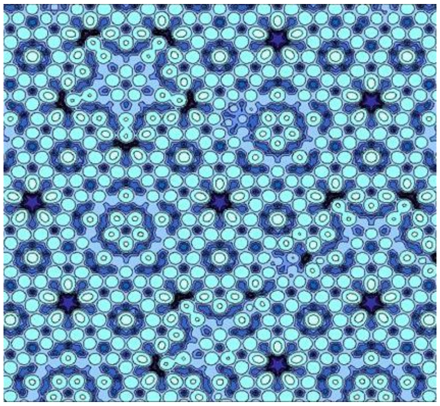
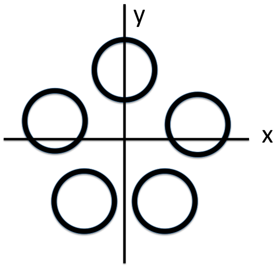
Chm 451 with Dr. Mattson Exam 2 **Name:**

27 October 2011



Earlier this month Dan Shechtman won the Nobel Prize in chemistry for his discovery of quasicrystals such as the one shown at right consisting of silver, aluminum (and other elements such as oxygen). Inspecting the structure, one can see atoms of one kind of element surrounded by a pentagonal plane of five other atoms of another element (AB_5) with D_{5h} local symmetry.

1a. (5 pts) Starting with the five pentagonal planar "B" atomic orbitals (that will form the SALC set) as shown at right, and the D_{5h} character table, determine the reducible representation and irreducible components for the σ-bonding SALCs.



D_{5h} Character Table (Note: cos72° = 0.309 and cos144° = -0.809)

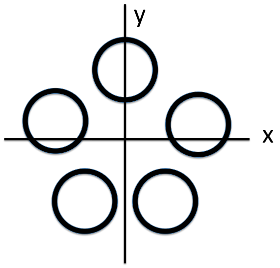
	E	**$2\ C_5(z)$**	**$2\ C_5^2$**	**$5\ C_2$**	**σ_h**	**$2\ S_5$**	**$2\ S_5^3$**	**$5\ \sigma_v$**		
A_1'	1	1	1	1	1	1	1	1		z^2
A_2'	1	1	-1	1	1	1	-1	-1		
E_1'	2	2cos72°	2cos144°	0	2	2cos72°	2cos144°	0	(x, y)	
E_2'	2	2cos144°	2cos72°	0	2	2cos144°	2cos72°	0		(x^2-y^2, xy)
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	z	
E_1''	2	2cos72°	2cos144°	0	-2	-2cos72°	-2cos144°	0		(xz, yz)
E_2''	2	2cos144°	2cos72°	0	-2	-2cos144°	-2cos72°	0		

	E	**$2\ C_5(z)$**	**$2\ C_5^2$**	**$5\ C_2$**	**σ_h**	**$2\ S_5$**	**$2\ S_5^3$**	**$5\ \sigma_v$**
Γ								

