

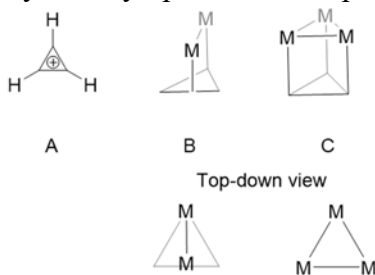
2018 Ch112 – Problem Set 2

Due: Thursday, October 25 – before class

Problem 1 (2 points)

The MO diagrams of complicated molecules can be constructed from the interactions of molecular fragments. The point groups of isolated fragments are often of higher symmetry than the actual molecule. It is useful to analyze the fragment in a lower symmetry point group that is a subgroup of the actual point group of the fragment. Consider the coordination of the cyclopropenium cation to M_2 and M_3 moieties, as shown below.

1) For molecules A and B, list the symmetry operations and point groups.



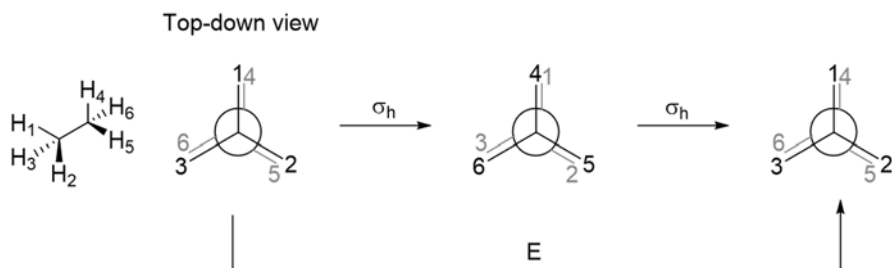
Consider the following multiplication table for C_{3v} , filled in according to the products of operations:

$$\text{Operation}_{\text{cell}} = \text{Operation}_{\text{column}} \times \text{Operation}_{\text{row}}$$

You will find that all possible products of operations (or squares of operations) are also operations that are members of this group (C_{3v}). Note that C_{3v} is NOT an Abelian group (multiplications of operations of C_{3v} are NOT necessarily commutative).

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E

2) We can obtain new characters corresponding to D_{3h} by adding additional operations to the C_{3v} point group, a subgroup of D_{3h} . Expand the multiplication table to the partial table for D_{3h} . Use ethane (eclipsed) to visualize operations as shown in the example below.



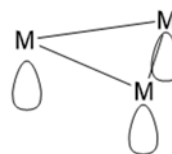
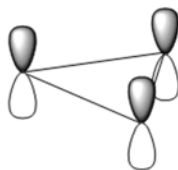
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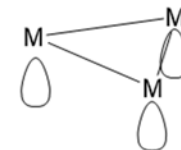
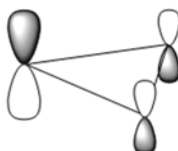
D_{3h}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''	σ_h	S_3	C_2
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''			
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v			
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'			
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3			
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2			
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E			
σ_h									
S_3									
C_2									

3) Analyze the interaction between cyclopropenium and the M_2 and M_3 fragments. For each metal, consider only a single orbital of sigma symmetry as basis set for interactions. For cyclopropenium cation only consider the HOMO and LUMO. Draw the HOMO and LUMO of cyclopropenium cation, and draw the SALCs of M_2 and M_3 fragments that have the correct symmetry to make bonds with the cyclopropenium cation HOMO and LUMO, respectively. Indicate if these SALCs are σ acidic/basic or π acidic/basic.

