2011

1. (4 points) Give the ground state electron configuration and identify as paramagnetic or diamagnetic:

a) Eu^{2+}

Eu [Xe] $4f^7 6s^2$

Eu^{2+} [Xe] $4f^7$ para

b) Mo^+

Mo [Kr] $4d^5 5s^1$

Mo^+ [Kr] $4d^5$ para

c) Se^{2-}

Se [Ar] $3d^{10} 4s^2 4p^4$

S^{2-} [Ar] $3d^{10} 4s^2 4p^6$ dia

d) Fe

Fe [Ar] $4s^2 3d^5$

2. Consider electron affinities for O, S, Se and Te.

a) **(2 points)** Distinguish between electron affinity and electronegativity?

EA energy for rxn $X(g) + e \longrightarrow X^-(g)$

EN ability of an atom, in a molecule, to attract electron density

b) **(2 points)** Is EA_1 positive or negative? Which will have the highest first electron affinity? Explain. EA_1 is generally negative and becomes less negative (generally) as you proceed down a group.
The most negative EA_1 is found for S (comparing O, S, Se, Te) although O is above it in periodic table, it is very small and incoming electron feels significant coulombic repulsn from other electrons in atom.

c) **(2 points)** Is EA_2 positive or negative? Which will have the largest second electron affinity? Explain. EA_2 always +ve → you are adding an electron to something that is already negative.

EA_2 largest for O → adding an e^- to a small high charge density ion.

3. Shown below for are the first ionization energies in kJ mol^{-1} for group 15 and 16 elements.

N: 1402	O: 1314
P: 1011	S: 1000
As: 947	Se: 941
Sb:834	Te: 869
Bi: 704	Po: 812

a) **(2 points)** Account for the ~~increasing~~ ionization energy as one proceeds down a group.

decreasing

– atoms getting large, e less strongly bound easier to remove

b) **(3 points)** Account for the decrease in ionization energy observed for N/O for P/S and As/Se.

removal of e⁻ from doubly occupied p vs. singly occupied p.

c) **(2 points)** Why is this trend not observed for Sb/Te and Bi/Po?

Sb/Te & Bi/Po are large; effect of coulombic repulsn between electrons not a significant

4. **(3 points)** Distinguish between an mineral, an ore and a rock.

mineral – defined structure
ore – has enough mineral to make it economic
rock – the stuff you skip

Bonus: What is your favourite mineral and why?

5. Determine the effective nuclear charge, based on Slater's rules, felt by

a) **(3 points)** 4d electron in silver

$(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2 4p^6)\overset{\downarrow}{(4d^{10})}(5s^1\ )$

$47 - 9(.35) - 36(1.00) = 7.85$

b) **(3 points)** 5s electron in

$47 - 18(.85) - 28(1.00) = 3.7.$

c) **(2 points)** Which electron will be ionized first and why? Does this make sense?

The e^- feeling lowest Zeff will be ionized 1st, ∴ 5s. This makes sense — based on expt we know 5s electrons are removed before 4d.

6. **(4 points)** MnO has a melting point of 1785 °C and Mn_2O_7 melts at 6 °C. Explain.

MnO high melting pt = Ionic
Mn^{2+} O^{2-}

Mn_2O_7 low melting pt, forces not bonds,
molecular covalent
Mn^{+7} is so small & high chrge density
O^{2-} is polarized to point bond no longer ionic

7. a) **(2 points)** What kind of bonding is found in solid $Mg(OH)_2$, $Ca(OH)_2$ and $Sr(OH)_2$? Explain.

ionic
metal cation / non metal anion
dissolves in water
ionic soln

b) **(1 points)** What trend in solubility was observed in the lab?

Increases from Mg → Ca → Sr

c) **(3 points)** Using concepts of bonding discussed in class explain the basis of this observed trend.