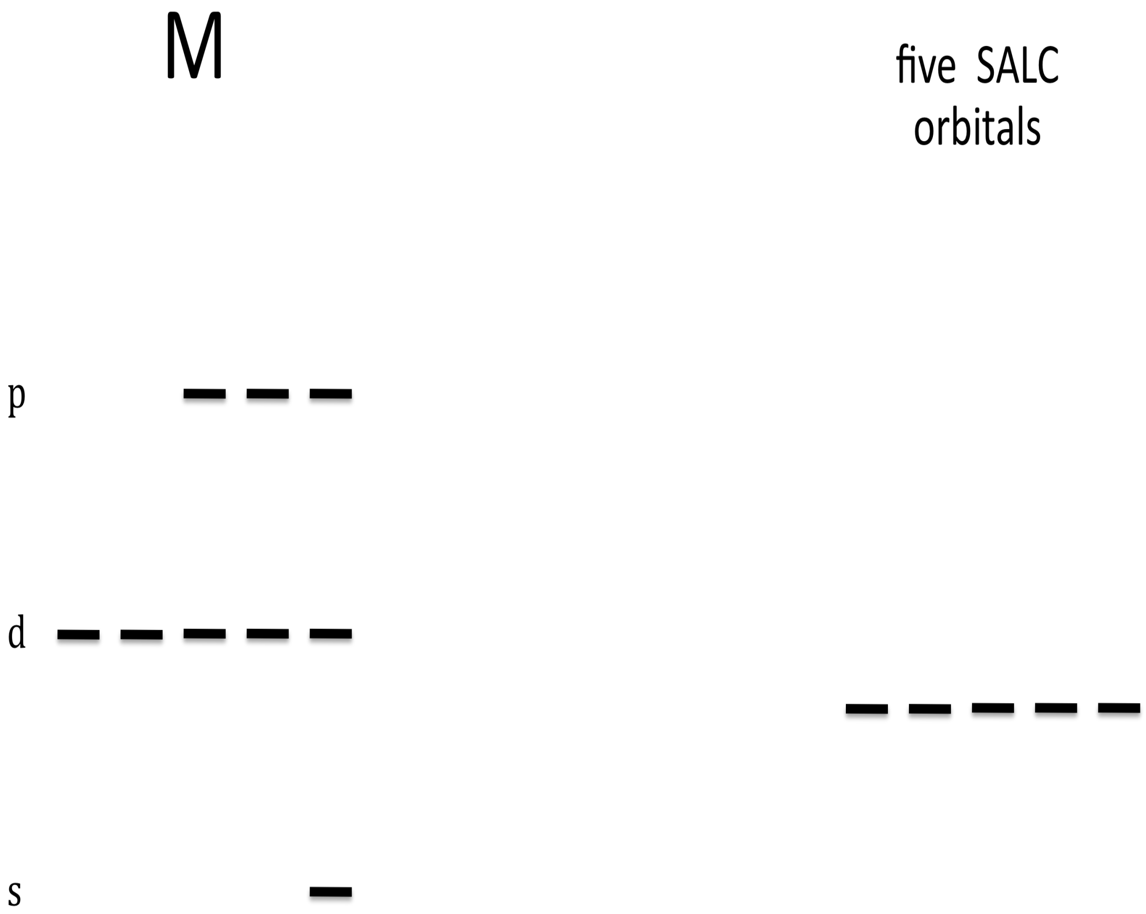
1b. (5 pts) Suppose the central atom has s-, p- and d-orbitals available for overlap. How would each transform according to the D_{5h} character table? Recall that for our purposes, "x" from the character table refers to the p_x orbital and "z^2" refers to the d_{z^2} orbital, etc. Which atomic orbitals will produce a MO with a SALC?

Orbital:	Transforms as:	Will this atomic orbital produce a MO with a SALC?
s		Yes No
p_x		Yes No
p_y		Yes No
p_z		Yes No
d_{z^2}		Yes No
$d_{x^2-y^2}$		Yes No
d_{xz}		Yes No
d_{yz}		Yes No
d_{xy}		Yes No

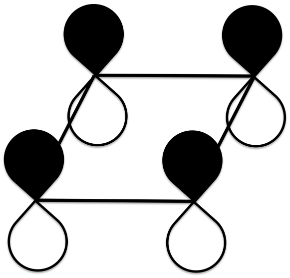
1c. (6 pts) For the s- and p-orbitals only (not the d-orbitals), that you indicated above (in 1b) would form a MO with a SALC orbital, sketch the molecular orbitals that result and give them symmetry labels (for example, a_1'). Use the template at right as your point of reference.

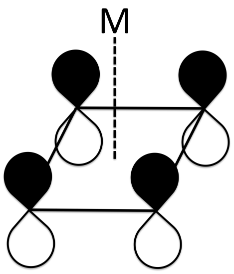


1d. (6 pts) Sketch the MO diagram showing all of the MOs indicated with a “Yes” in the table above. Include the MOs formed from d-orbitals. You do not need to sketch “lobe pictures” in this diagram, but do include symmetry labels. Include non-bonding orbitals in your sketch.

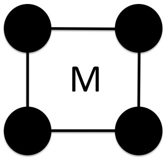


2. Cyclobutadiene, has formula C_4H_4. (You may want to sketch it in the margin here based on your knowledge of organic chemistry.) The diene part of structure results from four p-orbitals creating a π-manifold as shown at right. Cyclobutadiene can bond to a metal atom by donating π-electrons to a metal in a Lewis base → Lewis acid arrangement. The metal atom is situated above the plane of the carbon atoms as shown below. The “Top view” shows the tops of the p-orbitals with the metal situated in the center of the square of the carbon atoms. Together the metal atom and the C_4H_4 have C_{4v} symmetry.





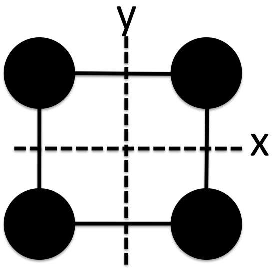
Top view:



C_{4v}	**E**	**2 C_4(z)**	**C_2**	**2 σ_v**	**2 σ_d**		
A_1	1	1	1	1	1	z	z^2
A_2	1	1	1	-1	-1		
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y)	(xz, yz)

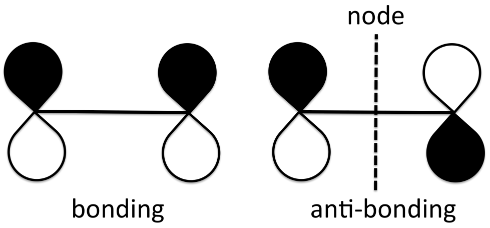
2a. (4 pts) Using the figure for the four p-orbitals (top of page), determine the reducible representation and the irreducible components. Use the figure at right as your perspective for the x- and y-axes. This is the top view again and the black circles are the tops of the p-orbitals; the view is down the z-axis.

