Inorganic Chemistry with Doc M.

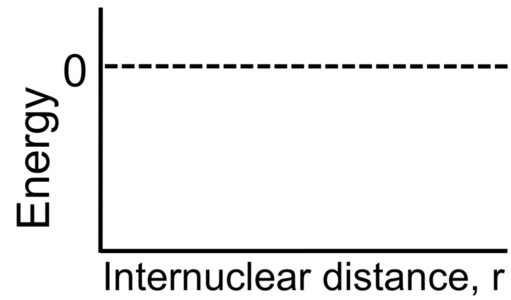
Day 6. Molecular Orbitals, Part 1

Topics:

1. MO diagram for two σ-orbitals
2. Symmetry
3. Homonuclear Diatomic Molecules
4. Heteroatom diatomic molecular orbitals

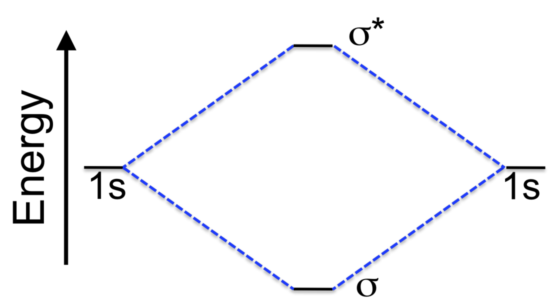
1. Molecular orbital diagram for two σ-orbitals:

A. From P-Chem, sketch on the plot of total energy (y) vs internuclear distance, r, for two hydrogen atoms. Somewhere on the plot, sketch what you picture what the hydrogen's s-orbitals look like at the energy minimum (overlapping?)



B. The hydrogen bond can be thought of as a linear combination of atomic orbitals, or simply a molecular orbital. Write the equation for the bonding molecular orbital MO for hydrogen, Ψ, from two atomic orbitals, Ψ_A and Ψ_B. Repeat for the antibonding orbitals.

C. The molecular orbital energy diagram for hydrogen, H_2 is given at right. The "outer" orbitals, labeled "s" are the two 1s atomic orbitals from the two hydrogen atoms. Add the labels "H $_A$" and "H_B" above the two s orbitals and place one electron ($1s^1$) in each orbital.

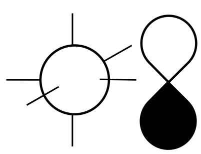


The outer atomic orbitals can be thought of as "the before" and the middle orbitals, the resulting molecular orbitals, can be thought of as "the after." Populate the MOs with the two electrons from the atomic orbitals, AOs.

D. Sketch the bonding and antibonding molecular orbitals using circles to represent the two atomic orbitals .

2. Symmetry.

A. There are three conditions for the formation of a molecular orbital: matching symmetry (constructive overlap must be possible), similar energy and appropriate internuclear distance (not too large). The first condition, matching symmetry, needs a bit more discussion. Sketch a p-orbital and show how it could overlap with an s-orbital, (a) with the s-orbital positioned along the p-orbital's primary axis, that is on the end of one lobe and (b) saddled up along the side. Use orbital sketches like those shown below. In one instance, there is no net overlap because the s-orbital overlaps equally with the + and – lobe of the p-orbital. This leads to no gain and is considered symmetry disallowed — we can ignore these sorts of overlaps.

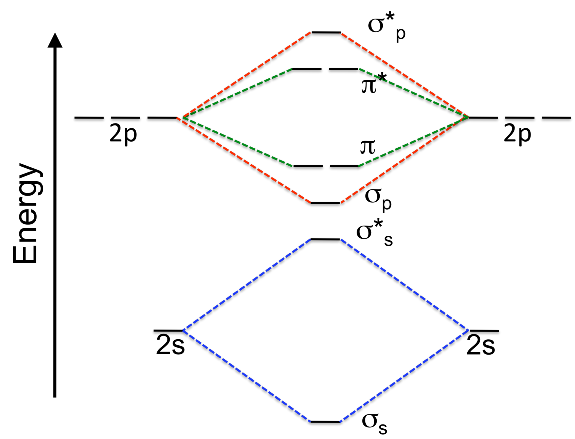


B. Repeat this with two p-orbital. Label the two orbitals you have sketched σ (direct overlap) and π (through space overlap).