Strong ionic bond ≡ high chrge density ions. Mg^{2+} smallest, ∴ highest charge density, strongest bond, lowest solubility

8.**(6 points)** Given the data below predict the type of cubic unit cell and number of anions found in that cell for each of (radii: Ba^{2+} 135 pm, Cu^{+} 96 pm; Cu^{2+} 73, Li^{+} 59 pm, O^{2-} 140 pm, I^{-} 220 pm and S_2^{-} 198 pm)

a) BaO

135/140 = 0.96 Big Cation CsCl cell
1 cation 1 anion

b) CuI

96/220 = 0.43 medium fcc & octahedral hole
4 anions 4 cations

11

c) LiS_2

59/198 = 0.29 small tetrahedral hole.
- [illegible]

4 anions ^{5}4 cations → every second hole.

125pm

9. **(5 points)** A particular metal has density of 7.2 g/cm^3 and an atomic radius of 123 pm; assuming it adopts a bcc crystal structure, determine its molar mass and identify the metal.

$bcc = \frac{1}{8}(8) + 1$

$= 2$ atoms.

body center-

atoms touch along body diagonal

$c^2 = (4r)^2 = b^2 + a^2 = a^2 + a^2 + a^2 = 3a^2$

$a = \frac{4r}{\sqrt{3}}$

123×10^{-12} m

123×10^{-10} cm

$V = a^3 = \left(\frac{4(123 pm)}{\sqrt{3}}\right)^3 = 28.4\ (pm)^3 = 2.\cancel{8}9 \times 10^{\overset{-23}{-\cancel{28}}}\ cm^3$

Mass of unit cell = density × V = $7.2 g/cm^3 \times 2.84 \times 10^{-28} cm^3$

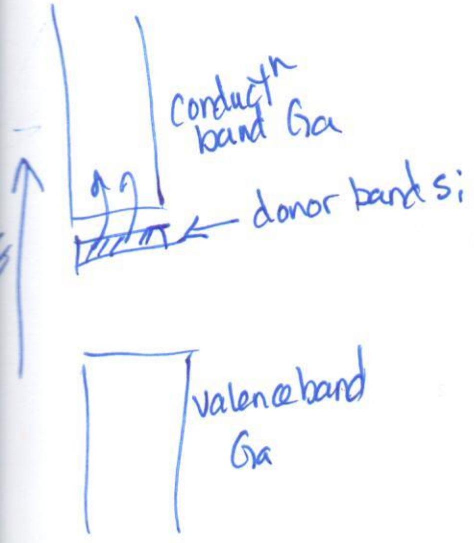
$= \cancel{2.0 \times 10^{-27}}$ g 1.65×10^{-22}

Mass per atom = $\frac{2.0 \times 10^{-27} \times 6.02 \times 10^{23}}{2}$ ~~mole~~ atoms/mol

$= 49.67$ g/mol → V

10. **(5 points)** Ga-doped Si is a semiconductor. Using band theory suggest whether it is n-type or p-type and explain how semiconducting properties arise.

Ga grp 13 Si is grp 14 (1 extra electron) ∴ n-type

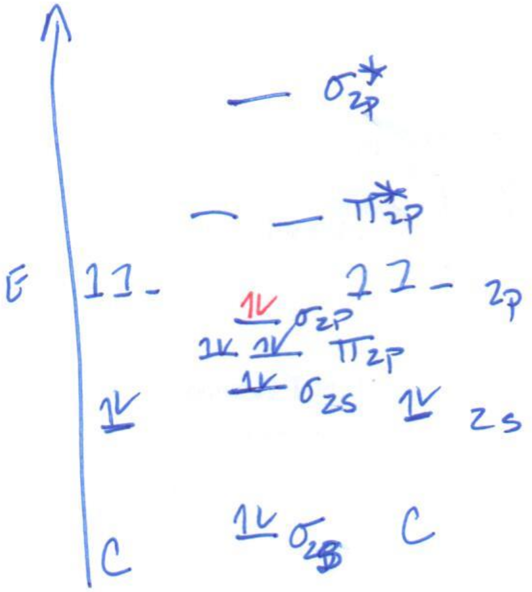


→ ~~A~~O (many many) combine to make a continuum of ~~va~~ orbitals, forming a conduct^n band lying several eV above the valence band. The Ga is doped with Si which is electron rich and the doped Si forms a donor band lying ~~the~~ within the band gap, and slightly below the conduction band. Electrons are readily promoted from the doping donor band to the empty conduction band.