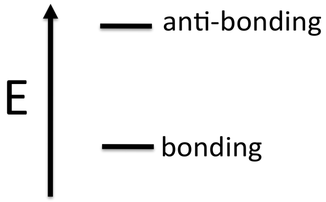
Top view:



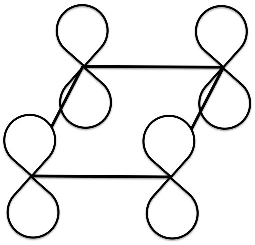
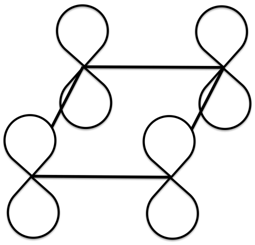
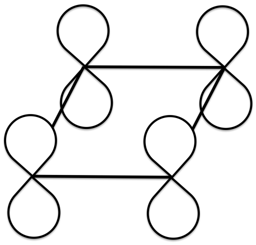
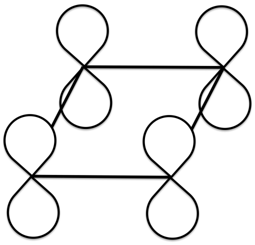
C_{4v}	**E**	**2 C_4(z)**	**C_2**	**2 σ_v**	**2 σ_d**
Γ					

Unlike the SALC sets we've constructed before, these four contributing orbitals are in close proximity to one another, so they form their own set of molecular orbitals (without the metal). Counting the nodes present between the carbon atoms tells us the relative degree of bonding vs. antibonding. For example, for ethene, the figure at left has zero nodes between carbons, while the one next to it (center figure) has one. This makes the former (zero nodes) bonding and the latter (1 node) antibonding as per the energy diagram at right.



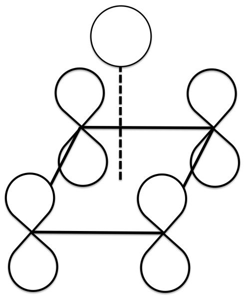
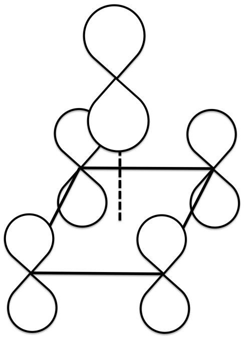
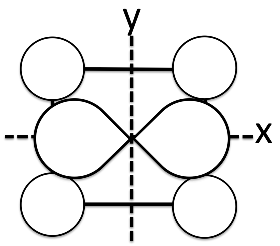
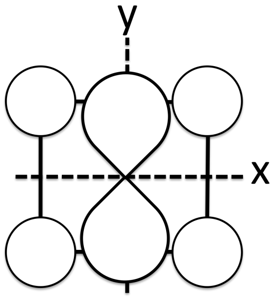


2b. (4 pts) Extending this to cyclobutadiene. Cyclobutadiene makes four π-MOs, one having zero nodes, two degenerate ones having one node and one having two nodes. Color in the lobes for these four cyclobutadiene MOs, creating the number of nodes indicated (you do not need to sketch in the nodal planes):

Zero nodes: 	One node: 	One node: 	Two nodes: 

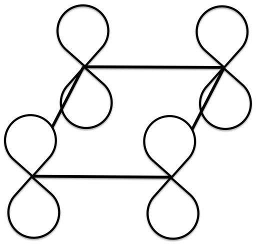
2c. (2 pts) Sketch the energy diagram for cyclobutadiene below. These MOs are the same as the SALCs we will use for the rest of the problem. The only difference is that they don't all have the same energy as SALCs have had in the past.

2d. (8 pts) Now back to our initial problem of how the cyclobutadiene π-manifold orbitals overlap with the metal. We usually inspect the character table to see what orbitals on the metal atom, M, would transform as each SALC we have created. This allows us to sketch and color in the MOs that result from each SALC orbital and atomic orbital on M. Complete the table below (by coloring in lobes) for the s- and p-orbitals on the metal, creating a MO, whenever possible. In the box below each orbital, write its symmetry label (e.g. a_1) or write "No MO."

MO formed with M's s-orbital?	with the p_z orbital?	with the p_x orbital? (Note: top view)	with the p_y orbital?
		Top view: 	Top view: 

2e. (1 pt) One of the irreducible representations has not been used yet. Which one is it? (give its symmetry label)

2f. (1 pt) Which cyclobutadiene MO from 2b is it?



