Chem 101 2017 Discussion #13 Chapter 10. Correlation diagrams for diatomic molecules.

Key

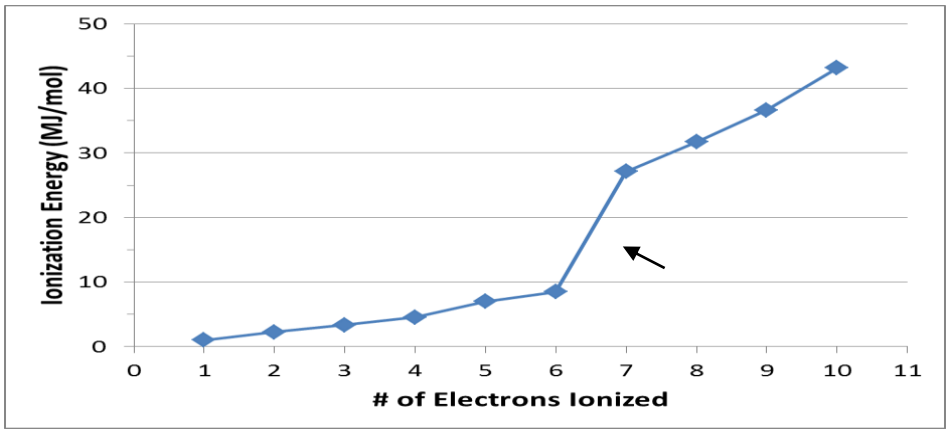
1. Below is a plot of the first 10 ionization energies for a single atom in 3rd row of the periodic table. The x-axis shows which ionization (e.g. IE_1, IE_2, etc) and the y-axis gives how much energy in MJ/mo

   a. What 3rd row element does the plot show? **S**
   b. First ionization energy IE_1 is 10.36eV calculate Z_{eff} for that element.
   (Useful information: 1ev=1.6021766·10^{-19}J; N_A = 6.022140857 × 10^{23}/mol;

   $IE = E_\infty - E_{initial} = 2.179 \cdot 10^{-18}(J)\frac{Z_{eff}^2}{n^2} = 13.6(eV)\frac{Z_{eff}^2}{n^2} = 1312(kJ/mol)\frac{Z_{eff}^2}{n^2}$)(Answer:2.62)

   $10.36 = E_\infty - E_{initial} = 13.6(eV)\frac{Z_{eff}^2}{n^2}$ and n=3; Z_{eff}=2.62

   c. The arrow points to the jump between the 6th and 7th ionization energy. Which of the following statements are true?
      i. The number of protons (Z) changed.
      ii. <u>The effective nuclear charge (Z_{eff}) changed.</u>
      iii. <u>The quantum number n of the electron that is ionized changed.</u>
      iv. <u>The radius of the ion decreased</u>



2. From the following neutral atom electron configurations, label the one with the highest *third ionization energy*, and lowest *third ionization energy*. Explain your answers.
   a. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ highest
   b. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
   c. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ lowest

3. Write the ground state electron configuration for Al, Al^{3+}, V, V^{3+}

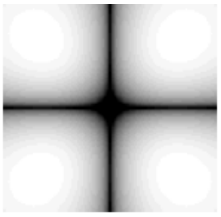
Al	=	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	paramagnetic
Al^{3+}	=	$1s^2\ 2s^2\ 2p^6\ 3s^0\ 3p^0$	diamagnetic
V	=	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	paramagnetic
V^{3+}	=	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^2$	paramagnetic

4. Answer the following questions about manganese (Mn):
   a. What is the electron configuration?

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

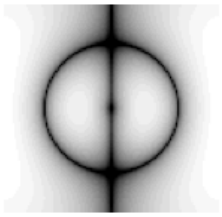
a. What are *n*, *l*, and *j* (number of loops) for one electron in each of the occupied electron clouds? **C and F not occupiee**

3d



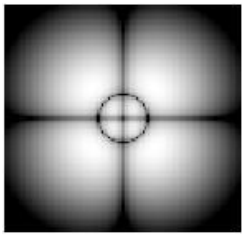
A

3p

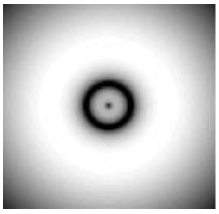


B

4d



C



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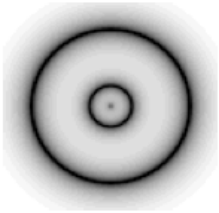
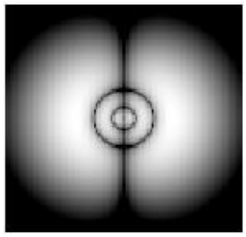


