

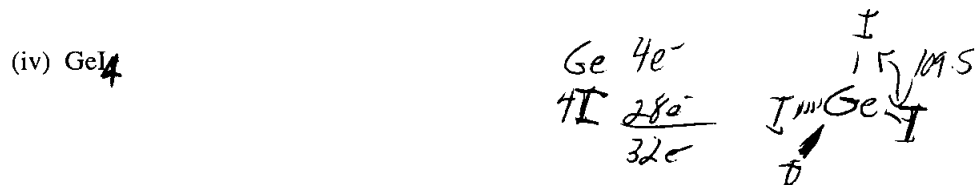
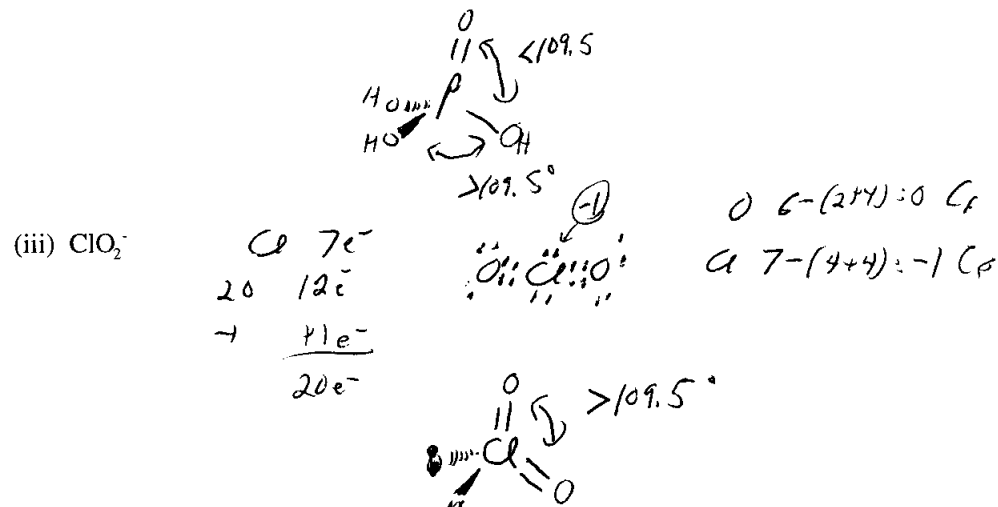
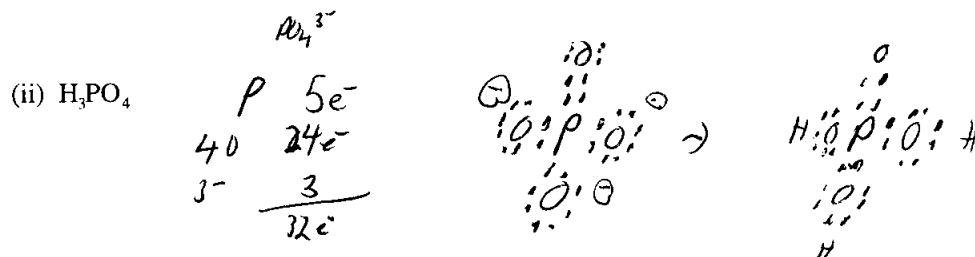
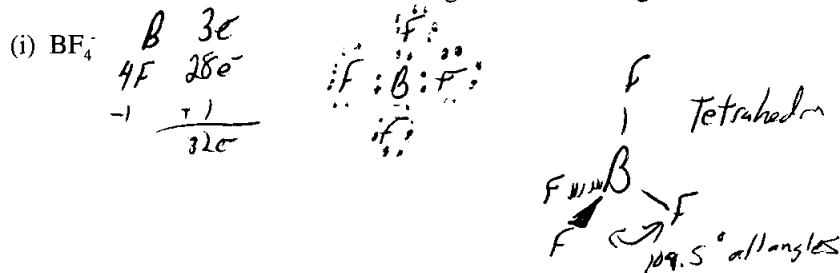
Chem 432 Exam 1. In Class Portion. Show all work where applicable.