2g. (1 pt) These two are the same (answers to 2e and 2f). What orbital on the metal transforms the same as this last orbital?

3. Aluminum chloride, $AlCl_3$ is an important reagent in organic chemistry.

3a. (2 pts) Sketch the Lewis dot structure of $AlCl_3$ and state why it is a Lewis acid in fewer than 5 words.

3b. (3 pts) Evidence suggests that unlike BF_3, which is a monomer, $AlCl_3$ is actually a dimer, Al_2Cl_6. Sketch a Lewis dot structure that shows how the electron pair groups on one Cl from each Al can function as a Lewis base by donating a pair of electrons to the other Al in the dimer. This allows each Al to have an octet.

4. H_3AsO_4 vs. H_3AsO_3.

4a. (1 pt) Which of these two acids would you expect to be the most acidic? H_3AsO_4 or H_3AsO_3? Circle one: H_3AsO_4 or H_3AsO_3

4b. (2 pts) Names these acids as an extension of your knowledge of the names of their phosphorus analogues H_3PO_4 or H_3PO_3.

H_3AsO_4

H_3AsO_3

4c. (2 pts) Suppose the pK_{a1} for H_3AsO_3 is 3.2. What would you predict for pK_{a2} and pK_{a3}?

5. Cesium iodide, CsI, is far less soluble in water than CsF.

5a. (2 pts) What theory explains why is this so?

5b. (2 pts) Using the same logic, predict the more soluble of this pair: LiF vs. LiI.

Circle one: LiF or LiI

6. Calcium exhibits a fcc lattice.

6a. (4 pts) Derive the equation for the relationship between the radius, r, and the volume, V, for the fcc lattice.

6b. (4 pts) Given the density of calcium, 1.55 g/cm^3, calculate the radius of elemental calcium.

6c. (2 pts) Would calcium's density be greater than 1.55 g/cm^3 or less than 1.55 g/cm^3 if the metal exhibited a simple or body-centered cubic lattice?

(i) Simple cubic unit cell:

A. > 1.55 g/cm^3 B. < 1.55 g/cm^3 C. equals 1.55 g/cm^3 D. Cannot predict

(ii) Body-centered cubic unit cell:

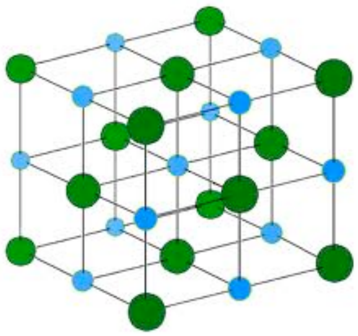
A. > 1.55 g/cm^3 B. < 1.55 g/cm^3 C. equals 1.55 g/cm^3 D. Cannot predict

7. (4 pts) What percent of a simple cubic unit cell is occupied by atoms? Show your work.

8. (7 pts) Consider these three ionic substances:

8a. Sodium chloride:

(i) What sort of sub-lattice is formed by the chlorides:



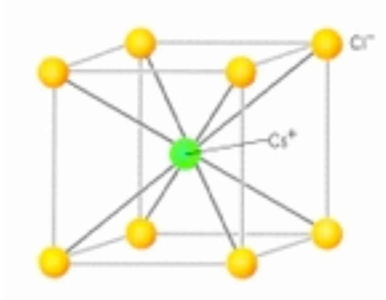
A. simple cubic
B. body-centered cubic
C. face-centered cubic
D. none of the above

(ii) What positions do the sodium ions occupy?

A. octahedral holes
B. tetrahedral holes
C. cubic holes
D. none of the above

8b. Cesium chloride:

(i) What sort of sub-lattice is formed by the chlorides:

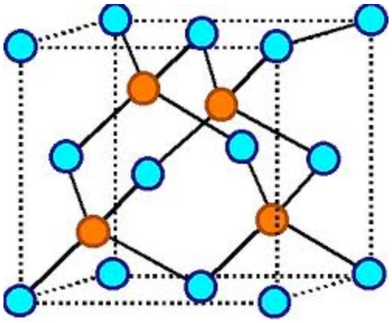


A. simple cubic
B. body-centered cubic
C. face-centered cubic
D. none of the above

(ii) What positions do the cesium ions occupy?

A. octahedral holes
B. tetrahedral holes
C. cubic holes
D. none of the above

8c. Zinc sulfide:



(i) What sort of sub-lattice is formed by the sulfides (blue):

A. simple cubic B. body-centered cubic

C. face-centered cubic D. none of the above

(ii) What positions do the zinc ions occupy?