Binding with HOMO:



Binding with LUMO:

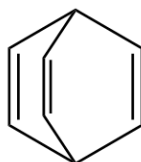


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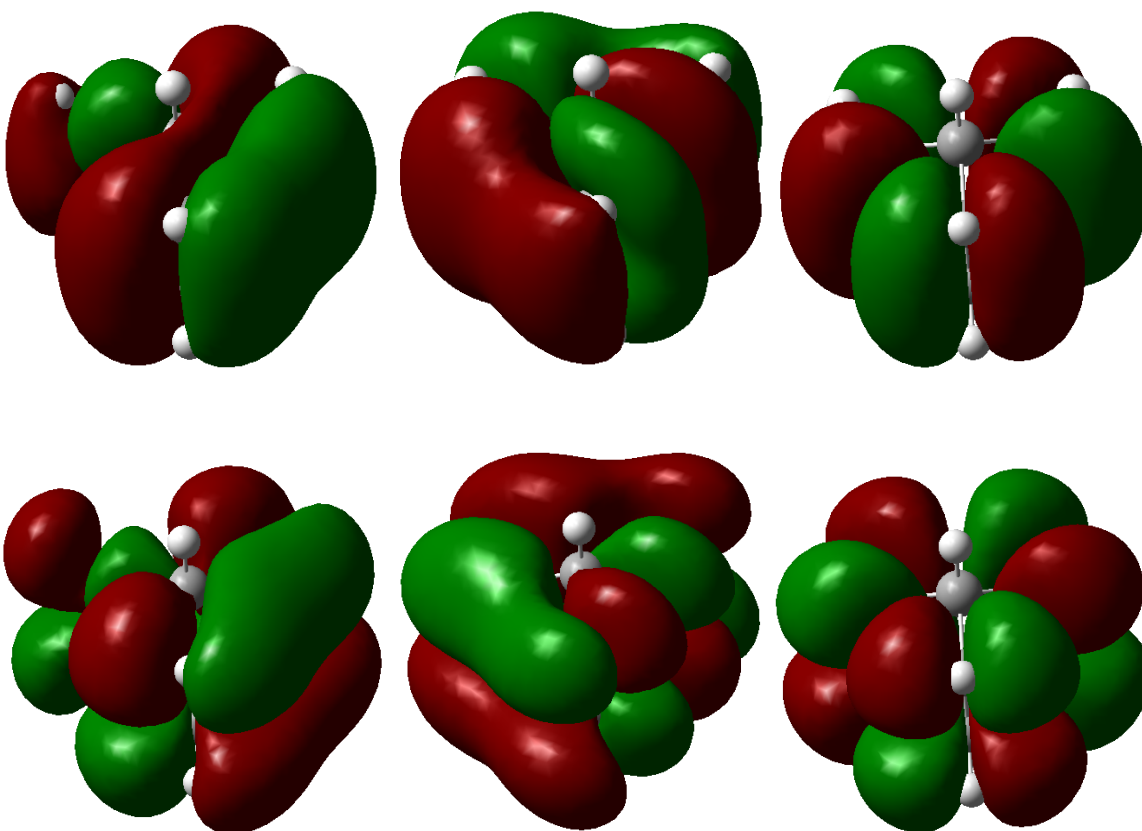
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Problem 2 (3 points)

Shown below is the structure of bicyclo[2.2.2]octa-2,5,7-triene, otherwise known as *barrelene*.



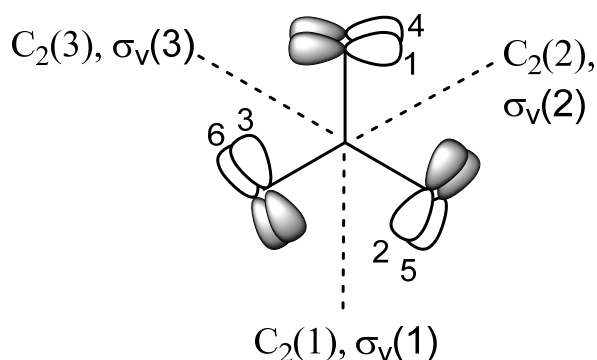
- Determine the point group of barrelene.
- Using the six p orbitals on each of the sp^2 hybridized carbon atoms as the basis set, generate a reducible representation Γ_{6p} .
- Express Γ_{6p} as a sum of irreducible representations, either by inspection or mathematically using the formula provided in class.
- Assign Mulliken symbols for each of the six calculated π orbitals shown below.