These conduct^n band electrons can carry charge through the material.

11. (8 points) When acetylene (ethyne) C_2H_2 is passed through a solution of copper(I) chloride a red precipitate of copper acetylide, Cu_2C_2, is formed. This is a common test for the presence of acetylene. Describe the bonding in the C_2^{2-} ion in terms of molecular orbital theory (draw the appropriate diagrams) and compare the bond order to that of C_2.

Comment



1. ~~[illegible]~~ MOs can be approximated by linear combinat^ns of AOs.
2. form from AOs of similar energy & appropriate symmetry
3. # AOs = # MOs
4. Show only valence P ~~[illegible]~~ orbitals for simplicity
3. In carbon 2s & 2p orbitals similar in energy so you get 4 σ type orbitals from combination of (2s) orbitals on each C & (2p) on each → the orbital labelled σ_{2p} will be higher in energy than the π_{2p}

BO of $C_2 = \frac{1}{2}(6-2) = 2$

BO of $C_2^{2-} = \frac{1}{2}(8-2) = 3$

Bond order for C_2^{2-} is higher than that for C_2 indicating that the C_2^{2-} species has a stronger bond than would C_2. Thus C_2^{2-} will make a very stable ion.

1+ 3(5) = 16 electrons

10:42
9:30

12. a) **(5 points)** Hydrogen azide, HN_3, a liquid, will explode violently when subjected to a physical shock. Draw all possible Lewis structures, assign formal charge, and identify which structures are significant contributors, explain why they are/arent significant

$\overset{(0)}{H}-\underset{\times\times}{\overset{(0)}{N}}=\overset{(+1)}{N}=\underset{\times\times}{\overset{\times\times}{N}}(-1)$

$+1-\overset{(+1)}{N}\equiv\overset{(+1)}{N}-\underset{\times\times}{\overset{(-2)}{\overset{\times\times}{N}}}{}^{\times}_{\times}$

↖ high formal charge, not good.

owest formal charge

uble & triple bonds

e good

$\overset{(0)}{H}-\underset{\times\times}{\overset{(-1)}{\overset{\times\times}{N}}}-\overset{(+1)}{N}\equiv\overset{(0)}{N}{}^{\times}_{\times}$

b) **(5 points)** Identify the VSEPR shape and suggest valence bond hydridization about each nitrogen atom in the significant structures. Indicate bond angles and relative bond lengths (i.e. short nitrogen—nitrogen bond, longer nitrogen- nitrogen bond) on your structures.

$H-\underset{\times\times}{\overset{①}{N}}=\overset{②}{N}=\underset{\times\times}{\overset{③}{\overset{\times\times}{N}}} \longleftrightarrow H-\underset{\times\times}{\overset{①}{\overset{\times\times}{N}}}-\overset{②}{N}\equiv\overset{③}{N}{}^{\times}_{\times}$

ll N-N bonds same

grps sp^2 bond angle ~ 120

grps sp bond angle 180

grps sp^2 not relevent as terminal.

- one short N≡N bond; N-N longer

① 4grps, sp^3, bond angle ~ 109.5

② 2grps sp bond angle 180

③ 2grps sp not relevant

c) **(2 points)** Experimental studies have identified N - N bond lengths of 113 and 124 pm and a H-N-N bond angle of 112°. Does your predicted Lewis structure support these findings? Why or why not?

Two different bond lengths, 113pm would be between N ② & ③

124pm would be between N ① & ②

Bond angle of 112° is intermediate between trigonal planar (sp^2) shape & tetrahedral (sp^3) hybridization. shape. the two dominant resonance forms, so yes my Lewis structures support Lewis structure.