E



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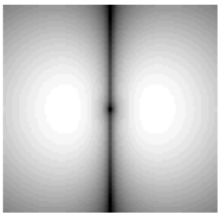

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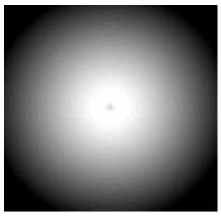
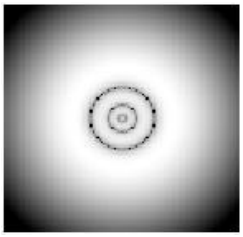


H



I

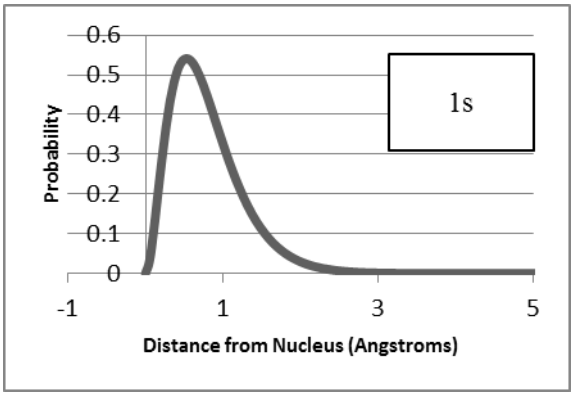
a. For the pictures below fill in the empty boxes with corresponding names of the orbitals(1s,2s,3s, 4s, 2p,3p,3d)

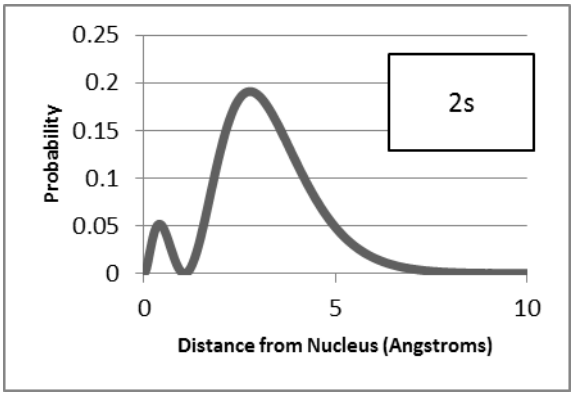
b. Use the radial probability densities below (electron cloud cross section below) to **estimate** the size of an atom of Mn. (Look at the x axis)

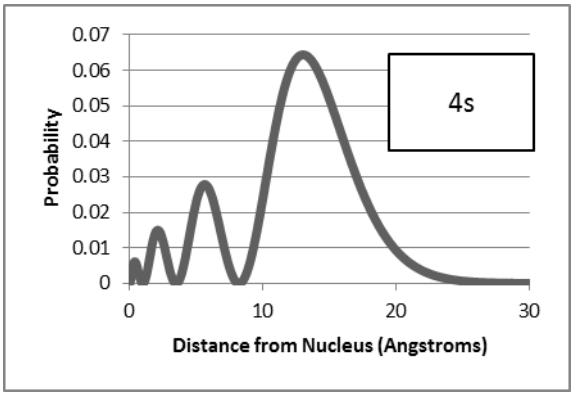
b. First ionization energy IE_1 is 7.43eV calculate Z_{eff} for that element(Answer:2.96)

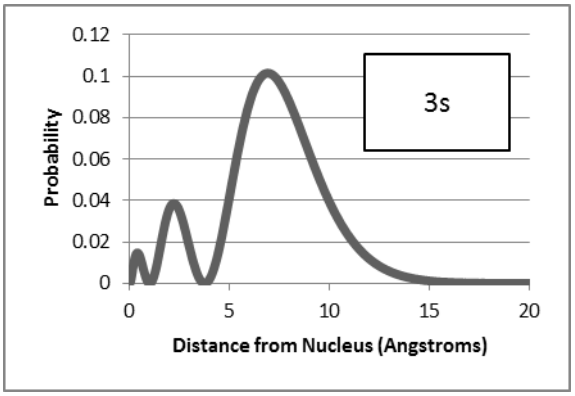
$$IE = E_\infty - E_{initial} = 13.6(eV)\frac{Z_{eff}^2}{n^2} = 7.43eV \text{ and } n=4;\ Z_{eff}=2.96$$