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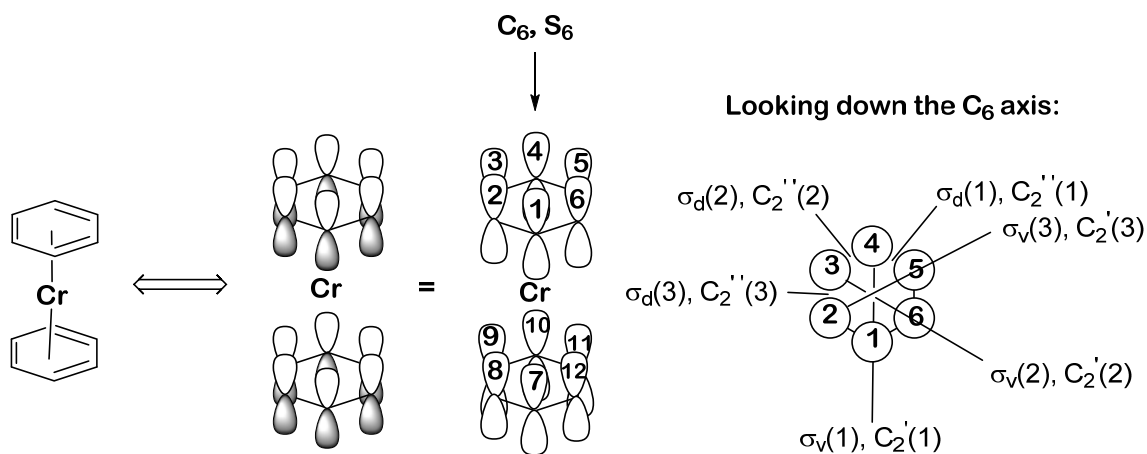
- e. Using the numbering scheme shown below, use the projection operator to obtain the coefficients of each carbon 2p for each of the six SALC's



- f. Draw the MO diagram for this π -system. Populate the diagram with electrons, and assign Mulliken symbols to each MO.

Problem 3 (5 points)

Bisbenzene chromium is an organometallic compound, shown below in the D_{6h} point group. The bonding in this molecule involves the interaction between the chromium orbitals and the π -system of the two benzene ligands. In this problem, only consider the π -system of the aromatic ligands.



- a. Use the twelve p orbitals on each of the benzene carbon atoms as the basis set to generate a reducible representation Γ_{12p} .

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b. Express Γ_{12p} as a sum of irreducible representations, determined either by inspection or mathematically using the formula provided in class.

c. By applying the projection operator to the p orbital labelled “1” in the diagram above, the SALC for one of the MOs of E_{2g} symmetry can be obtained using the following tables (*fill in the missing operations in the two tables*):

operation	E	C ₆		C ₃		C ₂	C' ₂ (1)	C' ₂ (2)	C' ₂ (3)	C'' ₂ (1)	C'' ₂ (2)	C'' ₂ (3)
on P1:	P1	P2	P6	P3	P5	P4	-P7	-P11	-P9	-P8	-P12	-P10
X _{E2g}	2	-1	-1	-1	-1	2	0	0	0	0	0	0

operation	i	S ₃		S ₆		σ _h	σ _d (1)	σ _d (2)	σ _d (3)	σ _v (1)	σ _v (2)	σ _v (3)
on P2:	-P10	-P9	-P11	-P8	-P12	-P7	P2	P6	P4	P1	P5	P3
X _{E2g}	2	-1	-1	-1	-1	2	0	0	0	0	0	0

