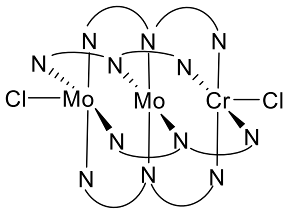
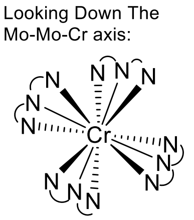
2015 Ch112 – problem set 5
Due: Thursday, Nov. 19 – before class
Remember to turn in your project abstract with this problem set

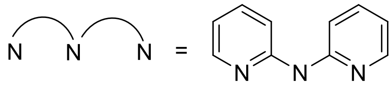
Problem 1 (2 points)

1. Consider the MoMoCr heterotrimetallic complex shown below (Berry, et. al. *Inorganica Chimica Acta* **2015**, p. 241). Metal-metal bonds are not drawn. The ligand framework distorts this structure so that it is in the C_4 point group, as seen by looking down the CrMoMo axis. For this problem assume C_{4v} symmetry.

a. Assign an average oxidation state for the metal centers and total number of d-electrons in this molecule:







b. Draw a qualitative MO diagram for the Mo-Mo interaction in the C_{4v} point group, using the ten Mo d-based orbitals as your basis set. Ignore Cr for this part. The z axis is along the M-M vector.
i. Assign Mulliken symbols
ii. Label each orbital with the type of interaction (nb, σ, σ^*, etc)
iii. Fill in the diagram with electrons assuming the average oxidation state as above. Predict the spin state of this fragment.
iv. Determine the Mo-Mo bond order

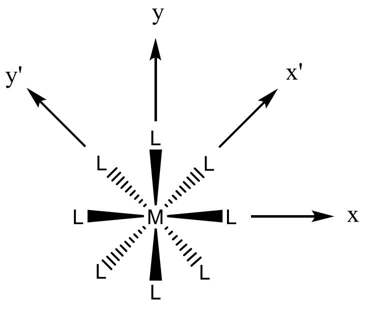
c. Starting from your answer to part b, draw the qualitative MO diagram for the Mo-Mo-Cr interaction. Consider whether atomic orbitals/molecular orbitals will mix significantly based *not only* on their symmetry, but also spatial overlap. Assume that the Mo & Cr based atomic orbitals are approximately equal in energy. Note that the crystallographic Mo-Mo bond distance is 2.098 Å and the Mo-Cr bond distance is 2.689 Å.
i. Assign Mulliken symbols
ii. Label each orbital with the type of interaction (nb, σ, σ^*, etc)
iii. Fill in the diagram with electrons
iv. Predict the Mo-Cr and Mo-Mo bond orders.

d. Draw the Mo-Mo-Cr molecular orbitals that correspond to the interactions between the three metals that have σ and π symmetry with respect to the z axis. Comment on their bonding / non-bonding / antibonding character.

e. Magnetic susceptibility experiments on the Mo-Mo-Cr trimetallic are consistent with a quintet ground state ($S = 2$). Rationalize the experimental result and discuss in the context of potential lower spin electronic configurations.

f. How do you expect the MO diagram to change for an analogous Mo-Mo-Mo complex of D_{4h} symmetry? Predict the bond orders of the two Mo-Mo interactions.

Problem 2 (3 points)



(view along the M-M vector)

In class, the electronic structure of bimetallic complexes of the form [$L_4M{-}ML_4$] in D_{4h} symmetry was analyzed. Consider here the staggered conformer. The z axis is perpendicular to the plane of the page. Using the coordinate system as given above (x,y for the metal in the front and x',y' for the metal in the back), answer the following questions:

1. What is the point group of [$L_4M{-}ML_4$]?

2. Considering σ interactions *only*, provide a qualitative d orbital splitting diagram for the square planar [ML_4] fragment. Label each orbital with its d orbital parentage. Label each orbital with the type of M−L interaction (nb, σ, σ*)

3. For the basis set consisting of the $d_{x2\text{-}y2}$, d_{xy}, $d_{x2\text{-}y2}'$, d_{xy}' orbitals determine which ones are related by symmetry and express them as a sum of irreducible representations. Provide the normalized wavefunction for each SALC. Show your work.