Circle your name Matt

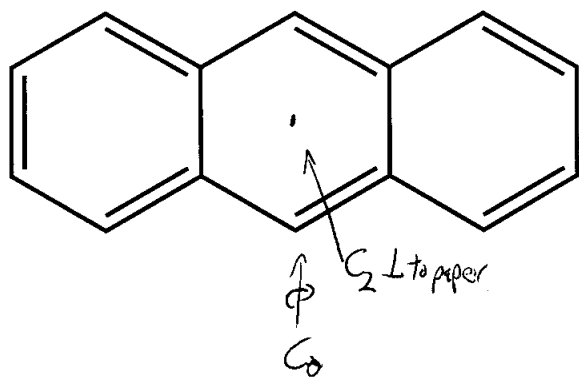
Lisa

Key

(1) For the following molecules, (a) draw the correct lewis dot structures and (b) draw the correct VSEPR structures with bond angles and indicating deviations from ideality.

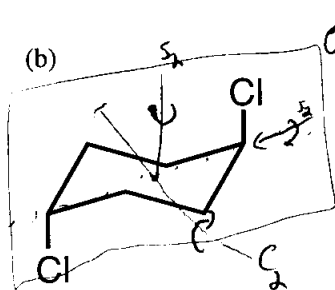


(2) List all of the symmetry elements and give the point groups for the following molecules
 (a) (this molecule is aromatic so ignore the double bonds)



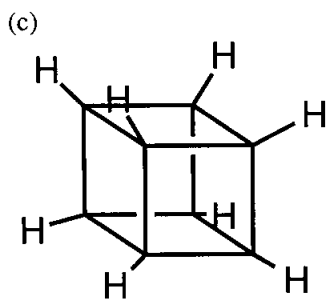
$E, C_2, 2C_2 \perp \text{to } C_2$
 $\leftarrow C_2, \sigma_h, 2\sigma_v, i$

D_{2h}



$\sigma_h, E, C_2, \sigma_h, i, S_2$

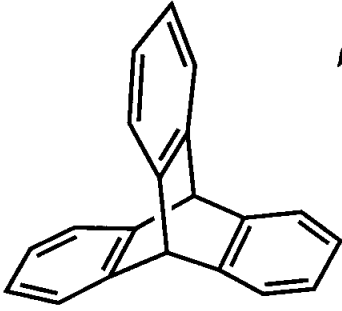
C_{2h}



$E, 4C_3, 3C_2, 3C_4, 3\sigma_h, 6\sigma_v, i$

O_h

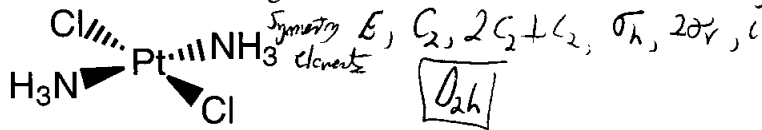
(d)



$E, C_3, \sigma_h, 3\sigma_v, 3C_2 \perp C_3, i$

D_{3h}

(3) Using the character tables provided, list the irreducible representations for the 5s, 5p, and 4d orbitals of the following molecule.



5s	A_g	4 d_{xy}	B_{1g}
5 p_x	B_{3u}	4 d_{xz}	B_{2g}
5 p_y	B_{2u}	4 d_{yz}	B_{3g}
5 p_z	B_{1u}	$d_{z^2}, d_{x^2-y^2}$	A_g

(4) Explain the differences between valence bond theory and molecular orbital theory. How are they similar?

Valence bond theory is concerned with forming bonds. Hybrid orbitals are constructed, each with 1 electron and pointing at the atom to bond with. The other atoms also have orbitals with 1 electron pointing in the right direction. The bonds formed are 2 electron bonds between two atoms with each atom donating 1 electron.

Molecular orbital theory mixes orbitals ~~from~~ from different atoms according to symmetry and energy ^{to form molecular orbitals}. Some orbitals are attractive (hold atoms together, bonding) when occupied by electrons. Some molecular orbitals are antibonding and ~~push~~ push atoms apart when occupied. Some orbitals are nonbonding. Orbitals can be delocalized over numerous atoms.

Take Home Portion of Exam 1. You may not receive help from any person but the instructor on this portion. You may use your notes and the course textbook (no other textbooks). This portion is due by 5:00 PM Wednesday, September 26.

