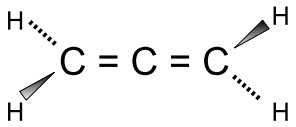
CHEM 352: Examples for chapter 4.

1. Find all the possible symmetry operations for 1,2-propadiene:



Solution:

The operations are: E, C_2, C_2', C_2'', S_4, S_4^3, σ_v, σ_v'.
The C_2 axis is along C = C = C. The C_2' and C_2'' axes are perpendicular to the C_2 axis and are locate long the plane of the paper and perpendicular to the plane.

---

2. Derive the C_{2v} multiplication table by applying two successive symmetry operations and identifying the resulting operation. Note that C_{2v} point group is Abelian.

Note that you need to construct a multiplication table not a direct product table.

Solution:

The group is Abelian, which means that the order of multiplication does not matter, which simplifies the problem. The products can be worked out as follows:

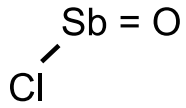
Multiplication by OE (the identity operation) always yields O as the result (where O is one of the symmetry operations in C_{2v}). Also operations such as OO give E (rotation and reflection). The only remaining operations are between C_2, $\sigma_v(xz)$ and $\sigma_v'(yz)$. The molecule is taken to reside in yz plane. Let's consider $C_2\sigma_v$ as an example. To visualize what is happening, think about NO_2 molecul and place p_x atomic orbitals on the oxygen atoms. Note that the x direction is out of the paper plane. C_2 will exchange the two oxygens and at the same time flip the p_x orbitals around. Then σ_v reflection just exchanges the oxygens again but without flipping the p_x orbitals. The

net effect was to get flip the p_x orbitals. This same effect may be obtained by σ_v' operation and therefore $C_2\sigma_v = \sigma_v'$. The same method can be used to go over all the remaineng elements in the product table.

---

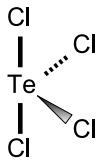
3. What are the symmetry elements and point groups for the following molecules:

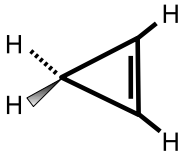
a) CH_2FCl

b) 

c) O = C = C = C = C = O

d) HI

e) $TeCl_4$: 

f) cyclopropene: 

Solution:

In a) and b) only C_s symmetry element. The point group is C_s.
In c) the symmetry elements are: C_∞ axis, ∞ number of perpendicular C_2 axes and σ_v planes and σ_h plane. The poing group is $D_{\infty h}$.
In d) the symmetry elements are: C_∞ axis and ∞ many σ_v planes. The point group is $C_{\infty v}$.
In both e) and f) the symmetry elements are: C_2 axis and two σ_v planes. The point group is C_{2v}.

---

4. What are the irreps for s, p and d atomic orbitals in D_{6h} point group?

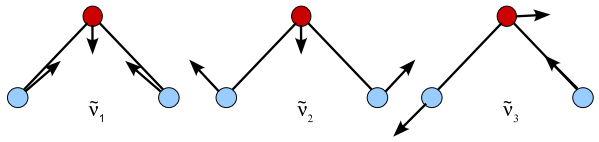
Solution:

From the character table we can see that both x and y correspond with the E_{1u} irrep. The p_x and p_y orbitals behave the same way and belong to E_{1u} as well. By using the same logic, p_z is A_{2u}. s orbitals are always spherically symmetric and hence this is A_{1g}. The Cartesian components of d orbitals are: $d_{xz}, d_{yz}, d_{x^2-y^2}, d_{xy}, d_{z^2}$. These behave spatially exactly like the spatial operatiors (subscripts). As such. we immediately identify these as: E_{1g}:

d_{xz}, d_{yz}, E_{2g}: $d_{x^2-y^2}, d_{xy}$, and A_{1g}: d_{z^2}.

---

5. The following are the normal vibration modes of water molecule:



Apply the C_{2v} symmetry operations for these modes and determine their irreducible representations (consider the directionality of the vectors shown).
Solution:

Mode 1 is unchanged under any symmetry operation in C_{2v} and hence it has A_1 symmetry. The mode would be labelled as a_1.
Mode 2 is unchanged under any symmetry operation and hence the label is a_1.
The arrows correspond demonstrate the direction of atomic motion in molecular vibration.
Mode 3 is unchanged with E and $\sigma_v'(yz)$ and the directions of the arrows get reversed (-1) with C_2 and $\sigma_v(xz)$. Thus the mode is labelled as b_2.

---

6. Consider H_2O molecule residing in yz plane (symmetry C_{2v}). Let H_1 and H_2 denote their $1s$ orbitals. What are the irreps for the following linear combinations: $S_1 = H_1 + H_2$ and $S_2 = H_1 - H_2$? Which oxygen atom valence orbitals may form molecular otabitals with S_1 and S_2?

Solution:

The orbitals S_1 and S_2 can be visualized as shown below (the first figure). From this we can see that S_1 corresponds to A_1 (all operations give 1) and S_2 to B_2 (characters 1 -1 -1 1). The symmetry labels for the orbitals are therefore a_1 and b_2, respectively. The oxygen atom orbitals are shown in the second figure below. The $2s$ O orbital is clearly A_1 (totally symmetric). According to the above picture, $2p_z$ is also A_1. p_y appears to be B_2 and p_x

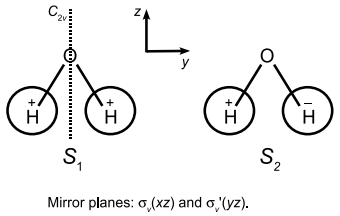


Figure 1: Visualization of S_1 and S_2 orbitals.

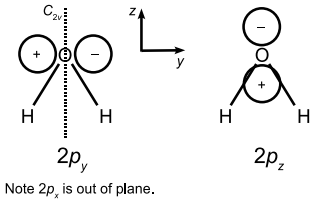


Figure 2: Visualization of oxygen atom orbitals.

B_1. To find possible non-zero overlap integral value (S), we have to find pairs that produce A_1 when multiplied. Essentially, this says that they must have the same symmetry. Thus S_1 can combine with $2s$ and $2p_z$ and S_2 with $2p_y$.

---

7. Function f_1 exhibits symmetry corresponding to irrep E_2 and function f_2 irrep A_1 in C_{6v} point group. Show that integral $\int f_1 x f_2 d\tau = 0$ (x represents multiplication by x coordinate).

Solution:

Operator x belongs to E_1 in C_{6v} (the operator column). Thus the product we need to look at is $A_1 \times E_1 \times E_2$. The product table tells us that this is equal to $B_1 + B_2 + E_1$ (a sum of three characters). Since A_1 is not present in this sum, the integral is zero.

---

8. The the ground state electronic wavefunction in H_2O has A_1 symmetry in C_{2v} point group. What the symmetries of the excited states that can absorb

liearly polarized light in a) x, b) y and c) z directions?

Solution:

The C_2 axis is along the z axis and the molecule is in the yz plane. The operator x belongs to B_1. The ground state is A_1 and by looking at the product table, we can see that the excited state must have B_1 symmetry ($B_1 \times B_1 = A_1$). For y (B_2) and z (A_1) the corresponding excited state symmetries must be B_2 and A_1, respectively.
