

20 September 2011

1. (1 pt each) Multiple Choice. What explanation accounts for these observations about periodic trends?

(a) The first ionization energy increases from left to right across the periodic table because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

(b) The atomic radius decreases from left to right across the periodic table because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

(c) The effective nuclear charge *in general* increases from left to right across the periodic table because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

(d) The electron affinity is zero for some groups despite the general trend because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

(e) The first ionization energy decreases from top to bottom within any family group of elements on the periodic table because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

(f) The atomic radius increases from top to bottom within any family group of elements on the periodic table because of...

- A. electronegativity. B. effective nuclear charge. C. atomic number.
D. the energy diagram. E. filled shells/subshells.

2. (3 pts) Why is the electron affinity larger for chlorine than for fluorine, even though the electronegativity is larger for fluorine?

3. Slater's rules and effective nuclear charge.

(a) (2 pts) Calculate the shielding felt by a valence electron on sulfur.

(b) (2 pts) Calculate the effective atomic number felt by a valence electron on bromine.

(c) (2 pts) Calculate the shielding felt by a valence electron on nickel.

4. Lewis dots, molecular geometry, resonance, paramagnetism and formal charge.

- (a) (6 pts) The compound AsF_2O is not known, however, we can predict the shape of the molecule, whether or not it has resonance, and whether it is paramagnetic or diamagnetic. Predict (i) its expected geometric shape, (ii) the number of resonance structures (if any) and (iii) its magnetic character.

- (b) (4 pts) The compound NOBr is known and resembles an interhalogen such as ICl . Sketch the Lewis dot structure of NOBr and assign formal charges to establish which is the best central atom (N or O or Br).

- (c) (6 pts) Continuing on with NOBr , predict (i) its expected geometric shape, (ii) state whether or not it has resonance and (iii) its magnetic character.

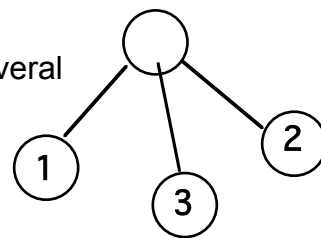
(d) (8 pts) Lewis never intended for us to use his method with the d-block elements. Nevertheless, we can sometimes do so for the very early (leftmost) transition metals. Using Lewis dot structures, predict the structures of:

(i) ScCl_3	(ii) TiCl_4	(iii) VF_3	(iv) CrO_3

(e) (3 pts) In order to reduce formal charge, we can draw resonance forms that expand the central atom's octet for those elements beyond $n = 2$. For example, this can be used to sketch resonance structures with minimal formal charge separation for SO_3^{2-} . Do so here:

5. Symmetry.

(a) (8 pts) Trigonal pyramidal species such as NCl_3 or SO_3^{2-} exhibit several properties of symmetry. Perform the symmetry operations listed below (in the boxes) on this numbered trigonal pyramidal species and give the results by writing the numbers 1, 2 and 3 in the circles provided.



E	C_3 (clockwise)	C_3 (counterclockwise)	σ_v

(b) We learned about several important symmetry operations including rotation axes, mirror planes (horizontal, vertical and diagonal), the inversion center, and identity. The molecule benzene belongs to the point group D_{6h} .

(i) (10 pts) Identify all of the rotation axes present. There are five unique rotation axes that add up to a total of eleven rotations. Complete the table in the format of the example (which is just an example and **not** a possible rotation axis for benzene.)

Rotation axis:	Number of equivalent axes (degeneracy)	Description of how the axis is related to the principle rotation axis
C_4	two	\perp to principle axis

(ii) (1 pt) Which one is the principle rotation axis?

(iii) (6 pts) Continuing with benzene, identify all of the mirror planes present. There are three unique mirror planes that add up to a total of seven mirror planes. Complete the table as you did above.