2007

1. **(2 points)** What is smelting and why was Cu smelting feasible 1000s of years before Fe smelting?

Smelting heat + reducing agent to make metal
Reducing agent could be coke.
Cu smelting before Fe because T required much lower.

2. **(2 points)** Name three of the six main mineral families in which metals are found in nature?

oxides
sulfides
silicates
phosphates
carbonates
halides.

3. What is the **ground state noble gas configuration** of and how many **unpaired electrons** are there in:

a) **(1 point)** Mo (Z=42) $[Kr]\ 5s^1 4d^5$ 6

b) **(1 point)** Co^{2+} (Z = 27) $[Ar]\ 3d^7$ 3

c) **(1 point)** P^{3-} (Z = 15) $[Ne]\ 3s^2 3p^6$ 0 unpaired

4) **(4 points) a)** For the ground state of Cd, [Kr] $4d^{10} 5s^2$

i) How many electrons have l = 2 as one of their quantum numbers? What are they?

s p d f
0 1 2 3

$l = 2$ means "d" for Cd there are 10 "3d" and 10 "4d electrons

ii) How many electrons have n =4 as one of their quantum numbers? What are they?

$n=4$ $4s^2$, $4p^6$ $4d^{10}$ = 18 electrons

iii) How many electrons have m_l = -1 as one of their quantum numbers? What are they?

$m_l = -1$ l = 1, 2.

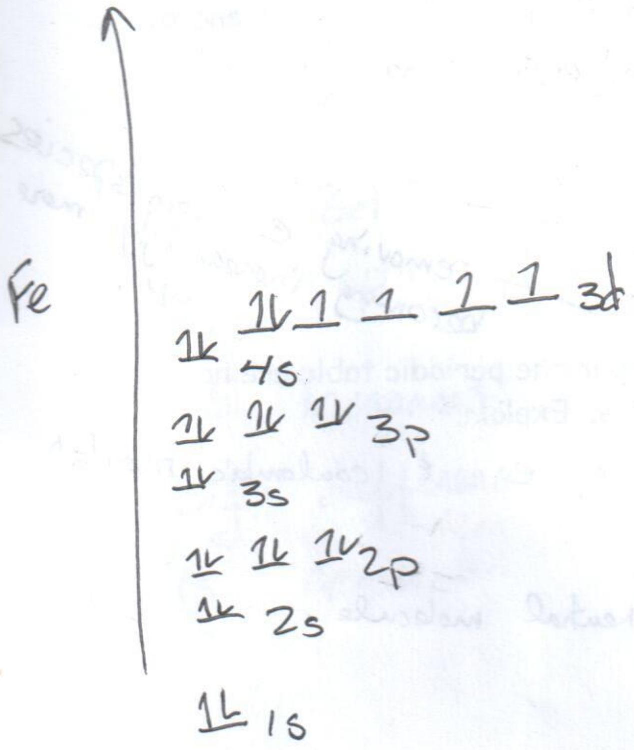
0 1 2 3
s p d f #

2p, (2)
3p, 3d (4)
4p, 4d (4)

10 electrons.

b) **(4 points)** Draw the complete atomic orbital energy diagram for Fe (in the ground state) showing how the electrons are distributed among the various orbitals. Ensure that your diagram is clearly labeled. Explain the significance of i) the Aufbau principle; ii) Hund's Rules; and iii) the Pauli Exclusion principle in the placement and orientation of electrons in this diagram.

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
26



i. Aufbau: Grnd state: e occupy lowest energy orbitals before moving to higher energy
4s filled then move on to 3d

ii) ~~Hund~~ Pauli
- every ~~od~~ e^- has its own address & no orbital has more than two e, one spin up $m_s = +\frac{1}{2}$ one spin dow ($m_s = -\frac{1}{2}$)

iii) ~~Paul~~ Hund's rules
Preferred electron config in energy degenerate orbitals is spin parallel.

5. a) **(3 point)** Indicate the smallest and largest species (atom or ion) in the following group: Al, F, As, Cs^+, I^- and N. Explain your answer.