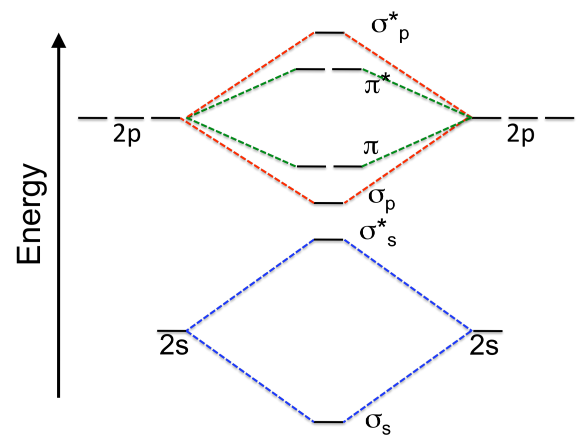
3. Homonuclear Diatomic Molecules

A. For atoms with s and p-orbitals only, such as B, C, N, O, and F, the σ-MOs (from s-orbitals) and the σ- and π-MOs from the p-orbitals, come together as shown here. This is the generic MO diagram for two identical atoms such as F_2 and O_2. Populate the MO diagrams for F_2 and O_2.

F_2



O_2



B. Bond order. Bond order is given by the equation:

Bond order = (number of bonding electrons – number of antibonding electrons)/2

Determine the bond order for both F_2 and O_2.

C. Electron configurations for molecular orbitals. Electron configurations for molecular orbitals can be written as shown for the example for F_2. Complete the electron configurations for O_2:

F_2: $(\sigma_s)^2\ (\sigma_s{}^*)^2\ (\sigma_p)^2\ (\pi)^4\ (\pi^*)^4\ (\sigma_p{}^*)^0$

O_2: $(\sigma_s)\ \ (\sigma_s{}^*)\ \ (\sigma_p)\ \ (\pi)\ \ (\pi^*)\ \ (\sigma_p{}^*)$

Determine the number of unpaired electrons for both F_2 and O_2.

Sketch a MO energy diagram for the superoxide ion, O_2^-.

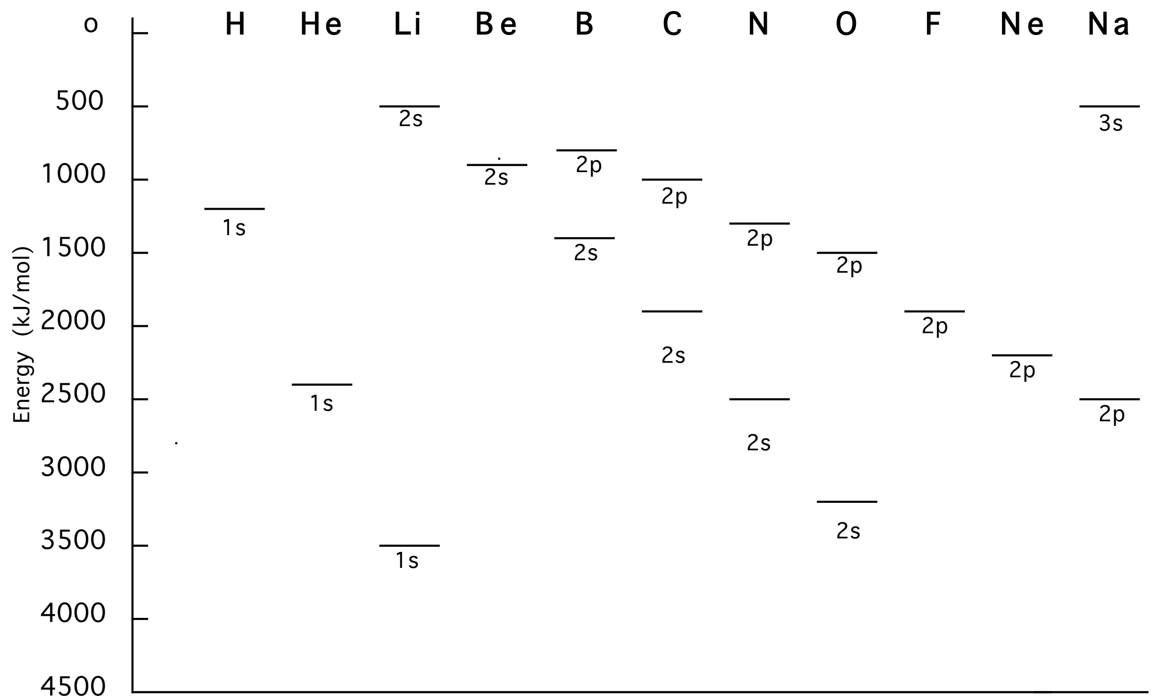
Based on your energy diagram for superoxide,