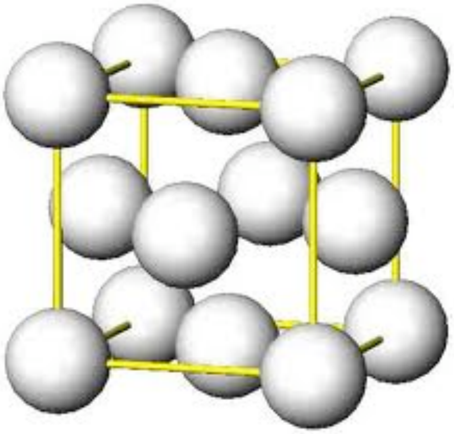
A. octahedral holes B. tetrahedral holes

C. cubic holes D. none of the above

(iii) What is the formula of zinc sulfide?

9. Close packing.

9a. Cubic-close packed (ccp) lattices



(i) (1 pt) Cubic close packing can be described by layers ABAB or ABC. Circle your choice: ABAB or ABC

(ii) (3 pts) Cubic close packing is the same as fcc. On the fcc lattice shown at right, write “A” and “B” (and “C”?) on each ball to show the equivalency of ccp and fcc.

(iii) (3 pts) How many:

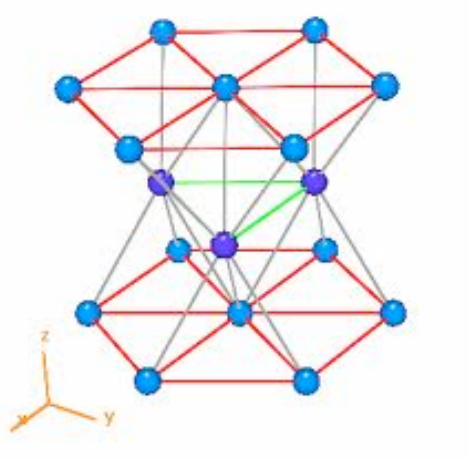
a. spheres are wholly contained within the ccp unit cell?
b. octahedral holes are contained within the ccp unit cell?
c. tetrahedral holes are contained within the ccp unit cell?

9b. Hexagonal-close packed (hcp) lattices

(i) (1 pt) How would the density of ccp compare to hexagonal close packed lattices for the same substance?

A. $d_{ccp} > d_{hcp}$ B. $d_{ccp} < d_{hcp}$ C. $d_{ccp} = d_{hcp}$

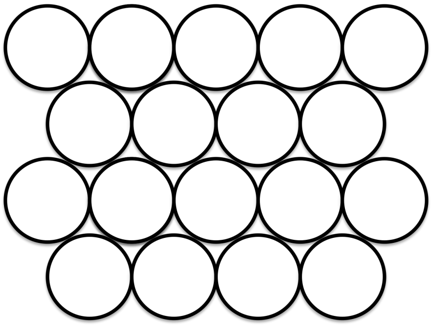
(ii) (2 pts) The hcp lattice is shown at right. Draw lines on the figure to outline one unit cell. (Use a highlighter pen if you have one available)



(iii) (3 pts) How many:

a. spheres are wholly contained within the hcp unit cell?
b. octahedral holes are contained within the hcp unit cell?
c. tetrahedral holes are contained within the hcp unit cell?

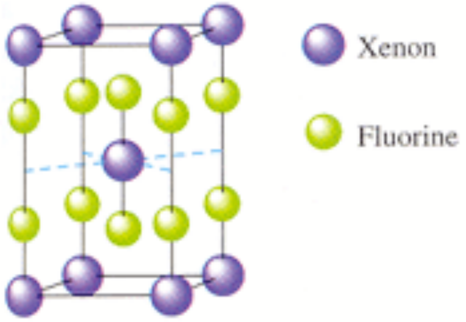
(iv) (2 pts) At right is a view of one layer of a hcp lattice. This amounts to a top view (2 dimensions). Outline one unit cell of the hcp lattice in the figure.



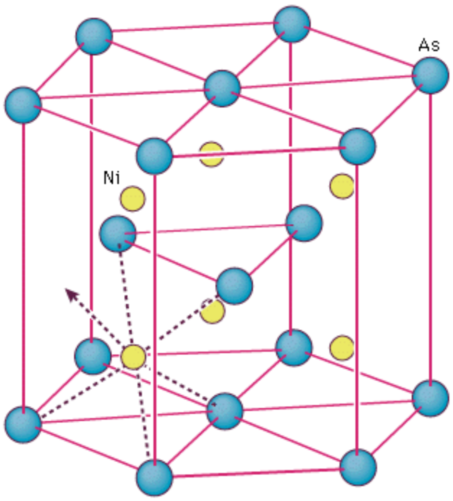
(v) (1 pt) Using the same figure and the unit cell you indicated in (iv), mark the location of the B layer(s) with “B”

10. Other compounds.

10a. (3 pts) The structure of a xenon fluoride compound is shown at right. What is its formula?