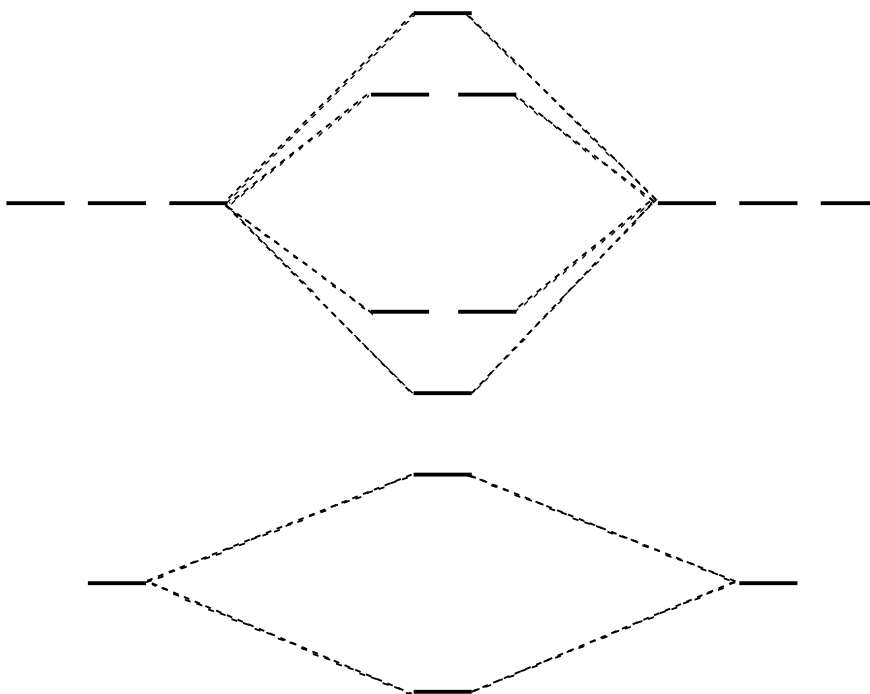
Mirror plane:	Number of equivalent mirror planes (degeneracy)	Description of how the mirror plane is related to the principle rotation axis

(iv) (2 pts) Benzene continued. Does benzene exhibit the symmetry operations E and i ?

E (identity)	i (inversion center)
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6. Molecular Orbital Theory. The diiodine cation, I_2^+ , is a rather rare species. It is prepared by oxidizing diiodine in oleum (a solution of sulfur trioxide in concentrated sulfuric acid) and the resulting solution is blue in color.

(a, 8 pts) Complete the MO diagram for I_2^+ by adding the appropriate number of electrons to the MO portion, labeling the atomic orbitals (2s or 2p) and every MO with either σ , σ^* , π or π^* .



(b, 1 pt) Is I_2^+ paramagnetic or diamagnetic? Circle your answer.

(c, 2 pts) What is the bond order in I_2^+ ? Show calculation.

(d, 4 pts) Sketch a drawing of each MO next to the MO energy line. Use the appropriate atomic orbital shapes as components (circles for s-orbitals, bowtie shapes for p-orbitals)

(e, 1 pt) Free iodine, I_2 , has a bond length of 266 pm. The I-I bond length in I_2^+ is either 256 pm or 276 pm. Which one is it?

(f, 5 pts) Which of these species could exist, at least in terms of MO theory? (More than one correct answer.)

- (i) I_2^{3-} (ii) I_2^{2-} (iii) I_2^- (iv) I_2^{2+} (v) I_2^{3+}

Answers.

1. (a) B; (b) B; (c) C; (d) E; (e) D; (f) E

2. Some people made a reasoned argument based on Z_{eff} , which is 5.2 for F and 6.1 for Cl. Others noted the larger size of Cl could probably accommodate the anion-forming electron better and have a larger ΔH .

3. (a) 10.55 p+; (b) 7.6 p+; (c) 20.45 p+

4(a) (6 pts) The compound AsF_2O is not known, however, we can predict the shape of the molecule.

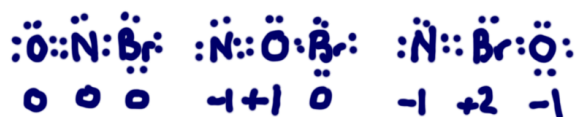
(i) Predict its expected geometric shape. Answer: trigonal pyramid (AB_3E)

(ii) Predict the number of resonance structures (if any). Answer: There are three reasonable resonance forms as shown here. The left one gives oxygen a $\text{FC} = -1$, but also an octet. The middle one gives the octet to arsenic and all FC are 0. The one at right, expands arsenic's octet to minimize FC (all are 0) while leaving the oxygen with an octet. Some atom has to have a non-octet value, and in this third structure, it is arsenic with 9 electrons. All three forms are reasonable.



