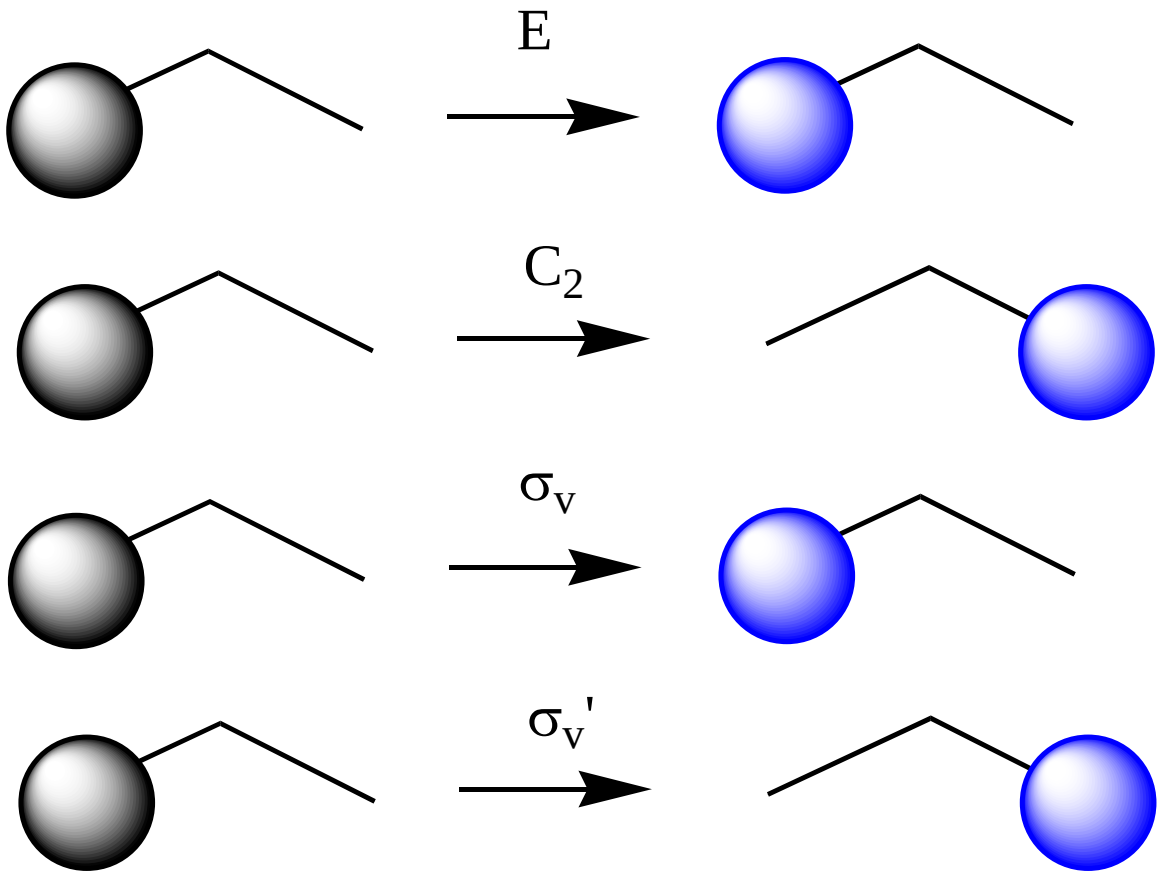
$$\chi_{A_1} = 1s_A + 1s_B$$



$$\chi_{B_1} = 1s_A - 1s_B$$

Method of Projection Operators

To use the projection operator method we choose one member of a symmetry related set of orbitals. We then apply the symmetry operations of the group to that orbital and observe how that AO is transformed into other orbitals in the molecule.



Method of Projection Operators

We can see that H_2 either remains in its location or is transformed into H_3 by the symmetry operations. Thus, we find that a table would look like

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
P	H_2	H_3	H_2	H_3
A_1	1	1	1	1
B_1	1	-1	1	-1

The row labeled P shows the projections. Finally, we apply the characters of the irreps for that set to construct MOs. We determined that there are two MOs, which transform as a_1 and b_1. We multiply the projected AOs by the characters of these irreps to find the two linear combinations.