10b. (3 pts) The structure of a nickel arsenide is shown at right. What is its formula?



Answers:

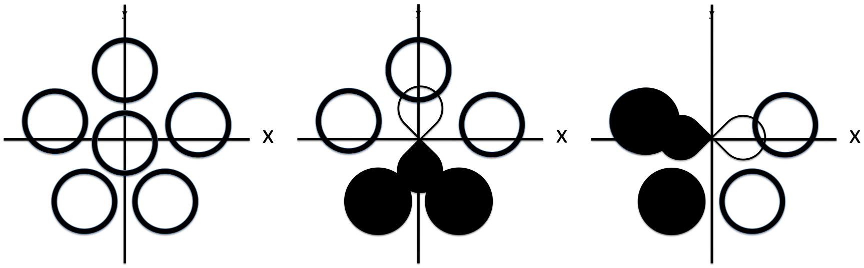
1a.

	E	**2 C_5(z)**	**2 C_5^2**	**5 C_2**	**σ_h**	**2 S_5**	**2 S_5^3**	**5 σ_v**
Γ	5	0	0	1	5	0	0	1
A_1‘	1	1	1	1	1	1	1	
E_1‘	$2\cos72^o$	$2\cos144^o$	0	2	$2\cos72^o$	$2\cos144^o$	0	$2\cos72^o$
E_2‘	$2\cos144^o$	$2\cos72^o$	0	2	$2\cos144^o$	$2\cos72^o$	0	$2\cos144^o$

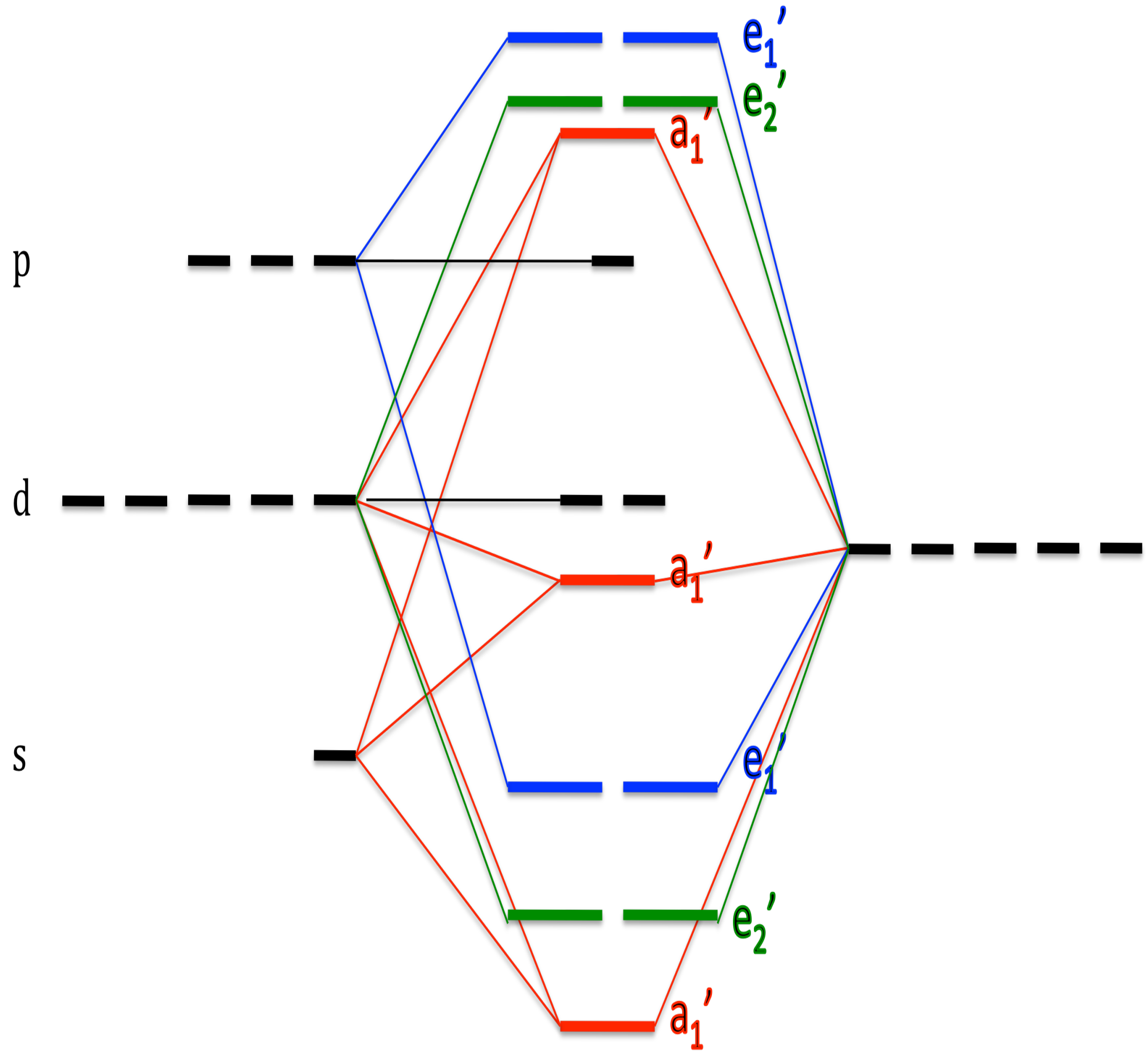
1b.