(a) What is the bond order?
(b) Write the electron configuration for superoxide.
(c) Is the superoxide ion diamagnetic or paramagnetic?
(d) Which would have a stronger oxygen-oxygen bond, molecular oxygen or the superoxide ion?
(e) Which would have a shorter oxygen-oxygen bond, molecular oxygen or the superoxide ion?

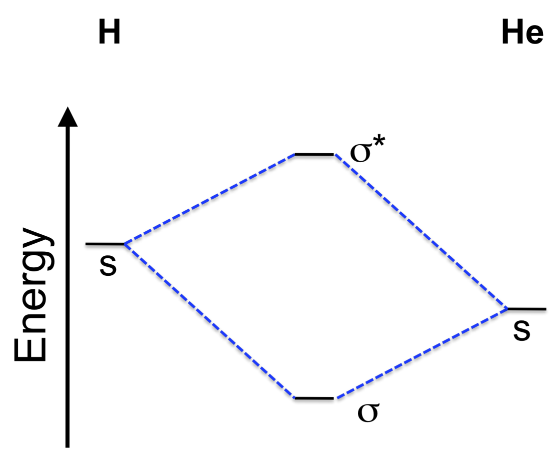
D. Some vocabulary: The highest occupied molecular orbital (including partially occupied) is abbreviated H.O.M.O. or simply "HOMO." The lowest unoccupied (empty) molecular orbital is abbreviated LUMO. Identify the HOMO and LUMO for F_2. (Answer should be in the format σ_s, etc.)

4. Heteroatom diatomic molecular orbitals

A. Relative orbital energy and orbital overlap. The relative energies of s and p orbitals for the first eleven elements are given here.



Thus, if one were to sketch the MO diagram for the hypothetical molecule HHe, it would look like:



B. Molecular orbitals tend to have characteristics that reflect the atomic orbitals closest in energy. As a result, the σ MO is more similar in energy to helium's 1s orbital and therefore is a little more "helium-like" than hydrogen-like. Conversely, the antibonding molecular orbital is more hydrogen-like. Because the s MO is also the HOMO for HHe^+, more of the electron density is on helium, simply because the s MO is helium-like. Sketch the bonding σ MO (using orbital shapes) and label the He end δ^- and the H end δ^+.

C. Sketch a MO energy diagram for nitrogen monoxide and related NO diatomics compounds. Also, prepare line sketches of each bonding and antibonding orbital.

Use the diagram to determine the bond order for:

NO
NO^+
NO^-

Refer again to the MO diagram you drew for NO. Is the unpaired electron in an orbital that is more nitrogen-like or oxygen-like?

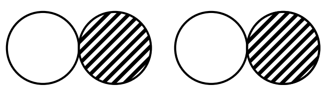
Review for ACS Final Exam in Inorganic Chemistry

Molecular Orbital Theory

1. Molecular orbital theory predicts that all of these are diamagnetic except:
   (a) N_2
   (b) NO^+
   (c) NO^-
   (d) O_2^{-2}
   (e) O_2^{+2}

2. Which of these has a bond order of 2?
   (a) N_2
   (b) NO^+
   (c) NO^-
   (d) O_2^{-2}
   (e) O_2^{+2}

3. For N_2, the following molecular orbital is described as:



   (a) σ_p
   (b) σ_p^*
   (c) π
   (d) π^*
   (e) σ_s^*

4. Which of the following is ***not*** expected to exist according to molecular orbital theory?
   (a) H_2^-
   (b) He_2^+
   (c) H_2^+
   (d) He_2
   (e) Be_2^+