Name _____

(5) Explain the bonding in metallocenes (i.e. ferrocene). First explain using molecular orbital theory. How do the metal and ligand interact to result in bonding? Try to explain ferrocene using valence bond theory (Assume there are 10 identical bonds between the iron and each carbon atom and construct suitable hybrid orbitals). How well does this work?

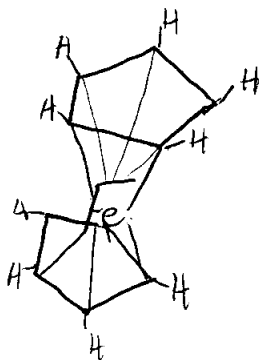
MO theory | The $p-\pi$ orbitals of the cyclopentadienyl rings interact with the d -orbitals of the iron to form bonding molecular orbitals. The bonding molecular orbitals are filled in ferrocene, and the antibonding are unfilled.



Valence bond | For valence bond theory, you need 10 orbitals all facing the points of the carbons in ferrocene. Technically, the Fe has unoccupied f -orbitals that could be used to form sp^3d^2f hybrids (assume they point to the carbons). It works, but

it suggests that the rings are not aromatic anymore.

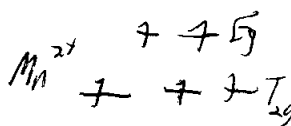
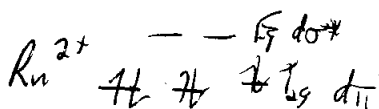
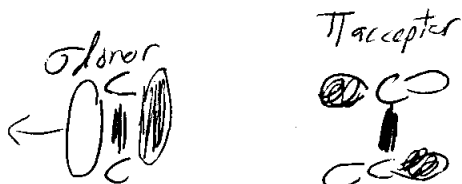
Also, this requires 20 valence electrons and this molecule only has 18.



Both views of bonding are rooted in the same basic quantum mechanical model of bonding. Bonding occurs because electrons are shared (or localized) between two or more atoms.

(6) Rank the relative bond strength between the following metals and ligands. Explain using ligand field theory and the orbital drawings of the ligands.

(a) Ethylene to Ru^{2+} (low spin), Mn^{2+} (high spin), and Ti^{4+}



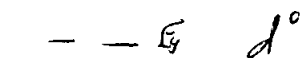
↑
 Empty E_g for donation to Ru^{2+}

↓ Filled E_g , weak σ bonds

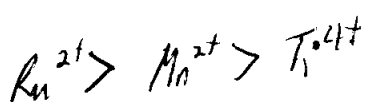
Filled T_{2g} , so good backbond

↓ Filled T_{2g} , not so good backbond

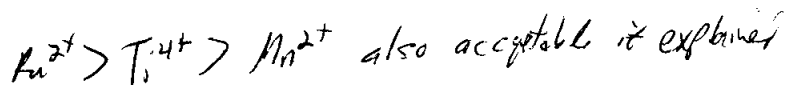
Ti^{4+}



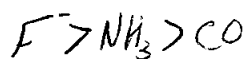
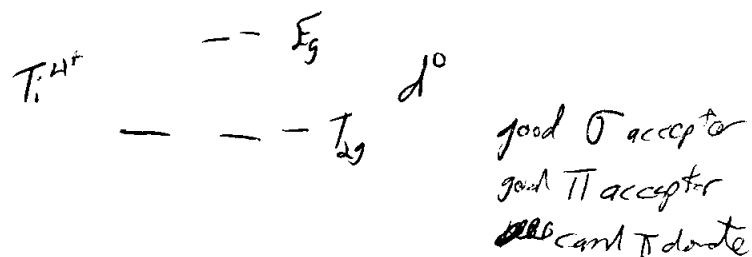
No backbonding by backbonding
 good σ bonds



This ordering assumes backbonding is stronger than σ donation with ethylene



(b) F, CO, and NH₃ to Ti⁴⁺



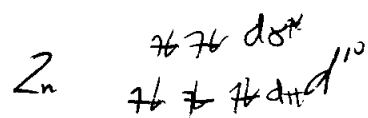
F⁻ both σ donor and π donor

NH₃ good σ donor

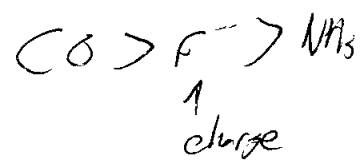
CO poor σ donor, good π acceptor (doesn't work here)

