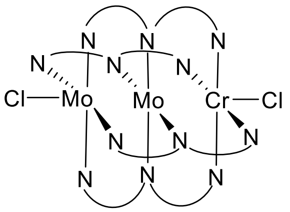
2016 Ch112 – Problem set 4
Due: Thursday, Nov. 10 – before class

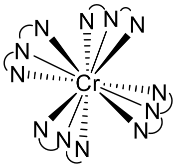
Problem 1 (2 points)

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:

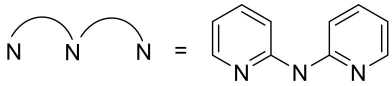


Looking Down The Mo-Mo-Cr axis:

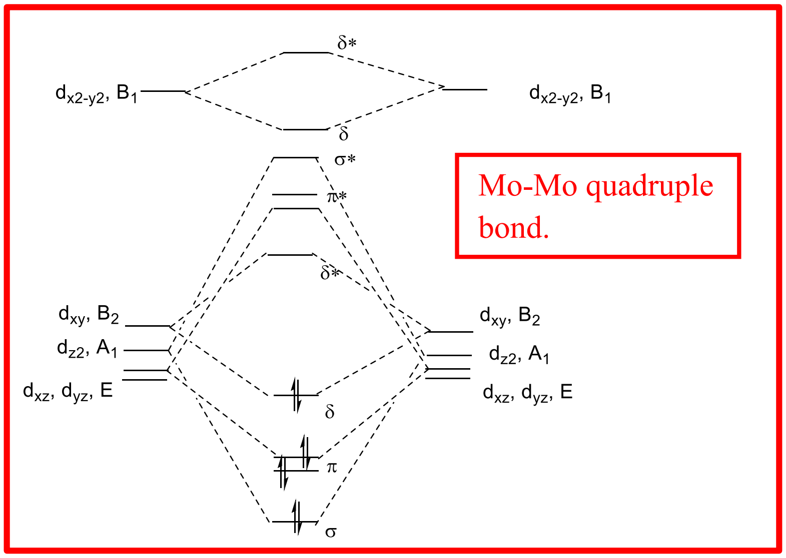


Mo^{2+}, Mo^{2+}, Cr^{2+}

12 electrons



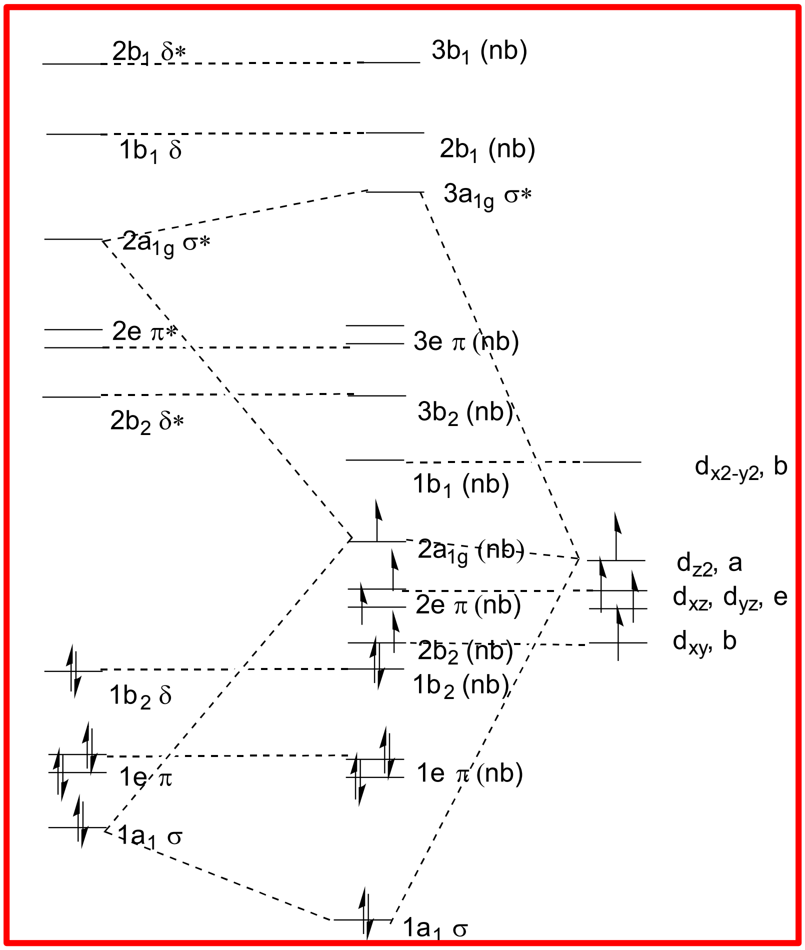
b. Draw a qualitative MO diagram for the Mo-Mo interaction in the C_{4v} point group, using the ten Mo d-based orbitals as your basis set. Ignore Cr for this part. The z axis is along the M-M vector.
i. Assign Mulliken symbols
ii. Label each orbital with the type of interaction (nb, σ, σ*, etc)
iii. 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