4. For the basis set consisting of the d_{xz}, d_{yz}, d_{xz}', d_{yz}' orbitals determine which ones are related by symmetry and express them as a sum of irreducible representations. Provide the normalized wavefunction for each SALC. Show your work.

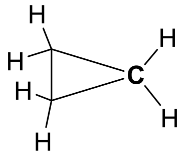
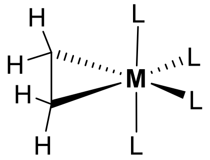
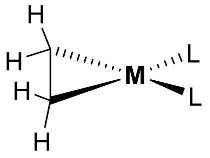
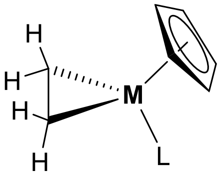
5. Starting from the d-orbital splitting diagram of the two [ML_4] fragments from part 2, sketch a qualitative molecular orbital diagram for [$L_4M{-}ML_4$]. Label each molecular orbital with the type of M−M interaction (σ, σ* etc.) and the Mulliken symbol. Draw the δ bonding interactions.

6. Assume that the donors L correspond to monoanionic L_2 chelating ligands and M = Mo to generate a fragment related to the complex analyzed in problem 1 part b, but of different symmetry. What is the Mo−Mo bond order under the symmetry of Problem 2? What is the spin state? Discuss the difference in bond order between the Mo_2 compounds of different symmetry, and provide an example of an organic molecule that undergoes a change in bond order upon rotation around a C-C bond.

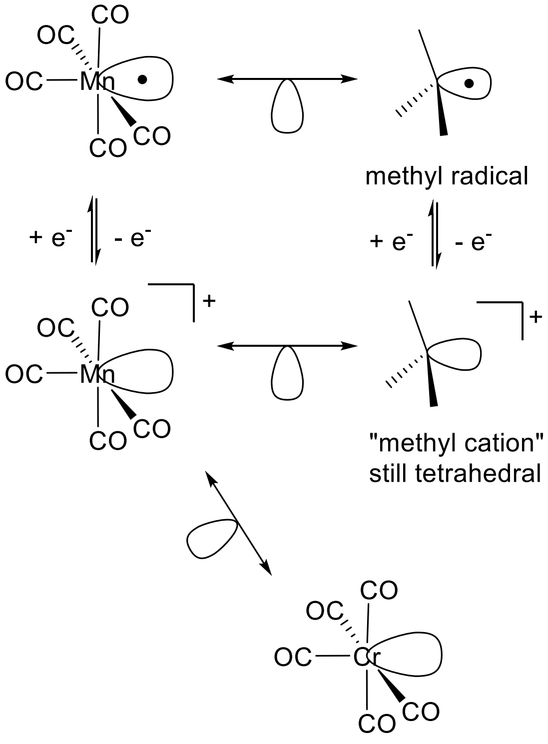
2015 Ch112 – problem set 5
Due: Thursday, Nov. 19 – before class
Remember to turn in your project abstract with this problem set

Problem 3 (2 points)

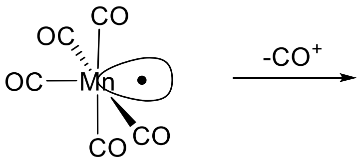
1. In class, the isolobal analogy was presented as a way to predict the stability and bonding of hypothetical organometallic compounds. Roald Hoffman describes it as a "bridge between organic and inorganic chemistry" (*Angew. Chem. Int. Ed.*, **1982**, *21*, p. 711). Using the isolobal analogy, several different metallacyclopropane fragments can be envisioned. For the neutral, closed shell structures below, fill in the table, and assign the identity of the first-row transition metal:

				
geometry	tetrahedral			
e^{-}s required for closed shell	8			
e^{-}s required from central atom	4			
identity of atom	Carbon			

2. To the right, it is shown that $Mn(CO)_5$ is isolobal with methyl radical, and $[Mn(CO)_5]^+$ is isolobal with methyl cation. Note that in describing these fragments, there is no need to consider the most stable geometry, as they are not isolated as species. You simply need to keep the geometry the same from fragment to fragment.