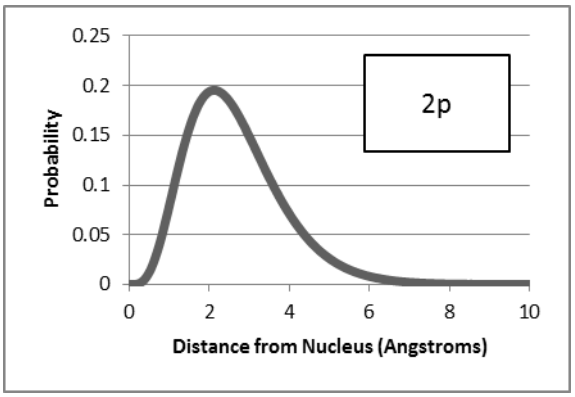
a. Use the radial distribution functions below to **estimate** the size of an atom of Mn.
4s IS THE BIGEST ORBITAL radius will be ≈15A; 15A·2≈30A

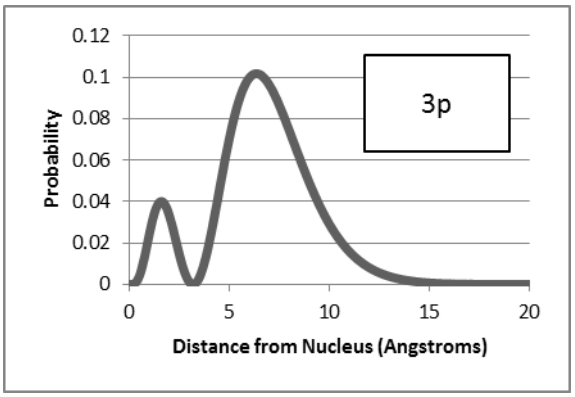


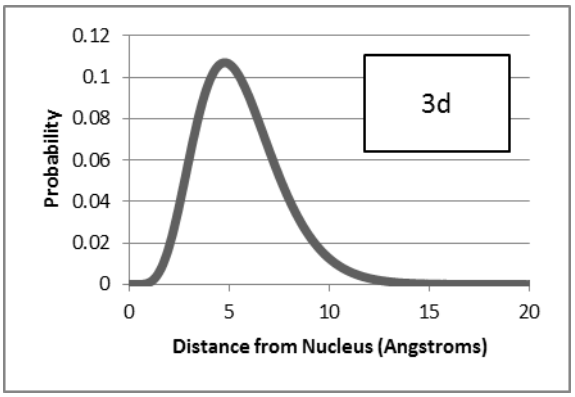












5. Which one will have the greatest ionization energy? Na^+ , Ne, F^- ,O^{2-}.

Na^+ highest

6. Rank the following in terms of increasing ionization energy: Na, Li, B, N, Ne

Na<Li< B< N<Ne

7. Rank the following in terms of increasing ionization energy: Li^+, B^+, N^+, Ne^+, Na^+

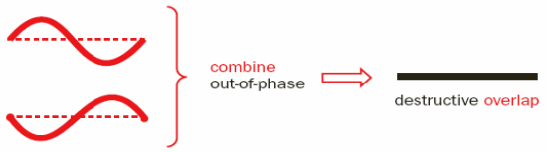
$B^+ < N^+ < Ne^+ < Na^+ < Li^+$

Things you should know when you leave Discussion today

- **Atomic Orbital** (s, p, d, f) vs.
  Molecular Orbital (σ, σ^*, NB, π, π^*, π_{nb})

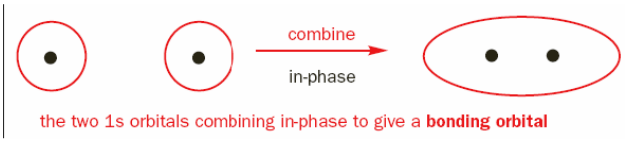
  a. **Total Number of MO =Total Number of AO**

- Constructive and destructive interference (in phase and out-of-phase interaction)

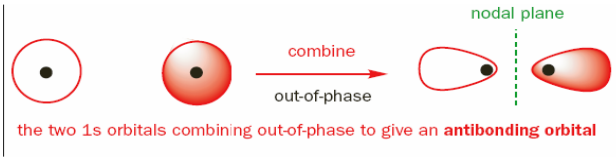


  a. Sigma bond is achieved by head–on–overlap

  b. **Bonding MO** (σ, π) - Constructive interference in phase interaction

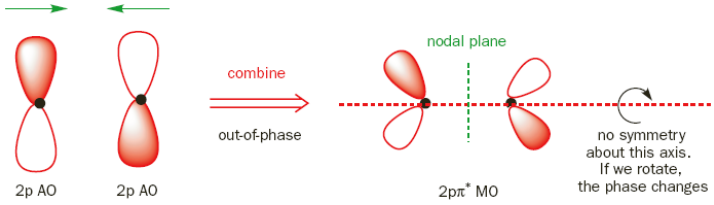


  c. **Antibonding MO** (σ^*, π^*) - Destructive interference out-of-phase interaction