Mo-Mo quadruple bond.

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.

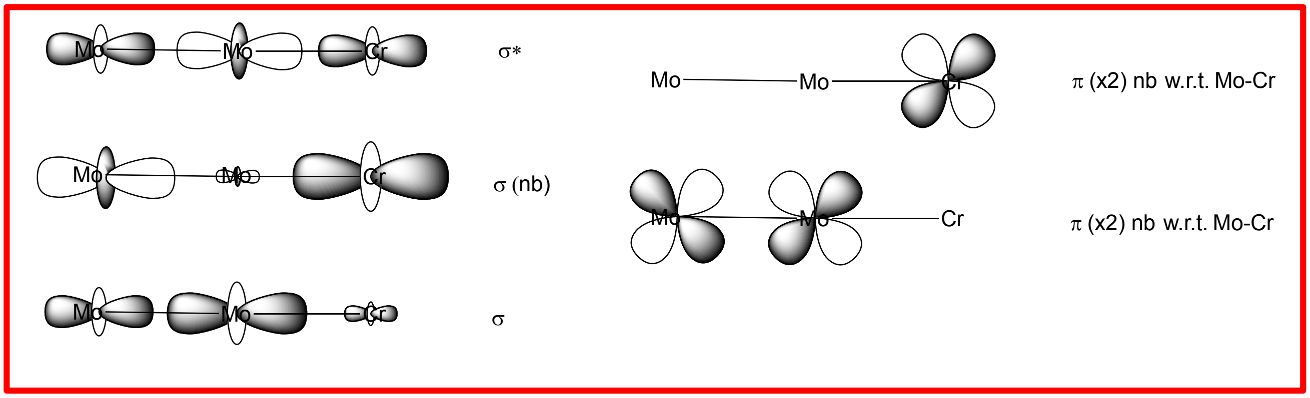


Mo-Mo: 3.5

Cr-Mo: 0.5

The labels in the center reflect the character of the interactions between Mo and Cr. The very long Cr-Mo distance compared to Mo-Mo indicate a much weaker interaction with the first row transition metal. Computationally, the bond Mo-Mo order is similar to the one observed in Mo_2 compounds (quadruple), although the Mo-Cr interaction is non-zero.

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.

The MO diagram drawn above is consistent with this picture, in which there are four unpaired electrons. Cr is effectively an isolated monometallic center, except for the d_{z^2} σ-interaction. These non-bonding orbitals are all close enough in energy for the electrons to overcome spin-pairing energy. Stronger field ligands on Cr or a stronger interaction with the Mo center could lead to a lower spin complex.

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.

The overall M-M bond order of the compound will be the same, assuming that the terminal Mo centers lead to equivalent interactions with the central one. The four M-M bonds will be shared equally over both M(central)-M(terminal) interactions for a total bond order of two each. No antibonding orbitals will be populated.

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Problem 2. (3 points)

1. Assign the point groups of both *trans*- and *cis*-$ML_4(O)_2^{n+}$.

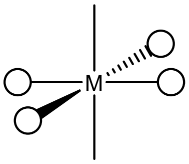
trans: D_{4h} *cis*: C_{2v}

2. Begin with the *trans* isomer only. First, determine the irreducible representations for the ligand-based SALCs in the point group from part *1* and the given coordinate system. Derive the irreducible representations for the four equatorial L ligands ($\Gamma_{4L\sigma}$), the axial oxo σ interaction (Γ_{2Opz}), and the axial oxo π interactions (Γ_{4Opxy}) in the appropriate symmetry.

