2016 Ch112 − Problem Set 2
Due: Thursday, October 20 – before class

Problem 1 (1 point)

1) The character table for the C_{2v} point group is given below in the bolded section of the table. We will consider the D_{2d} character table in its entirety by adding an additional operation (C_2') to the C_{2v} point group and doing operation multiplication to find additional operations in the D_{2d} group.

$\text{operation}_{\text{product}} = \text{operation}_{\text{column}} \times \text{operation}_{\text{row}}$

Recall that you will find that all possible products of operations (or squares of operations) are also operations that are members of this group (C_{2v}); this is part of the definition of a group. In the table below, fill in the row and column headed by the operation C_2' with the product of operations. Consider using a molecule of appropriate symmetry (for example, allene) to help visualize the symmetry transformations taking place.

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	C_2'
E	E	C_2	σ_v	$\sigma_{v'}$	
C_2	C_2	E	$\sigma_{v'}$	σ_v	
σ_v	σ_v	$\sigma_{v'}$	E	C_2	
$\sigma_{v'}$	$\sigma_{v'}$	σ_v	C_2	E	
C_2'					

2) Fill in the multiplication table below for operations of point group D_{2d}. The operations found in the first table are given below, although the mirror planes are denoted with σ_d and σ_d' in this higher symmetry group. Note that point group D_{2d} is not Abelian (that is, multiplication of operations is not necessarily commutative).

D_{2d}	E			C_2	C_2'		σ_d	σ_d'
E								
C_2								
C_2'								
σ_d								
σ_d'								

2016 Ch112 − Problem Set 2
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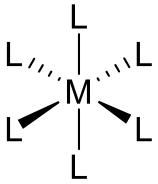
Problem 2 (3 points)

a) Consider an octahedral metal complex ML_6. Show an MO diagram taking into account σ interactions only (including the derivation is not necessary). For basis set, consider an s orbital for each L, and the s, p, and d orbitals for M. Label with Mulliken symbols. Fill with electrons assuming that the d-count is 6. Clearly label the d orbitals with their parentage (d_{z2}, d_{xy}, etc) and character (bonding, non-bonding, antibonding with respect to the M-L interaction).



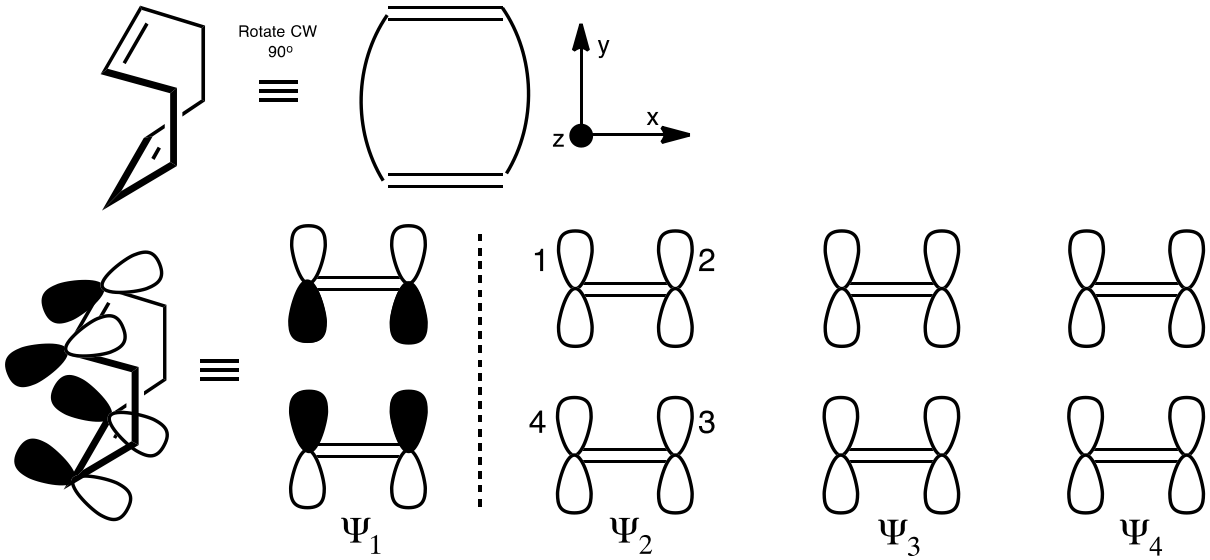
b) Now consider the substitution of two L ligands on the metal complex for 1,5-cyclooctadiene (COD) as shown in the following reaction scheme. First derive the MO diagram of the isolated fragment COD.

i. What is the point group of COD?