Largest I^- 54 e^- 53 protons, isoelectronic with Cs^+ but lower effective nuclear charge on outer e^-, so larger.

F smallest number of shells (2nd period.) & located right on periodic table, high Zeff for 2nd period

b) **(3points)** You measure the electron affinities for elements from Al, Si, P, S and Cl and because you were never taught good lab skills, you write the energies without noting to which element they belong. The energies you record are -44, -348.7, -200.4, -74 and -120 kJ mol^{-1}. Using your knowledge of trends in EA, assign the measured EA to each of the atoms. Explain your answer.

EA should increase across periodic table left to right as Zeff increases

↑ _ _ ↑↑ _ ↑↑↑ ↑↓↑↑ ↑↓↑↓↑

Al Si P S Cl

Al -44
Si -120
P -74
S -200.4
Cl -348.4

Si / P switched as P you are adding e to ½ filled orbital

c) **(2 points)** Rank the following ions/atoms in order of increasing ionization energy. Explain your ranking.
S^{2-}, S^{2+}, S

Anions big, cations small
extra e.

$\overset{small}{S^{2+}} \longrightarrow S \longrightarrow \overset{big.}{S^{2-}}$

Ionizatn energy smallest $S^{2-} \longrightarrow S - S^{2+}$ — removing e from species becoming increasingly more +ve.

Bonus: The changes in EA as one goes down a group in the periodic table are not nearly as large as the variation in ionization energies. Explain.

EA balance between Zeff felt by incoming e & coulombic repulsn
Adding e to "neutral atom"

IE removing e⁻ from outer most orbital of neutral molecule.

6 a) **(1 point)** What is the electronic configuration for gallium ($_{31}Ga$)?

$[Ar]\,3d^{10}4s^{2}4p^{1}$

b) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 4s electron on Ga? $(1s^2)(2s^2\,2p^6)\underbrace{(3s^2\,3p^4)(3d^{10})}(4s^2\,4p^1)$

$Z_{eff} = 31 - 2(.35) - 18(0.85) - 10(1.00) = +5$

c) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 4p electron on Ga?

$+5$

d) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 3d electron on Ga?

$31 - 9(.35) - 18(1.0) = 9.85.$

e) **(1 point)** Based upon these values of effective nuclear charge, what trends do you expect of observe in terms of 1st, 2nd, 3rd, and 4th ionization energies? Be specific.

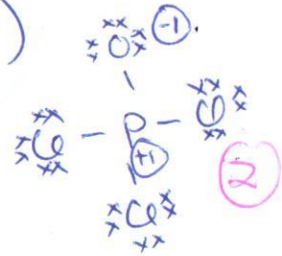
Since Zeff is much larger for 3d e I would expect 4th IP to be HUGE.

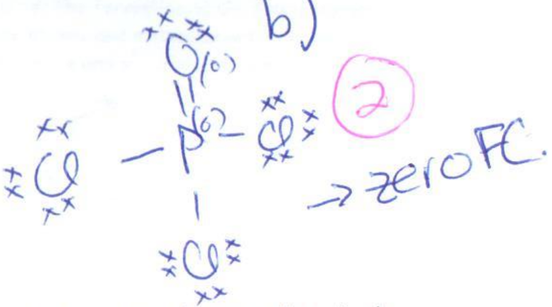
IE increases 1st to 2nd + 3rd than very big difference 4th when the 3d electron is removed.

7) **(4 points) a)** Draw two possible resonance Lewis structure for $POCl_3$ (use trends in electronegativity to identify the central atom) and determine the formal charge on each atom in the resulting molecules.

32 electrons

a)





b)**(1 point)** Based on calculation of formal charges on each atom in the molecule, which resonance structure is expected to be dominant?. Explain.

Stable structure will have 0 formal charge on all atoms → b

c) **(2 points)** Based on VSEPR theory, would you predict the same molecular geometry from each resonance structure? What electron configurations and molecular geometry are predicted?