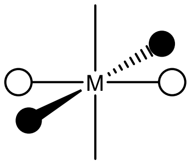
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{4L\sigma}$	4	0	0	2	0	0	0	4	2	0
Γ_{2Opz}	2	2	2	0	0	0	0	0	2	2
Γ_{4Opxy}	4	0	-4	0	0	0	0	0	0	0

$\Gamma_{4L\sigma} = A_{1g} + B_{1g} + E_u$
$\Gamma_{2Opz} = A_{1g} + A_{1u}$
$\Gamma_{4Opxy} = E_g + E_u$

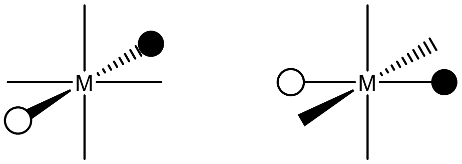
3. Provide graphical representations of the SALCs and assign their Mulliken symbols. Represent the σ-symmetry orbitals on L as *s* orbitals. You need not use the projection operator, but rather use the character table and symmetry-associated functions within the table to help construct the SALCs.



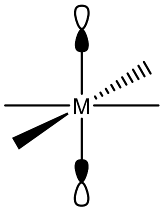
A_{1g}



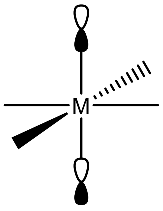
B_{1g}



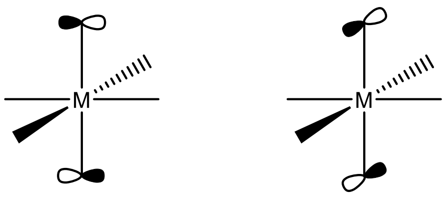
E_u



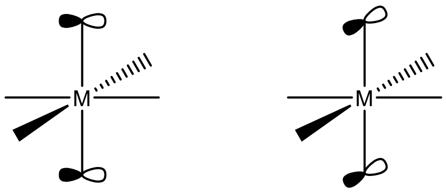
A_{1g}



A_{2u}

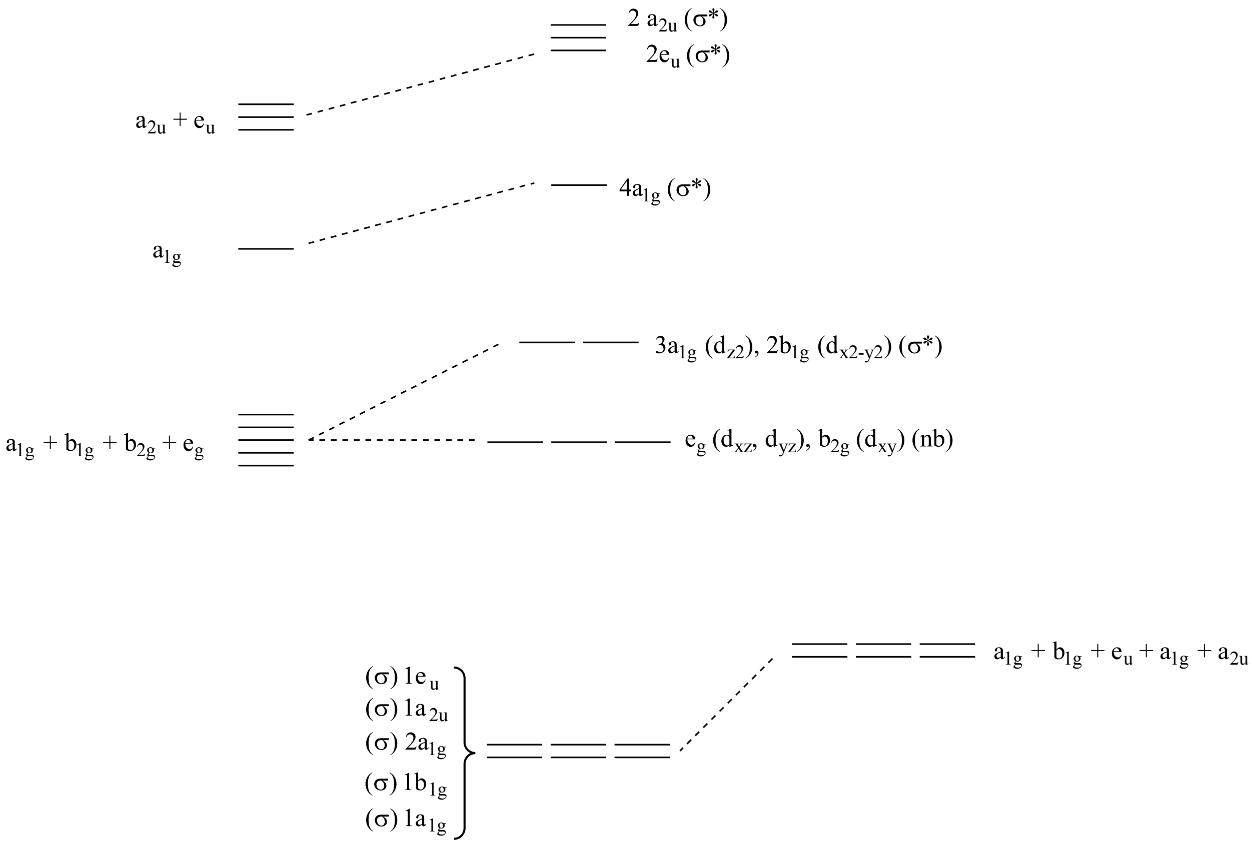


E_g

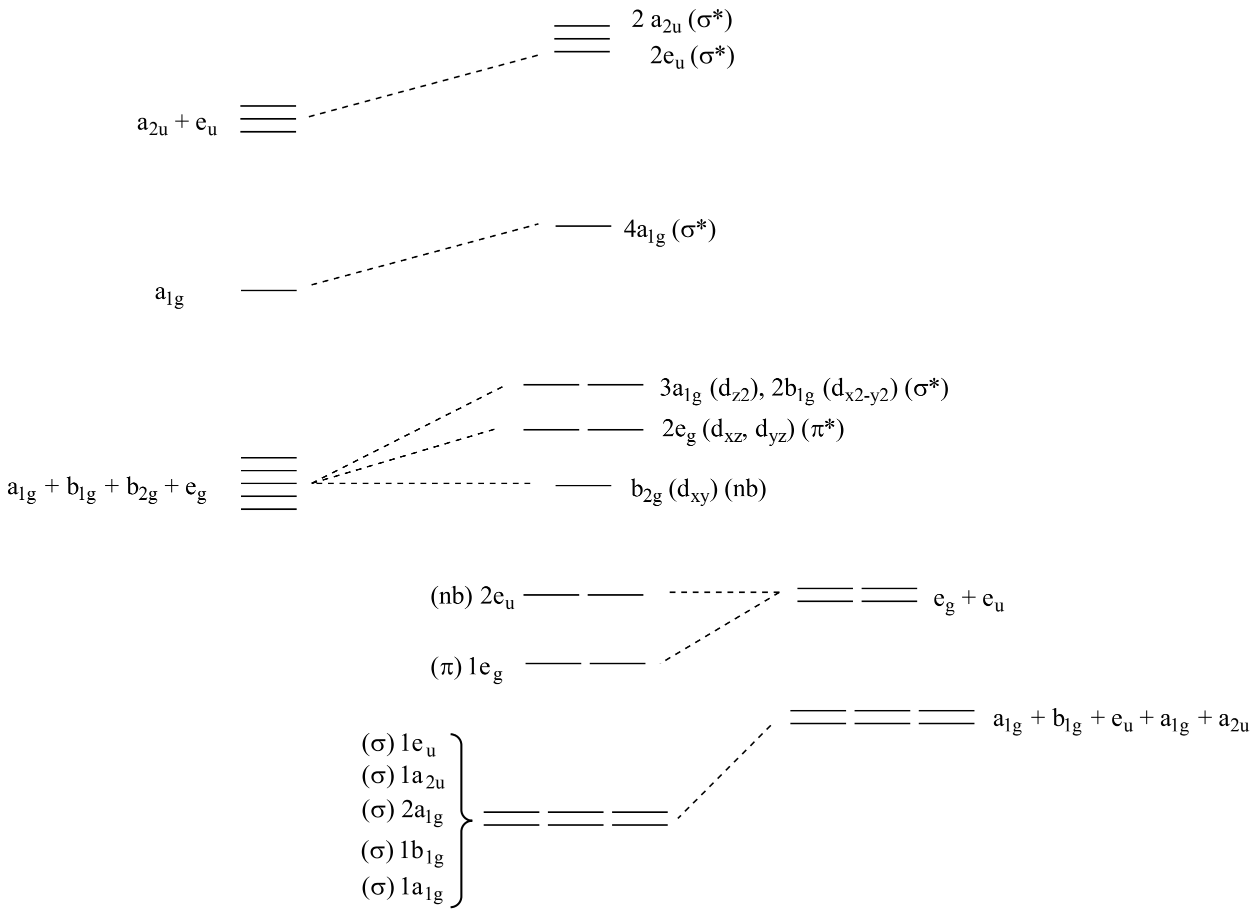


E_u