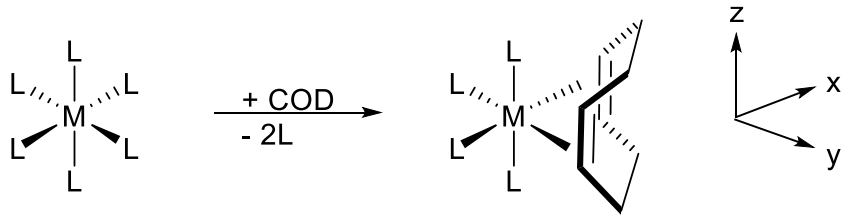
ii. Using the four p orbitals on each of the sp^2 hybridized carbon atoms as the basis set, generate a reducible representation Γ_{4p}. Express Γ_{4p} as a sum of irreducible representations, derived either by inspection or mathematically.

iii. Find the normalized wavefunctions for the four SALCs, using the projection operator to determine its coefficients. Use the following diagrams of the p-orbitals to represent the SALCs graphically and provide normalized wavefunctions for each. An example is shown below to highlight the selected view. Assign Mulliken symbols to each SALC.

iv. The SALCs derived above correspond to the MOs for the π system of COD. Assume that, because the double bonds are not conjugated, there is only a small energy difference compared to isolated double bond interactions. Sketch the MO diagram, populate with electrons and include Mulliken symbols. Indicate the character of the MOs (bonding, antibonding) with respect to the interaction between adjacent carbon atoms.

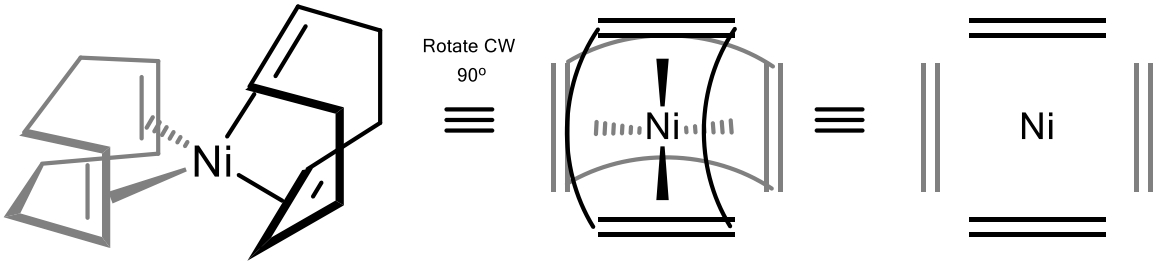


c) Assuming that L and each olefin of COD have similar σ-donating properties, develop a simplified MO diagram of the $ML_4(COD)$ complex. Begin with the orbitals of d-parentage from the diagram you derived in part *a* and interact this set with the appropriate COD SALCs. Assume that the energy of the metal-based d-orbitals is between the π-bonding and the π-antibonding orbitals of COD. Label the parentage of the d-orbitals, considering the given coordinate system, fill with electrons (keeping a d-electron count of 6), and indicate the character of the MOs (σ, π and bonding, non-bonding, antibonding) with respect to M-olefin interaction.



Problem 3 (4 points)

Nickel(0) bis(cyclooctadiene), $Ni(COD)_2$, has a pseudo-tetrahedral coordination environment around nickel:



1) Give the oxidation state, d-count, and electron count for $Ni(COD)_2$.

2) Approximate $Ni(COD)_2$,as Td NiL_4. Show an MO diagram taking into account σ interactions only (including the derivation is not necessary). For a basis set, consider an s orbital for each L, and the s, p, and d orbitals for M. Label with Mulliken symbols. Fill with electrons assuming that the d-count is 10. Clearly label the d orbitals with their parentage (d_{z2}, d_{xy}, etc) and character (bonding, non-bonding, antibonding with respect to the M-L interaction).