Polyatomic molecules

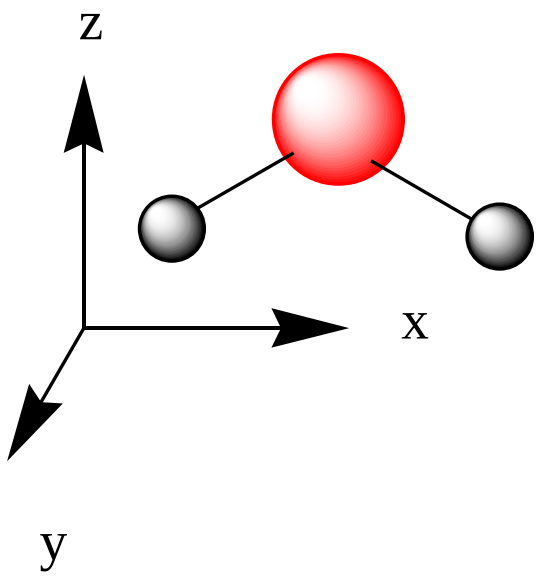
The reducible representations for hydrogen SALCs are a_1 and b_1. The oxygen orbitals (read from the character Table are:

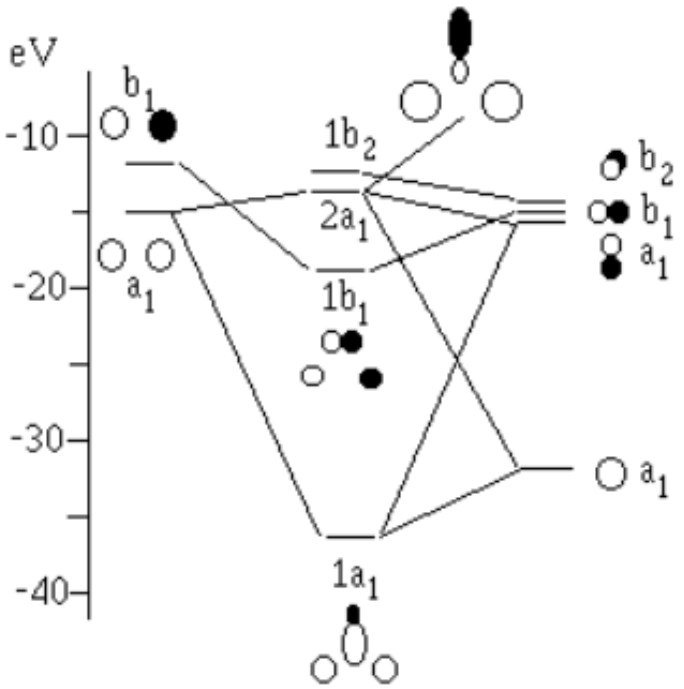
$2s = a_1$

$2p_z = a_1$

$2p_x = b_1$

$2p_y = b_2$

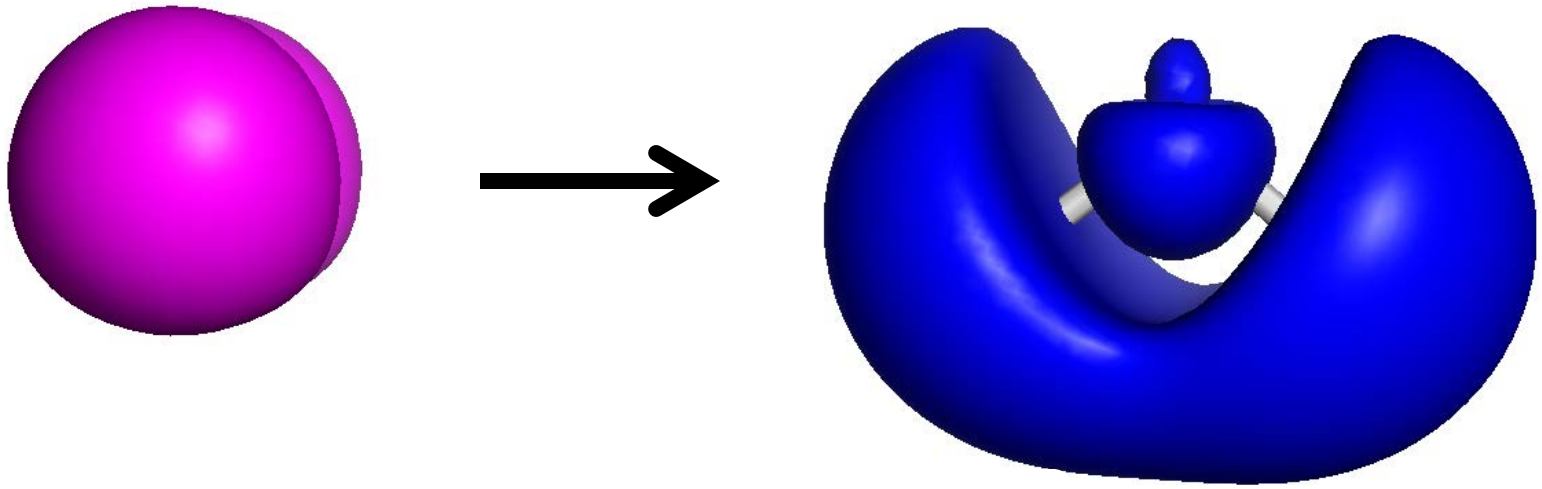




Note that the energies are obtained from a calculation. However, the forms of the orbitals can be predicted based on symmetry considerations.