4. Construct the σ-only molecular orbital diagram for *trans*-$ML_4(O)_2^{n+}$, using the metal *d*, *s*, and *p* atomic orbitals and the SALCs derived in parts *2* and *3* for the σ symmetry ligand orbitals. You may consider the O and L-based SALCs of σ symmetry to be isoenergetic. Label each molecular orbital with the correct Mulliken symbol and provide the character of the interaction (bonding, non-bonding, anti-bonding). Label the d-based orbitals with their d-orbital parentage.



5. Now construct the full molecular orbital diagram for *trans*-$ML_4(O)_2^{n+}$, including the SALCs derived in parts *2* and *3* for the π symmetry O^{2-}orbitals.



6. Redraw only the d-splitting diagram derived from the MO diagram in part *5* for *trans*-$ML_4(O)_2^{n+}$. Consider now the effect of switching the position of one of the oxo and L ligands to generate *cis*-$ML_4(O)_2^{n+}$. Draw this new d-splitting diagram starting relative to the diagram for *trans*-$ML_4(O)_2^{n+}$. Clearly illustrate which d-orbitals change in energy and which remain the same. Label all orbitals with their d-parentage and bonding/non-bonding/anti-bonding character. Note that both diagrams should be derived under the same coordinate system, as shown above.

With the oxygen atoms in the xz plane, d_{xz} is π antibonding with two oxygen p orbitals for both geometries. d_{yz} is π antibonding with two O orbitals on the left and only one on the right. d_{xy} is nonbonding on the left and antibonding with respect to one of the O π orbitals on the right.

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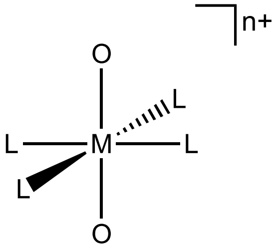

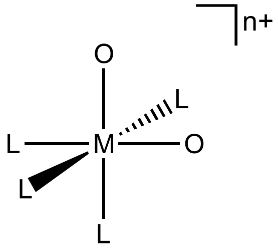

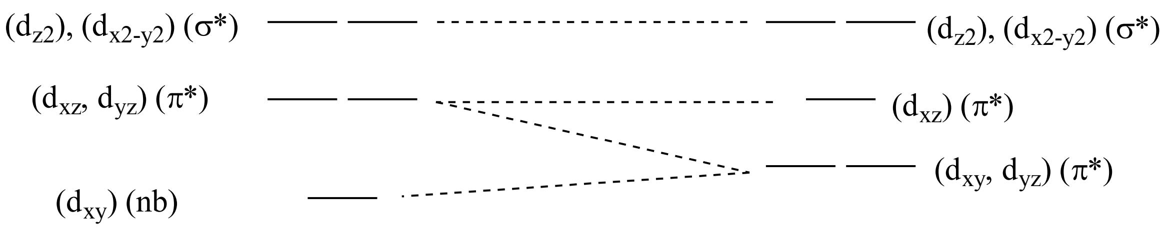

d_{z2} and d_{x2-y2} are σ-antibonding and remain unchanged as the σ framework is unperturbed between the two isomers. d_{xz} retains its high energy π* character, whereas d_{yz} loses overlap and lowers in energy in the cis isomer. d_{xy} rises in energy to be approximately degenerate with d_{yz} due to new π* character.