Orbital:	Transforms as:	Will this atomic orbital produce a MO with a SALC?
s	a_1‘	Yes
p_x	e_1‘	Yes
p_y	e_1‘	Yes
p_z	a_2“	No
d_{z^2}	a_1‘	Yes
$d_{x^2-y^2}$	e_2‘	Yes
d_{xz}	e_1“	No
d_{yz}	e_1“	No
d_{xy}	e_2“	Yes

1c.



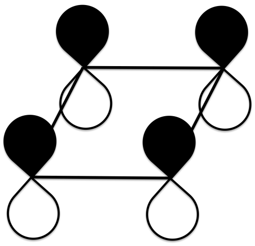
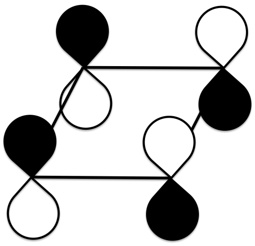
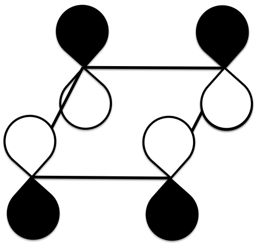
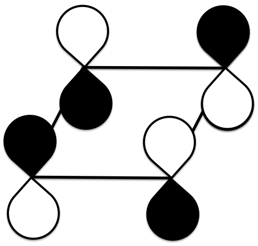
1d.



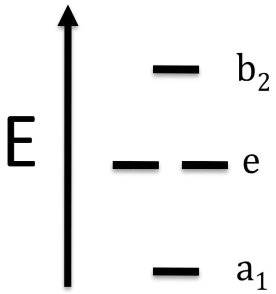
2a.

C_{4v}	E	2 C_4(z)	C_2	2 σ_v	2 σ_d
Γ	4	0	0	0	2
A_1	1	1	1	1	1
E	2	0	-2	0	0
B_2	1	-1	1	-1	1

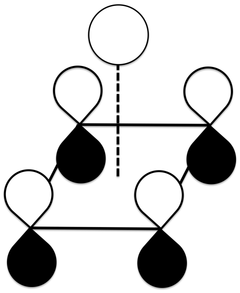
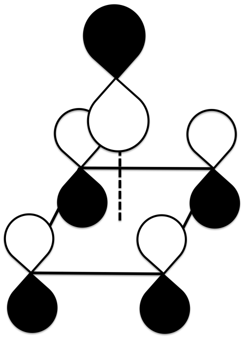
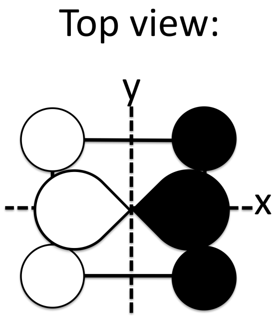
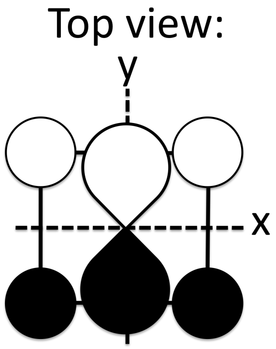
2b.

Zero nodes:	One node:	One node:	Two nodes:
			

2c.

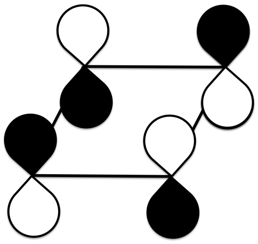


2d.

MO formed with M’s s-orbital?	with the p_z orbital?	with the p_x orbital? (Note: top view)	with the p_y orbital?
			
a_1	a_1	e	e

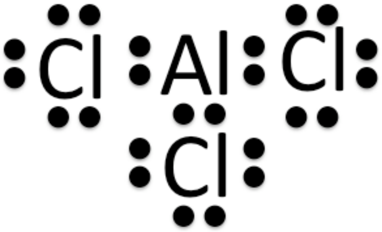
2e. b_2

2f.