Consider the reaction shown below. A Mn-C bond of $Mn(CO)_5$ (*cis* to the open site) is homolyzed, releasing CO^+. What is the resultant Mn fragment? What first-row metal can you swap in for Mn to make this an isoelectronic neutral compound?



2015 Ch112 – problem set 5
Due: Thursday, Nov. 19 – before class
Remember to turn in your project abstract with this problem set

3. To extend the analogy, provide the identity of four neutral $M(PR_3)_x$ fragments (x = 4, 5, or 6) that are each isolobal to the following organic fragments. Provide the identity of the transition metal, M.

a. methane b. methyl radical c. methylene d. methyl anion

4. For each of the four metal fragments drawn in part 3, use the isolobal analogy to predict if each of them might react with an incoming carbon dioxide molecule to generate a product with the CO_2 fragment in bent geometry, and if so, draw the structure of the product of that reaction.

Problem 4 (3 points)

Part A

In class, we considered a free ion with the $1s^2 2s^2 2p^2$ electronic configuration. Consider now the case in which p orbitals with different principal quantum numbers are populated with one electron each, as in $1s^2 2s^2 2p^1 3p^1$, abbreviated as $p_a{}^1 p_b{}^1$.

1. Determine the total number of possible microstates for the $p_a{}^1 p_b{}^1$ configuration.
2. Determine the ground state term using the shortcut presented in class.
3. Prepare a microstate table and populate with all possible microstates. Example notation: $(1_a{}^+, 1_b{}^+)$
4. Reduce the microstate table for the p^1p^1 configuration to its component free-ion terms. Include the terms resulting from spin-orbit coupling. Order all terms based on energy strictly following Hund's rules.

Part B

Consider a free ion with a d^3 electronic configuration.

1. By inspection, obtain the term symbol (^{2S+1}L) for the ground state.
2. For this ground state, obtain all possible *J* values and order them from lowest to highest in energy.
3. The first excited state for the d^3 ion is the ^4P state. How many microstates does the ^4P state contain?
4. Splitting of terms and orbitals in a chemical environment

2015 Ch112 – problem set 5
Due: Thursday, Nov. 19 – before class
Remember to turn in your project abstract with this problem set

Consider an octahedral ligand field on a set of atomic wave functions. The full symmetry of the octahedron is O_h but we can work with the rotational subgroup O. An atomic orbital can be represented as follows (radial, angular (θ, φ), and spin wavefunctions):

$$\Psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi) \cdot \psi_s$$

We can ignore ψ_s assuming negligible spin-orbit coupling. The radial function R has no directionality, so it can also be ignored. The angular function Θ is invariant with respect to rotation in the z axis (principal rotation axis), so it can be ignored as well. Working only with Φ, we show without derivation that the character of the reducible representation under C_α for a basis set in which the orbital angular momentum is l is given by:

$$\chi(\alpha) = \frac{\sin\,[\left(l + \frac{1}{2}\right)\alpha]}{\sin\,(\alpha/2)}$$

For example, for the set of *f* orbitals ($l = 3$) :

$$\chi(C_3) = \frac{\sin\,[\left(3 + \frac{1}{2}\right)\left(\frac{2\pi}{3}\right)]}{\sin\,(\pi/3)} = \frac{\sin\,(7\pi/3)}{\sin\,(\pi/3)} = 1$$

In the limit where $\alpha = 0$, $\chi(E) = 2l+1$.

These characters belong to irreducible representations of the spherical point group of atoms (K). The table below allows conversion to the lower symmetry point group, O.

a) By applying the formula, complete the table below.

	E	6 C_4	3 C_2 (= C_4^2)	8 C_3	6 C_2'
S ($l = 0$)	1				1
P ($l = 1$)	3				−1
D ($l = 2$)	5				1
F ($l = 3$)	7			1	−1
G ($l = 4$)	9				1
H ($l = 5$)	11				−1
I ($l = 6$)	13				1

b) Each row is a reducible representation in the O point group. Represent each row as a sum of irreducible representations.