7. Consider the two hypothetical complexes $Mo(PR_3)_4(O)_2$ and $Mo(PR_3)_4(O)_2^{2+}$. Assign the oxidation states, d-electron counts, and valence electron counts of both molecules.

$Mo(PR_3)_4(O)_2$: Mo^{IV}, d^2, 18e^-
$Mo(PR_3)_4(O)_2^{2+}$: Mo^{VI}, d^0, 16e^-

8. Which geometry, *trans* or *cis*, would you expect each complex, $Mo(PR_3)_4(O)_2$ and $Mo(PR_3)_4(O)_2^{2+}$, to prefer? Explain given the molecular orbital and d-splitting diagrams derived above. Indicate the nature of the HOMO in each case and the average M-O bond order. Use only d-orbitals for π bonding.

$Mo(PR_3)_4(O)_2$ will prefer the *trans* geometry as the two d electrons will be placed in the non-bonding d_{xy} orbital (HOMO) rather than an antibonding orbital in the *cis* geometry (Mo-O π bond order = 2). $Mo(PR_3)_4(O)_2^{2+}$, on the other hand, will prefer the *cis* geometry. There are no d electrons so no antibonding orbitals will be populated and the *cis* geometry maximizes the π-bonding interactions with the d-orbitals (Mo-O π bond order = 3).

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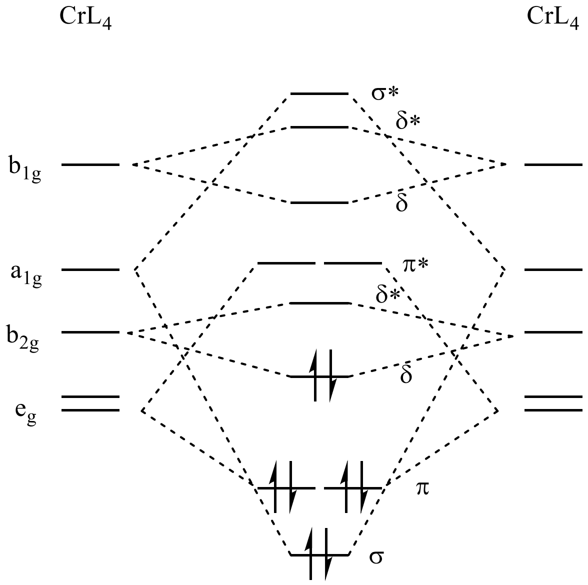
Problem 3. (2 points)

1. Assign oxidation state and d-count for the Cr centers in complexes **A** and **B**.

   A - Cr^{II}/Cr^{II} (d^4/d^4)

   B - Cr^{II}/Cr^{I} (d^4/d^5)

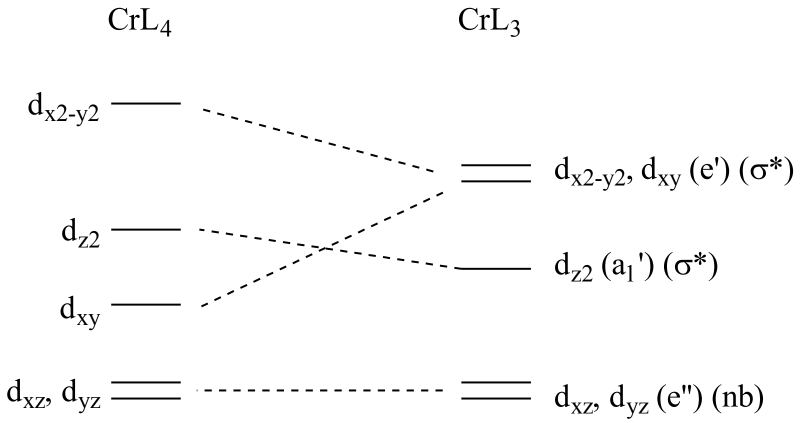
2. Interact the two [CrL$_4$] fragments to arrive at an MO diagram depicting the M-M interactions, similar to [ReCl$_4$]$^-$ from lecture to construct [Re$_2$Cl$_4$]$^{2-}$. We will assume an eclipsed geometry (D$_{4h}$) even though these structures display some distortions. Label each orbital with its Mulliken symbol, and label the type of interaction (σ, σ*, π, etc) with respect to both M-M and M-ligand interactions. For simplicity assume that the ligands only act as σ donors.