Yes, 4 groups, therefore tetrahedral electron configuration, no lone pairs, therefore tetrahedral geometry

d) **(1 point)** What valence bond hybridization is dictated by these structures? Explain?

Tetrahedral so VB says sp^3

e) **(3 points)** In the valence bond analysis, what type of orbitals are involved in each of the central atom to terminal atom bonds?

P-Cl sp3 and p ; P-O sp3 and p; P-O d and p

↑ ↑ ↑ ↑ ↑ ↑

P Cl P Cl P Cl

if say σ for P-Cl & σ & π for P-O give +2

8) Based on VSEPR theory identify the geometry of the electron groups, the shape of the molecule, whether if the molecule is polar or non polar and the valence bond hybridization required for the predicted shape. Use the space provided to draw molecule as needed.

DRAW LEWIS STRUCTURE FOR MOLECULE HERE

a) (4 points) SeO_3

Geometry ______trigonal planar______

Shape______trigonal planar______

Bond angle___120 ______

Polar ?______no______

VB hybridization______sp2______

-0.5 for each error

b) **(4 points)** PH_3

Geometry ______tetrahedral______

Shape______trigonal ~~planar~~ pyramidal

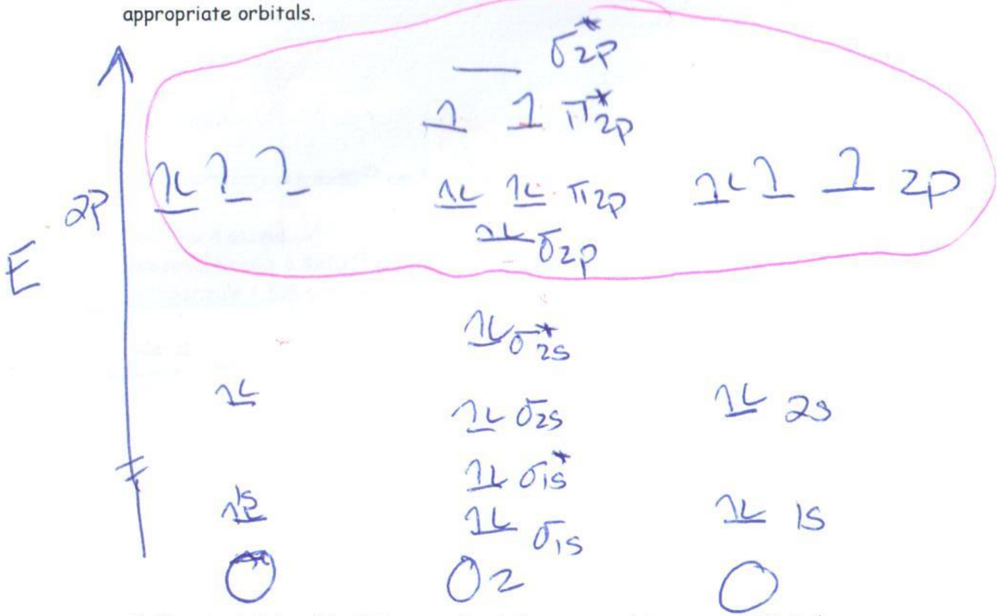
Polar ?______yes______

Bond angle______< 109.5______ if they say 109.5 -0.25

VB hybridization______sp3______

-correct # electrons -correct ordering MO -labelled σ σ* -ok if only showin P

9) a) **(4 points)** Construct MO diagrams for the formation of O_2. Your diagram should show the relative energies of the atomic and molecular orbitals and the molecular orbitals should be labeled as σ σ*, π and π*. Show the electrons in appropriate orbitals.