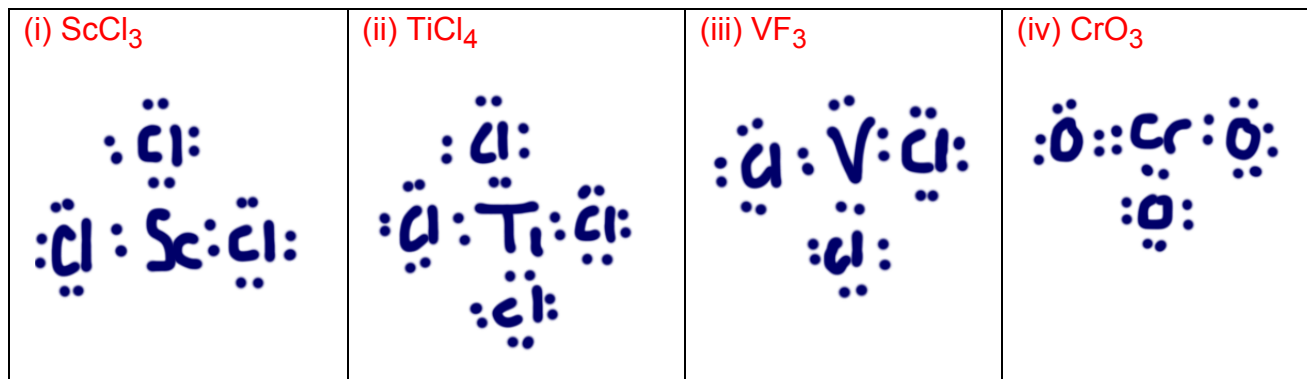
(iii) Predict its magnetic character. Answer: paramagnetic

4(b) Here are three structures (top row) showing each atom as the central atom. The best one is clearly the first one in which nitrogen is the central atom. The middle one has +1 and -1 formal charges, which isn't by itself a terrible thing, however, very electronegative oxygen has $\text{FC} = +1$, which is not good. The structure shown in the second row is not unreasonable at first blush. It uses bromine's ability to expand its octet to achieve formal charges less than ± 2 . Expanding the octet is largely limited to fluorine chemistry, however, so this structure is probably not very reasonable after all, leaving us with the very first one as our final choice.



4(c) (i) Predict its expected geometric shape (Answer: bent), (ii) state whether or not it has resonance (Answer: No) and (iii) its magnetic character (Answer: diamagnetic).

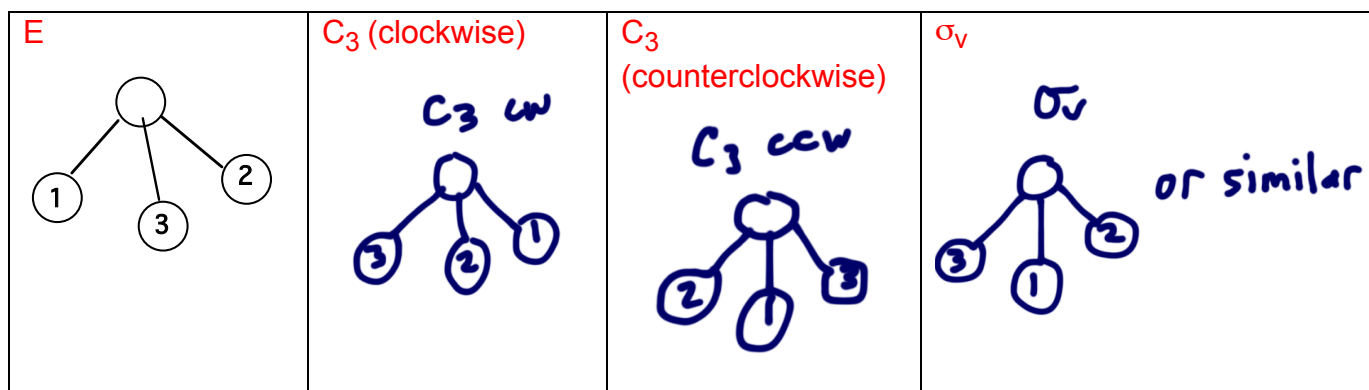
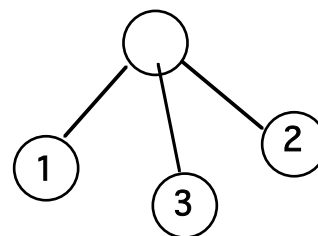
4(d) (8 pts) Lewis never intended for us to use his method with the d-block elements. Nevertheless, we can sometimes do so for the very early (leftmost) transition metals. Using Lewis dot structures, predict the structures of:



4(e) By sketching double bonds between sulfur and oxygen for one (not three) of the oxygen atoms, one achieves a structure with minimum formal charges for all atoms. Using two or three double bonded oxygen atoms to sulfur creates a FC = -1 or -2 for sulfur, respectively. Of course, there are three equivalent resonance structures with this expanded octet structure. Keep in mind that these expanded octet structures are debatable unless F is the B group.