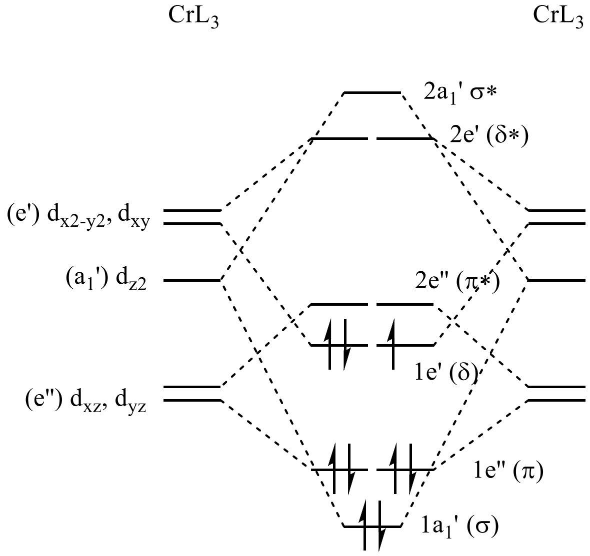
3. Fill in the d-splitting diagram from question 3 with the appropriate number of electrons. What is the Cr–Cr bond order?

   Bond Order = 4

4. Starting from the MO diagram of [CrL$_4$], derive a d-splitting diagram for one of the [CrL$_3$] fragments in **B** clearly showing how you expect the orbital energies to change. Label each orbital with its d-parentage, Mulliken symbol, and type of interaction with L (σ, σ*, or nonbonding).



5. Interact two [CrL_3] fragments from question 4 to arrive at a qualitative MO diagram of complex **B**. Make sure your diagram reflects the change in Cr–Cr bond length (shortening is indicative of an increase in Cr–Cr bond order). What is the Cr–Cr bond order? Label each orbital with its d-parentage, type of M-M and M-ligand interaction, and Mulliken symbol.



Bond order = 4.5

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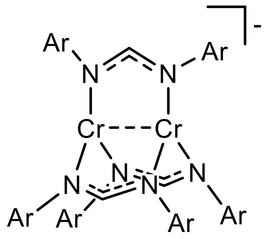
Complex **B** can be reduced with 1 equivalent of KC_8 to form the anionic species **B**$^-$.

B$^-$



6. What is the oxidation state, d-electron count of each Cr center in **B**$^-$?

Cr^I/Cr^I (d^5, d^5)

7. Do you expect the Cr–Cr distance to lengthen or shorten when reducing **B** to **B**$^-$? What is the Cr–Cr bond order of **B**$^-$? What is the Cr–Cr bond order for the hypothetical molecule **A**$^-$?

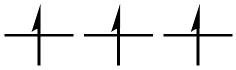
One would expect the Cr-Cr distance to shorten as the bond order increases to 5. The Cr-Cr bond order for **A**$^-$ would be 3.5.