F⁻ > CO > NH₃ or F⁻ > CO \approx NH₃ accepted

(c) F, CO, and NH₃ to Zn²⁺



$d\sigma^*$ filled, lousy σ bond
 $d\pi$ filled, good π donor



(7) In order to explain molecules such as SH_6^- , valence bond theory creates hybrid orbitals using the unoccupied 3d orbitals to create 6 hybrid orbitals. Below are two molecular orbital diagrams of SH_6^- . One only uses the s and p orbitals on S and the other includes the d orbitals.

(a) How does the MO diagram change when the d orbitals are added? Is SH_6^- predicted to be stable or unstable in each diagram (explain why). An extra 2 bonding, 3 nonbonding, and 2 antibonding orbitals are added. 2 nonbonding orbitals disappear. SH_6^- is predicted to be stable

in both diagrams, because in the first, all bonding and nonbonding orbitals are filled. In the second, all bonding orbitals are filled, and the nonbonding and antibonding are unfilled.

(b) Label the molecular orbitals as bonding, antibonding, and nonbonding on each of the two MO diagrams.

(c) If you know that orbitals 5 and 6 have E_g symmetry, which d-orbitals are used in those molecular orbitals? Are they the ones you expect (why or why not)? Oh symmetry

$E_g = d_{x^2-y^2}, d_{z^2}$. These are the ones you would expect, because they are of the proper symmetry for σ bonding to the H's.

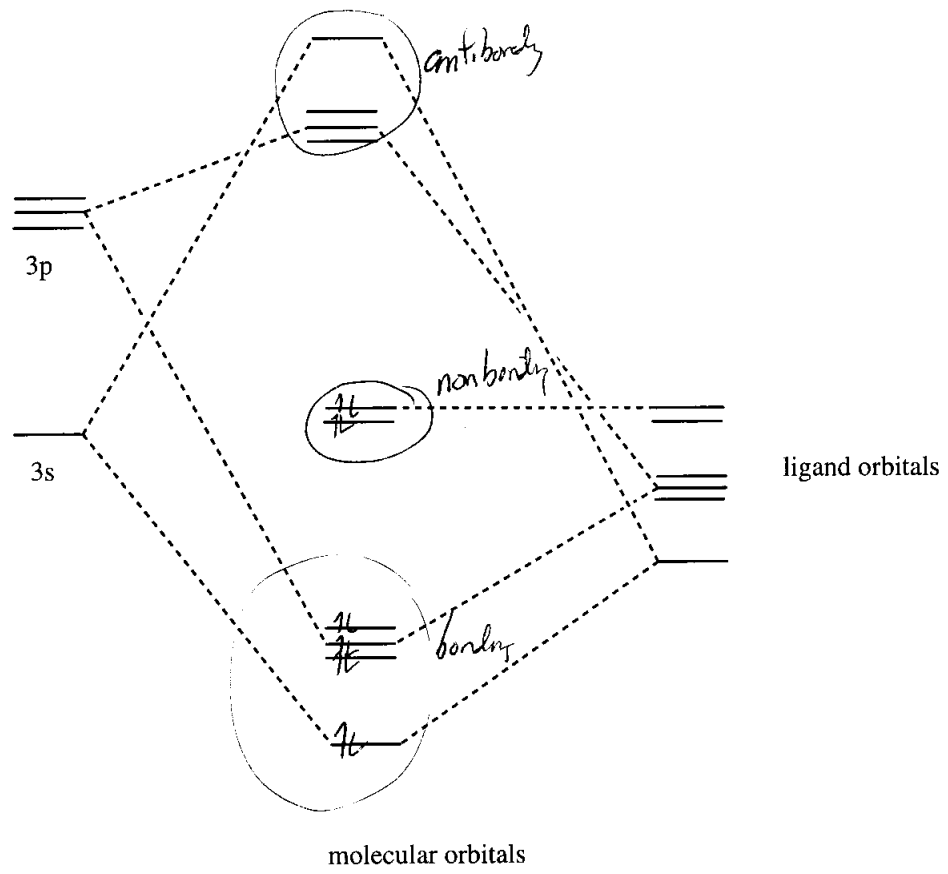
(d) Should the molecule SH_6^- be stable according to these MO diagrams (answer for each individually)? Why or why not?