Taking the products of these characters and the p-orbitals from the basis set of 12 p-orbitals, the following symmetry-adapted linear combination can be achieved:

$$\begin{aligned}\Psi_{E_{2g}1} &= 2P1 - P2 - P6 - P3 - P5 + 2P4 - 2P10 + P9 + P11 + P8 + P12 - 2P7 \\ &= 2P1 - P2 - P3 + 2P4 - P5 - P6 - 2P7 + P8 + P9 - 2P10 + P11 + P12\end{aligned}$$

Normalize this result to give the final wavefunction:

$$\Psi_{E_{2g}1} =$$

d. Draw a picture of this E_{2g} MO:

e. Repeat this process (applying projection operator to P2) to find a second MO of E_{2g} symmetry:

p-orbital												
X _{E2g}												

p-orbital												
X _{E2g}												

$$\Psi_t =$$

Is this new “test” wavefunction orthogonal to the one we obtained in part (c)? Show mathematically.

If the wavefunctions are not orthogonal, then find a function $\Psi_{E_{2g}2}$ orthogonal to $\Psi_{E_{2g}1}$ by taking a linear combination of $\Psi_{E_{2g}1}$ and $\Psi_{E_{2g}t}$ according to:

$$\Psi_{E_{2g}2} = c_1\Psi_{E_{2g}1} + c_2\Psi_{E_{2g}t}$$

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If needed, find c_1 and c_2 such that $\Psi_{E_{2g}2}$ is orthogonal to $\Psi_{E_{2g}1}$ and provide the normalized wavefunction, $\Psi_{E_{2g}2}$.

f. Draw the molecular orbital defined by Ψ_2 :

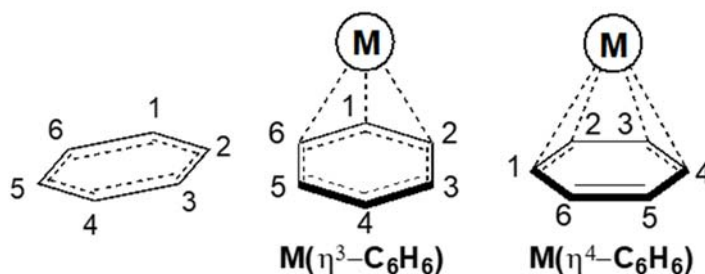
g. *By inspection*, sketch the MOs and determine the normalized wavefunctions for the rest of the bisbenzene π -system. Hint: Utilize irreducible representations and the symmetry of the functions listed on the right side of the D_{6h} character table to predict the form of the SALCs, where possible, and use the coefficients determined in class for the π -system of benzene to help in finding the expressions of the wavefunctions for the π -system of bisbenzene.

h. What is the oxidation state and d electron count of chromium in this complex? What is the valence electron count?

i. Looking at the character table for D_{6h} , list the symmetries of the metal d, s, and p orbitals.

j. Using your answers from parts g-i, sketch a qualitative MO diagram of bisbenzene chromium and populate with electrons. Label each orbital with the appropriate Mulliken symbol and indicate the type of bonding interaction (i.e. σ , π). Determine whether each MO is bonding, non-bonding, or anti-bonding.

k. Hapticity (η) is defined as the number of contiguous atoms in a ligand interacting with the metal center. Following the numbering scheme provided and assuming that the metal based orbitals fall between the energy of the HOMO and the LUMO of benzene, answer the following questions:



1) Consider the metal ion interacting with benzene in a η^3 fashion. The metal ion has two orbitals available: one σ -acidic and one π -basic. Sketch only the most significant interactions between benzene and the metal ion. Sketch a qualitative MO diagram starting from the two metal orbitals and six benzene frontier orbitals.

2) Consider the metal ion interacting with benzene in a η^4 fashion. The metal ion has three orbitals available: one σ -acidic, one π -basic, and one π -acidic (the two π orbitals are orthogonal to each other). Sketch only the most significant interactions between benzene and the metal ion. Sketch a qualitative MO diagram starting from the three metal orbitals and six benzene frontier orbitals.