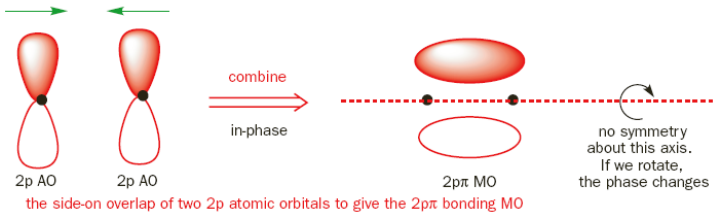


  d. ***π*** formed from side-by-side overlap of available ***p*** AO

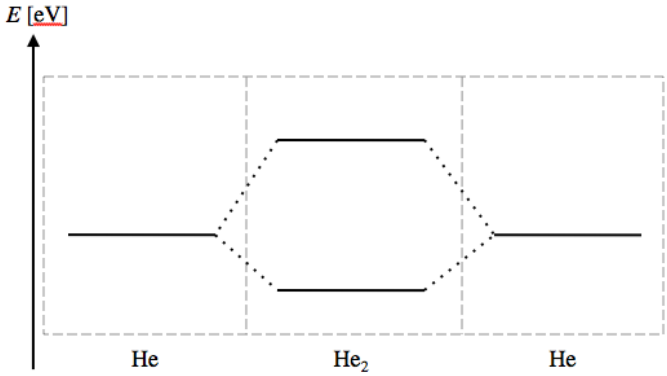
    - ***π**** is out-of-phase overlap of available ***p*** AO

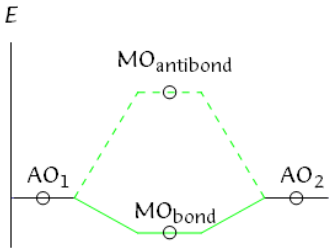


    - ***π*** is in-phase side-by-side overlap of available ***p*** AO



1. Draw correlation diagram for He_2^+:
Keep in mind that: 1sσ* is more unstable than 1sσ is stable.





a. What is the bond order of He_2^+? 0.5

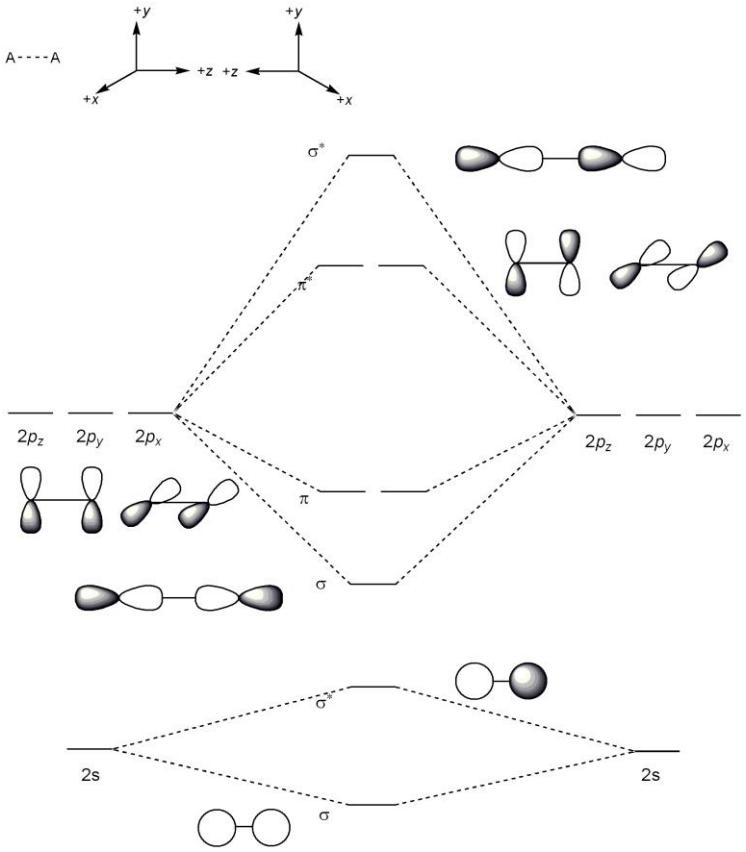
b. Put in the order of increasing bond length H_2; H_2^+ and He_2^+. (hint : find the bond orders for all the molecules or molecular ions)

bond length: $H_2 < H_2^+ < He_2^+$
BO: 1 0.5 0.5

2. Draw the correlation diagram for the HeH molecule. Which molecule or molecular ion will have the shortest bond HeH^{3+},HeH^{2+}, HeH^+, HeH, HeH^-? (Answer: HeH^+)

	HeH^{3+}	HeH^{2+}	HeH^+	HeH	HeH^-
BO:	0	0.5	1	0.5	0

- General MO Correlation Diagram for second row in the Periodic table.