For the first one, the extra electron would have to be placed in an antibonding orbital. This would tend to make the molecule unstable. In the second (with the d-orbitals) the extra electron goes into a nonbonding orbital, ~~at the top~~ which should not affect the stability.

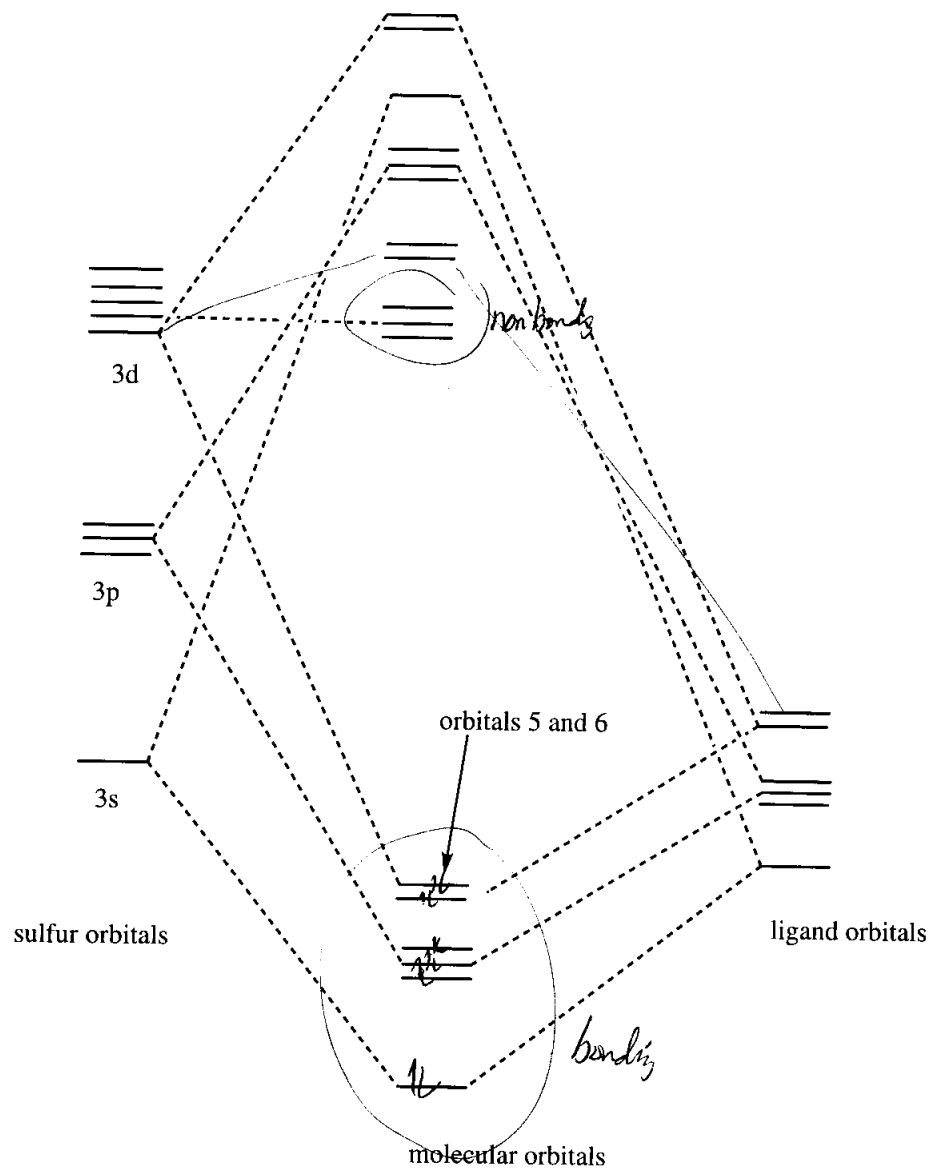
MO 2 - stable SH_6^-

MO 1 - at least less stable than MO-2 predicts

6e⁻
6e⁻
2e⁻



SH_6 using only the s and p orbitals on S



MO diagram for SH_6 including the d orbitals