Problem 4. (3 Points)

Part A

1. Determine the total number of possible microstates for the $1s^2 2s^2 2p^3$ configuration. Determine the ground state term using the shortcut presented in class.

$$\# \, Microstates = \frac{6 \cdot 5 \cdot 4}{3 \cdot 2 \cdot 1} = 20$$



Ground State = ^4S

2. Prepare a microstate table and populate with all possible microstates.

	3/2	1/2	-1/2	-3/2
2		$(1^+, 1^-, 0^+)$	$(1^+,1^-,0^-)$	
1		$(1^+, 0^+, 0^-)$ $(1^+, 1^-, -1^+)$	$(1^-, 0^+, 0^-)$ $(1^+, 1^-, -1^-)$	
0	$(1^+, 0^+, -1^+)$	$(1^+, 0^+, -1^-)$ $(1^+, 0^-, -1^+)$ $(1^-, 0^+, -1^+)$	$(1^+, 0^-, -1^-)$ $(1^-, 0^-, -1^+)$ $(1^-, 0^+, -1^-)$	$(1^-, 0^-, -1^-)$
-1		$(-1^+, 0^+, 0^-)$ $(1^+, -1^-, -1^+)$	$(-1^-, 0^+, 0^-)$ $(1^-, -1^-, -1^+)$	
-2		$(-1^+, -1^-, 0^+)$	$(-1^+, -1^-, 0^-)$	

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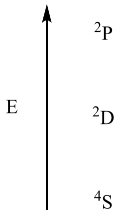
3. Using the microstate table for the $1s^2 2s^2 2p^3$ configuration, derive the state symbols. Include the terms resulting from spin-orbit coupling. Order all terms based on energy strictly following Hund's rules (ignoring J).

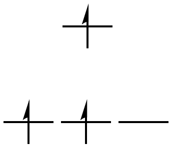
$^2D_{5/2}$, $^2D_{3/2}$; $^2P_{3/2}$, $^2P_{1/2}$; $^4S_{3/2}$



Part B

1. Determine the total number of possible microstates for the $2p^2 3s^1$ configuration. Determine the ground state term using the shortcut presented in class.

$$\# \mathit{Microstates} = \frac{6 \cdot 5 \cdot 2}{2 \cdot 1 \cdot 1} = 30$$



Ground state = ^4P

2. Prepare a microstate table and populate with all possible microstates. Remember that all microstates will maintain a $1s^2 2s^2 2p^2 3s^1$ configuration. Example notation: $(1_p^+, 0_p^-, 0_s^+)$

	3/2	1/2	-1/2	-3/2
2		$(1_p^+, 1_p^-, 0_s^+)$	$(1_p^+, 1_p^-, 0_s^-)$	
1	$(1_p^+, 0_p^+, 0_s^+)$	$(1_p^+, 0_p^-, 0_s^+)$ $(1_p^-, 0_p^+, 0_s^+)$ $(1_p^+, 0_p^+, 0_s^-)$	$(1_p^+, 0_p^-, 0_s^-)$ $(1_p^-, 0_p^+, 0_s^-)$ $(1_p^-, 0_p^-, 0_s^+)$	$(1_p^-, 0_p^-, 0_s^-)$
0	$(1_p^+, -1_p^+, 0_s^+)$	$(1_p^+, -1_p^+, 0_s^-)$ $(1_p^+, -1_p^-, 0_s^+)$ $(1_p^-, -1_p^+, 0_s^+)$ $(0_p^+, 0_p^-, 0_s^+)$	$(1_p^+, -1_p^-, 0_s^-)$ $(1_p^-, -1_p^+, 0_s^-)$ $(1_p^-, -1_p^-, 0_s^+)$ $(0_p^+, 0_p^-, 0_s^-)$	$(1_p^-, -1_p^-, 0_s^-)$
-1	$(-1_p^+, 0_p^+, 0_s^+)$	$(-1_p^+, 0_p^-, 0_s^+)$ $(-1_p^-, 0_p^+, 0_s^+)$ $(-1_p^+, 0_p^+, 0_s^-)$	$(-1_p^+, 0_p^-, 0_s^-)$ $(-1_p^-, 0_p^+, 0_s^-)$ $(-1_p^-, 0_p^-, 0_s^+)$	$(-1_p^-, 0_p^-, 0_s^-)$
-2		$(-1_p^+, -1_p^-, 0_s^+)$	$(-1_p^+, -1_p^-, 0_s^-)$	

3. Using the microstate table for the $1s^2 2s^2 2p^2 3s^1$ configuration, derive the state symbols. Include the terms resulting from spin-orbit coupling. Order all terms based on energy strictly following Hund's rules (ignoring J).

$^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$, $^2D_{5/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$, $^2S_{1/2}$