5. Symmetry.

5(a) (8 pts) Trigonal pyramidal species such as NCl_3 or SO_3^{2-} exhibit several properties of symmetry. Perform the symmetry operations listed below (in the boxes) on this numbered trigonal pyramidal species and give the results by writing the numbers 1, 2 and 3 in the circles provided.



5(b) We learned about several important symmetry operations including rotation axes, mirror planes (horizontal, vertical and diagonal), the inversion center, and identity. The molecule benzene belongs to the point group D_{6h} .

- (i) (10 pts) Identify all of the rotation axes present. There are five unique rotation axes that add up to a total of eleven rotations. Complete the table in the format of the example (which is just an example and not a possible rotation axis for benzene.)

Rotation axis:	Number of equivalent axes (degeneracy)	Description of how the axis is related to the principle rotation axis
C_6	two	contains principle axis
C_3	two	identical to C_6^2 and contains principle axis
C_2	one	identical to C_6^3 and contains principle axis
C_2	three	\perp to principle axis and runs through two atoms
C_2	three	\perp to principle axis and runs mid-bond between two pairs of atoms

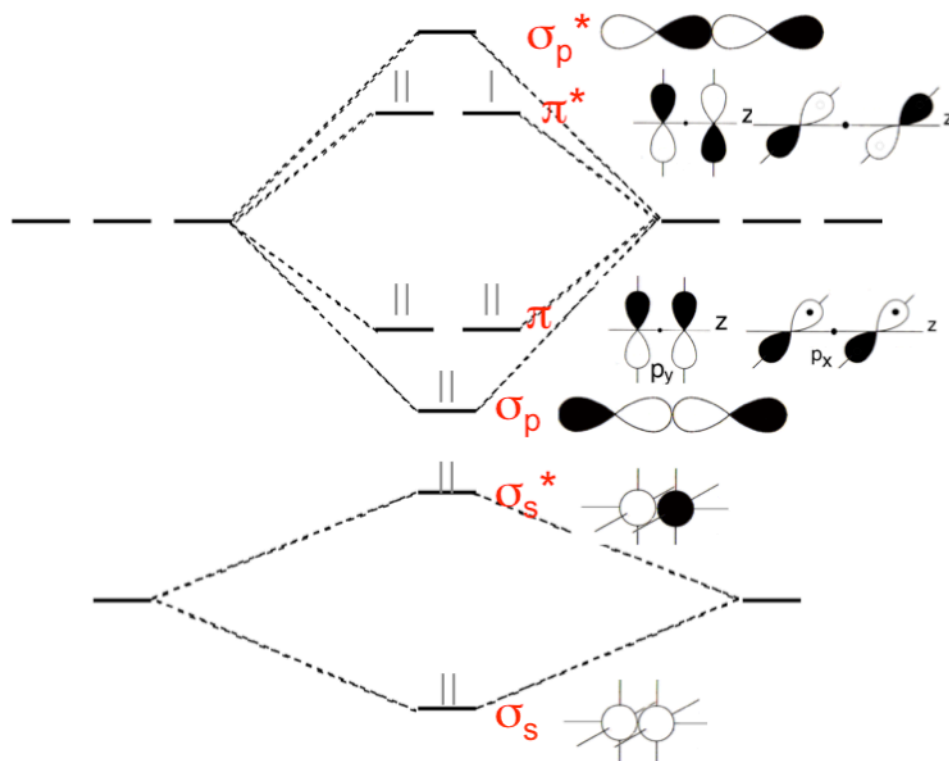
- (ii) C_6 is the principle rotation axis?

- (iii) (6 pts) Continuing with benzene, identify all of the mirror planes present. There are three unique mirror planes that add up to a total of seven mirror planes. Complete the table as you did above.

Mirror plane:	Number of equivalent mirror planes (degeneracy)	Description of how the mirror plane is related to the principle rotation axis
σ_h	one	\perp to principle axis
σ_v	three	contains principle axis and two carbon atoms
σ_d	three	contains principle axis and bisects carbon-carbon bonds

- (iv) Yes to both

6a.



b. paramagnetic

c. 1.5

d. see diagram

e. 256 pm

f. (iii) I_2^- (iv) I_2^{2+} (v) I_2^{3+}