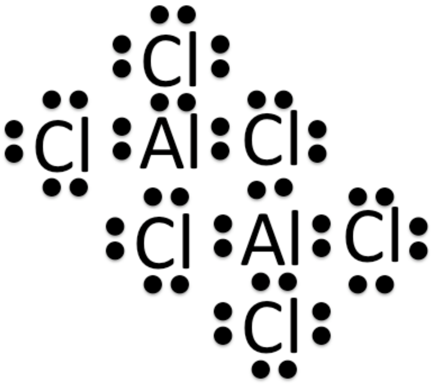


2g. d_{xy}

3a. (2 pts) Lewis acids are electron pair acceptors.



3b.



4a. H_3AsO_4

4b.

Arsenic acid H_3AsO_4

Arsenous acid H_3AsO_3

4c. If pK_{a1} is 3.2, pK_{a2} should be about 8 and pK_{a3} about 13

5a. Hard-soft acid-base theory

5b. LiI

6a. See notes, show derivation, step by step. Answer is $V = 16\sqrt{2}r^3$ or equivalent.

6b. 197 pm

6c. B, B

7. 52.4%

8a. (i) C; (ii) A

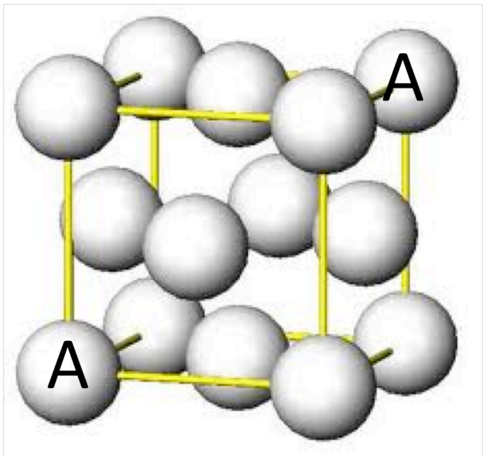
8b. (i) A; (ii) C

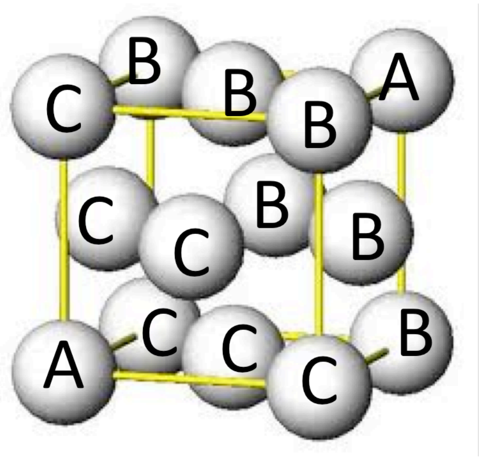
8c. (i) C; (ii); (iii) ZnS

9a. Cubic-close packed (ccp) lattices

(i) ABC

(ii) The most important thing to realize is that the cpp is the same as the fcc, only situated on its corner atoms, so that opposite corners are both Layer A, as shown in the figure at left. The B and C layers fill in as shown at right.





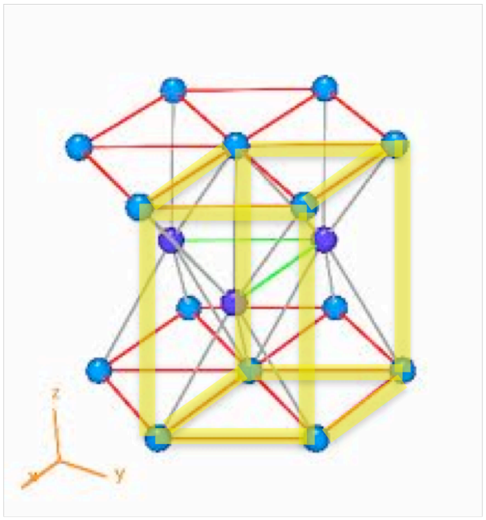
(iii) (3 pts) How many:

a. 4; b. 4; c. 8

9b. Hexagonal-close packed (hcp) lattices

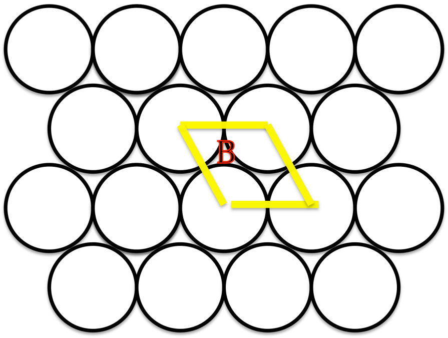
(i) C

(ii)



(iii) a. 2; b. 2; c. 4

(iv) and (v)



10a. XeF_2

10b. NiAs