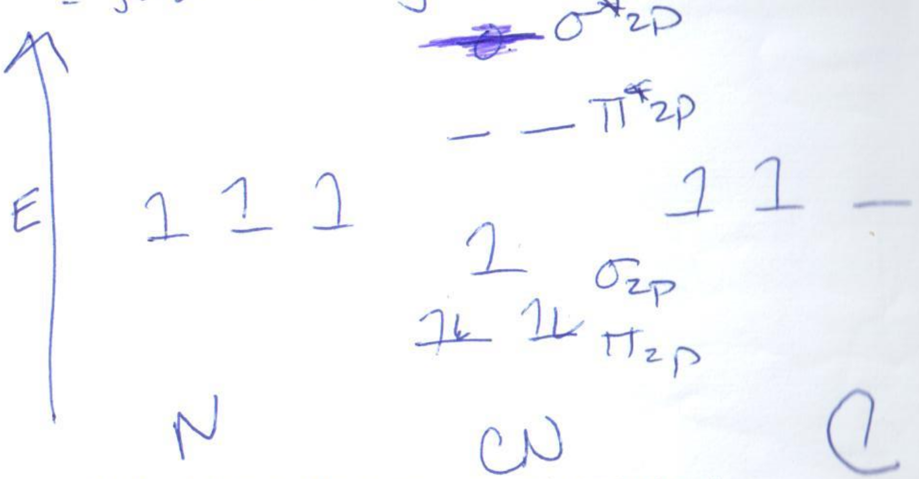
b) **(3 points)** Using this MO energy-level diagram, would you expect O_2 to have lower or higher first ionization energy than atomic oxygen? Explain.

Would expect O_2 to have a lower IE because the outermost electrons ion O_2 occupy antibonding orbitals, this means the highest occupied orbital will have higher energy in O_2 than in O

should have assumptions if any made

10) **(4 points)** Construct an MO diagram for CN. Your diagram should show the relative energies of the atomic and molecular orbitals and the molecular orbitals should be labeled as σ σ*, π and π* etc. Show the electrons in appropriate orbitals. Indicate clearly any assumptions you make in constructing this diagram.

- assume P orbital energy same for C
- assume "N or lower" MO ordering
- just showing P.



b) **(4 points)** Based on this diagram, determine the bond order and diamagnetism/paramagnetism of CN^-, CN, and CN^+. Which of these three species will have the shortest bond length.

CN^- $(\sigma 2s)2$ $(\sigma^* 2s)2$ $(\pi 2p)4$ $(\sigma 2p)2$ BO = 3 , dia(SHORTEST)
CN $(\sigma 2s)2$ $(\sigma^* 2s)2$ $(\pi 2p)4$ $(\sigma 2p)1$ BO = 2.5, para
CN^+ $(\sigma 2s)2$ $(\sigma^* 2s)2$ $(\pi 2p)4$ BO = 2, dia

① shortest = CN^-
(0.5) for each BO
0.5 for each para/dia.

11. **(5 points)** You are given a small bar of an unknown metal. The density of the metal is found to be 10.5 g cm^{-3}. X-ray diffraction experiments indicate the metal assumes a face centered cubic unit cell, with an atomic radius of 144.6 pm. What is your metal?

fcc → $8(\frac{1}{8}) + 6(\frac{1}{2}) = 4$ atoms

touch along face diagonal

$(4r)^2 = 2a^2$

$$a = \sqrt{\frac{(4r)^2}{2}} = \sqrt{\frac{(4 \times 144.6 \times 10^{-10}\,\text{cm})^2}{2}}$$

$$= 4.09 \times 10^{-8}\,\text{cm}$$

$V = a^3 = 6.84 \times 10^{-23}\,\text{cm}^3$

mass $= 6.84 \times 10^{-23} \times 10.5\,\text{g/cm}^3 = 7.18 \times 10^{-22}\,\text{g}$ (4 atoms)

$= 1.796 \times 10^{-22}\,\text{g}$ 1 atom

$M = m \times N_A = 108.2\,\text{g}$ $\underline{\underline{\text{Ag}}}$

12) **(2 points)** Carbonic acid (H_2CO_3) is a weak acid formed when CO_2 is bubbled through water. Write the chemical reactions that occur as a result of hydrolysis of carbonic acid and its conjugate base.