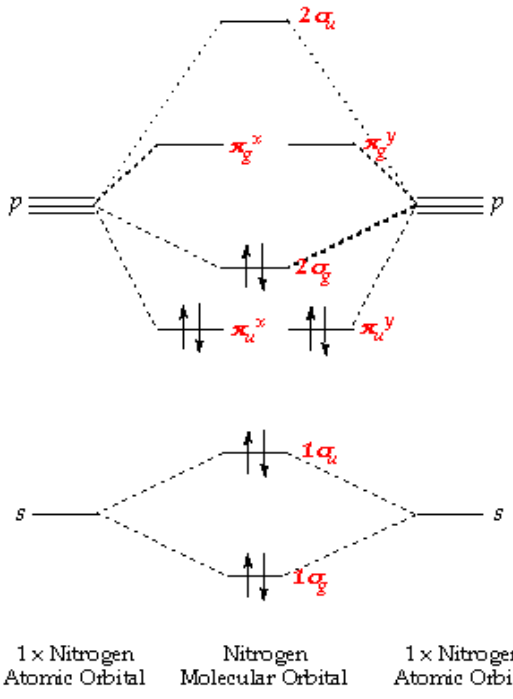


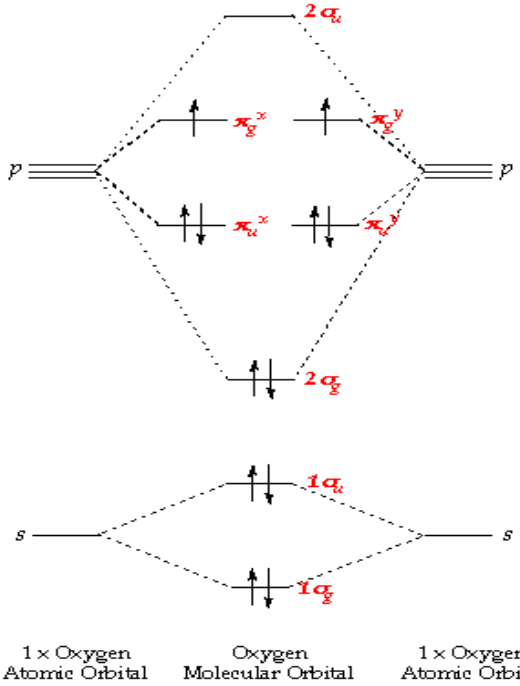
a. **Bond Order**

$$B.O. = \left[\frac{(\#\ of\ \ e\ in\ \ filled\ bonding\ orbitals) - (\#\ of\ \ e\ in\ \ filled\ antibonding\ orbitals)}{2} \right]$$

or

$$B.O. = (\#\ of\ \ filled\ bonding\ orbitals) - (\#\ of\ \ filled\ antibonding\ orbitals)$$





1. Draw two AO energy diagrams for the atoms in O_2^- one atom on the left and one atom on the right, leaving space in the middle. Draw a picture of each AO. Draw the MO energy diagram and pictures of the resulting MOs in between and fill them with the electrons for the molecule.

a. Draw the MO diagram(hint : count how many AO you start with and how many valence electrons you have)

b. Calculate the bond order. (8-5)/2 = 1.5

c. Is O_2^- diamagnetic or paramagnetic? Yes

d. Write the molecular electron configuration. $(1\sigma_{2s})^2(1\sigma_{2s}^*)^2(2\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$

e. If an electron is removed, will this make the bond longer or shorter? shorter

2. (At home on a separate piece of paper) Draw two AO energy diagrams for the following atoms in [C_2, N_2, O_2, F_2, F_2^+, F_2^-], one atom on the left and one atom on the right, leaving space in the middle. Draw a picture of each AO. Draw the MO energy diagram and pictures of the resulting MOs in between and fill them with the electrons for the molecule.

a. Calculate the bond order for each molecule.
b. Discuss which of the molecular orbitals are responsible for single, double bonds, etc.
c. Discuss the relative length, reactivity and 'strength' of these bonds.
d. What are the magnetic properties of these molecules? (Which one is diamagnetic and which one is paramagnetic.

TF's name:_____ Your name: _____ Discussion Section: _____