HOMO to LUMO transition in H_2O

top



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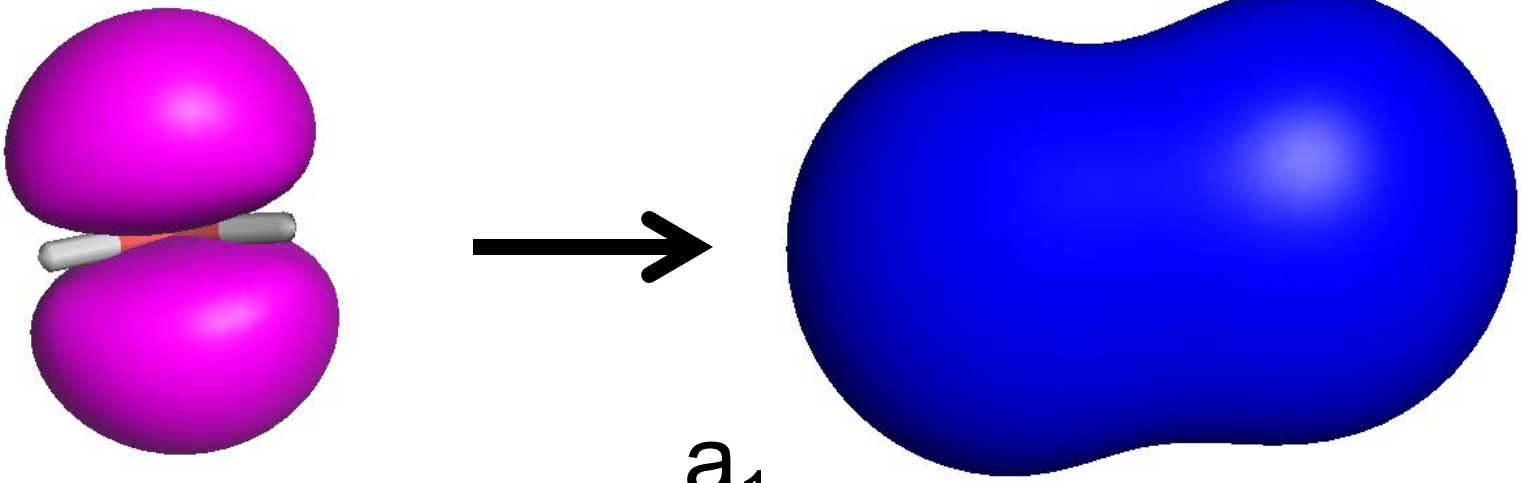

b_2

a_1

Eigenstate	Irrep	Hartrees	eV	Occupation
1 + 1	a1.1	-18.748477	-510.1	2.000
3 + 2	a1.1	-0.917545	-24.968	2.000
5 + 1	b1.1	-0.471788	-12.838	2.000
7 + 3	a1.1	-0.333240	-9.068	2.000
9 + 1	b2.1	-0.253144	-6.888	2.000
11 + 4	a1.1	0.023886	0.650	0.000
13 + 2	b1.1	0.093912	2.555	0.000
19 + 2	b2.1	0.563271	15.327	0.000
27 - 1	a2.1	0.926496	25.211	0.000