2016 Ch112 – Problem Set 2
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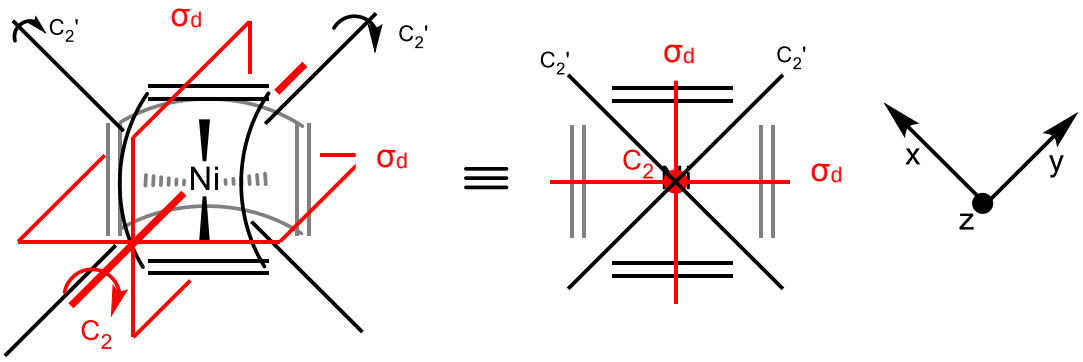
Now consider $Ni(COD)_2$ in the D_{2d} point group:



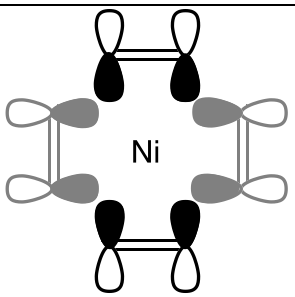
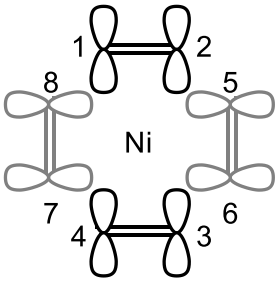
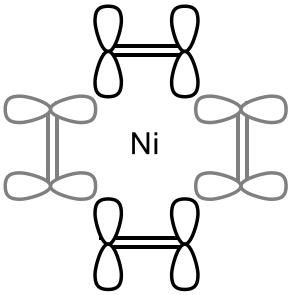
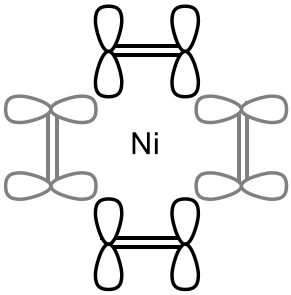
Note the new coordinate system, where the z-axis remains perpendicular to the page, and the x- and y-axes contain the C_2' axes that are perpendicular to the principle rotation axis.

3) Using the given coordinate system and the D_{2d} character table at http://symmetry.jacobs-university.de/cgi-bin/group.cgi?group=702&option=4, list the irreducible representations for the Ni 4p, 4s, and 3d orbitals. Check the selection of the coordinate system with the transformations of x^2-y^2 (you don't have to show any work).

4) The SALCs for the p orbitals of the two COD moieties in $Ni(COD)_2$ can be determined by following the procedure below:

a) What is the reducible representation for the 8 p-orbitals of COD in $Ni(COD)_2$? What irreducible representations is it composed of?

b) Fill in the following table by starting from the SALCs constructed in Problem 2 for COD. Provide in phase and out of phase combinations of SALCs of same symmetry from the two COD ligands (Ψ_1 and Ψ_1', respectively). Assign Mulliken symbols for the resulting SALCs in D_{2d}.

 $\Psi_1 + \Psi_1$'	 $\Psi_1 - \Psi_1$'	 $\Psi_2 + \Psi_2$'	 $\Psi_2 - \Psi_2$'
D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :

2016 Ch112 − Problem Set 2
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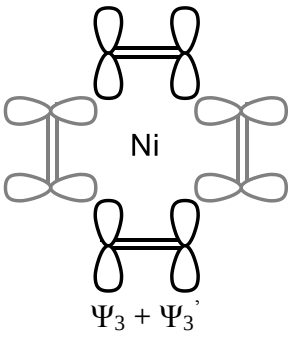
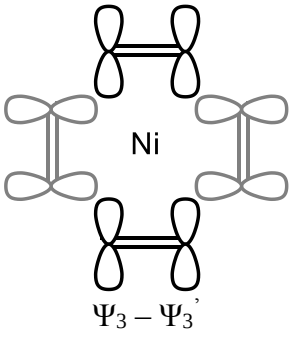
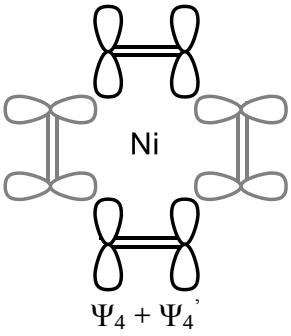
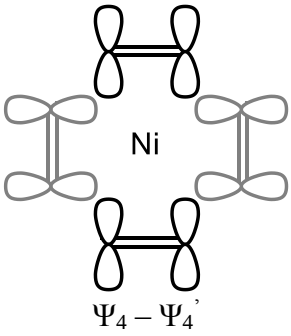
 $\Psi_3 + \Psi_3'$	 $\Psi_3 - \Psi_3'$	 $\Psi_4 + \Psi_4'$	 $\Psi_4 - \Psi_4'$
D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :	D_{2d} Mulliken Symbol :

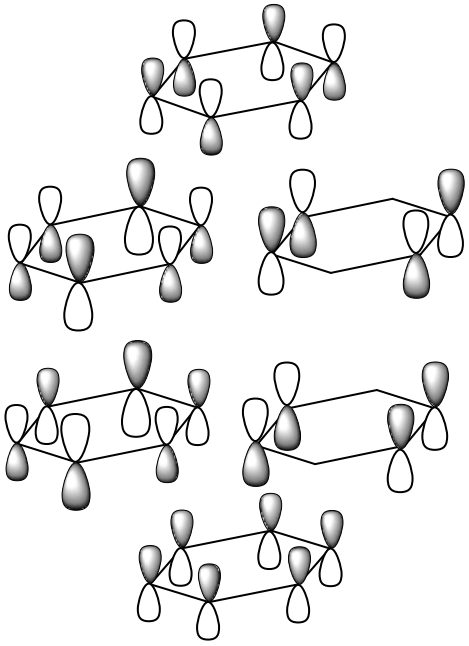
5) Provide normalized wavefunctions for all SALCs. Show that $\Psi_2 + \Psi_2'$ and $\Psi_2 - \Psi_2'$ are orthogonal. Show that atomic orbitals p1 and p5 contribute equally to the set of $\Psi_2 + \Psi_2'$ and $\Psi_2 - \Psi_2'$. Verify that atomic orbital p1 is used fully in the derived SALCs.

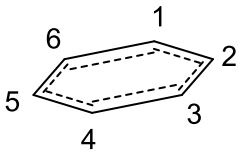
6) Draw the MO diagram of $Ni(COD)_2$ using the metal atomic orbitals and SALCs analyzed above. Assume that the SALCs displaying bonding olefin character (adjacent carbons) are lower in energy than the d orbitals and the ones displaying antibonding olefin character are higher in energy than the d orbitals. Clearly label the parentage of the MOs based on d-orbitals. Include Mulliken labels, fill with electrons, and indicate the character of the MOs (σ, π and bonding, non-bonding, antibonding) with respect to M-olefin interaction. Label the HOMO and LUMO.

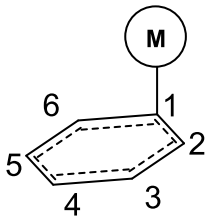
Problem 5 (2 points)

Compounds displaying interactions of metal centers with the π-system of benzene are common in coordination chemistry, including as intermediates for CH activation and cross coupling reactions. Shown below is the molecular orbital depiction of the π-system of benzene, derived in class. 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:

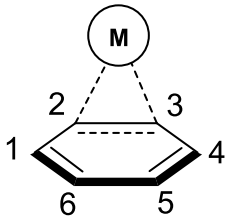
Problem 5, cont.



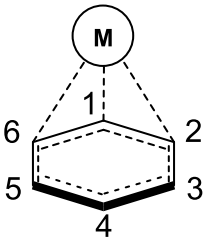




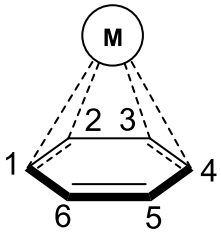
M(η^1–C$_6$H$_6$)



M(η^2–C$_6$H$_6$)



M(η^3–C$_6$H$_6$)



M(η^4–C$_6$H$_6$)

1. Consider the metal ion interacting with benzene in a η^1 fashion. The metal ion has one orbital available along the axis of interaction: σ-acidic (empty). Sketch only the most significant interaction between benzene and the metal ion. Sketch a qualitative MO diagram starting from the one metal orbital and six benzene frontier orbitals.

2. Consider the metal ion interacting with benzene in a η^2 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.

3. 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.

4. 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.