Answers: C, C, B, D

Answers to Day 5

1. Symmetry operations

Our work	answer
a. SO_3 (trigonal planar)	two C_3 (cw and ccw) and three C_2
b. OH_2	C_2
c. NH_3	two C_3 (cw and ccw)
d. IF_7 (pentagonal bipyramid)	two C_5 (cw and ccw) and five C_2
e. XeF_4 (square planar)	two C_4 (cw and ccw), one C_2 and four C_2
f. BrF_5(square pyramid)	two C_4 (cw and ccw), one C_2
g. HCl	$C_{infinity}$
h. CO_2	Infinite C_2 and $C_{infinity}$

C. The principle rotation axis

Our work	answer
a. SO_3	C_3
b. OH_2	C_2
c. NH_3	C_3
d. IF_7	C_5
e. XeF_4	C_4
f. BrF_5	C_4
g. HCl	$C_{infinity}$
h. CO_2	$C_{infinity}$

D. Reflection planes

Molecule:	σ_v	σ_h	σ_d
a. SO_3	yes, 3	yes, 1	no
b. OH_2	yes, 2	no	no
c. NH_3	yes, 3	no	no
d. IF_7	yes, 5	yes, 1	no
e. XeF_4	yes, 2	yes, 1	yes, 2
f. BrF_5	yes, 2	no	yes, 2
g. HCl	yes, an infinite number	no	no
h. CO_2	yes, an infinite number	Yes, 1	no

E. Inversion center.

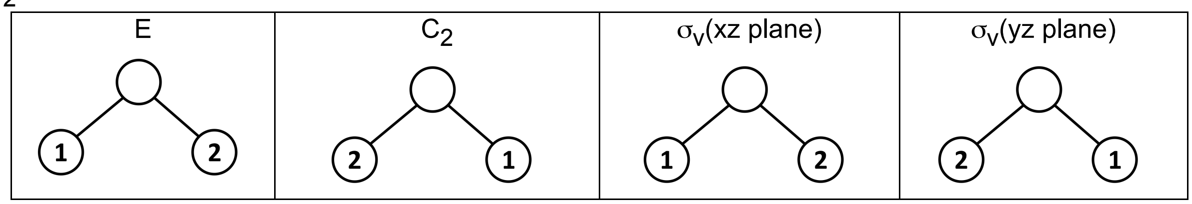
Our work	answer
a. SO_3	no
b. OH_2	no
c. NH_3	no
d. IF_7	no
e. XeF_4	yes
f. BrF_5	no
g. HCl	no
h. CO_2	yes

2. Point groups: The C_{nv} groups, D_{nh} groups

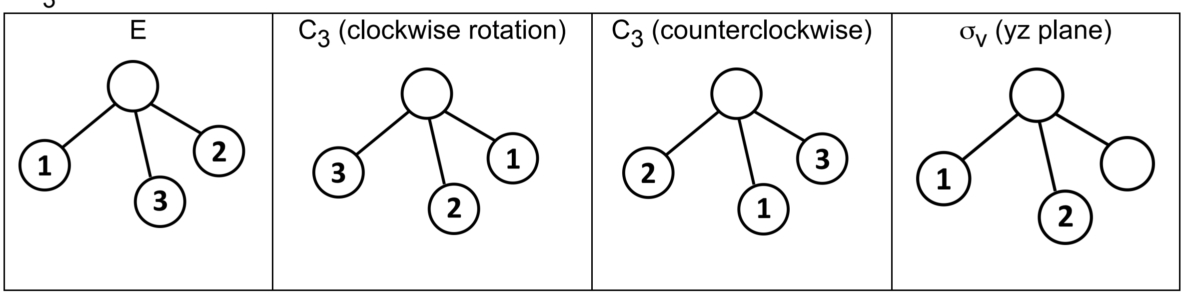
C_{nv} family point groups	Symmetry elements:
C_{2v}	E, C_2, σ_v(xz plane), σ_v(yz plane)
C_{3v}	E, two C_3, three σ_v
C_{4v}	E, two C_4, C_2, two σ_v, two σ_d
C_{5v}	E, two C_5, two C_5^2, five σ_v
C_{6v}	E, two C_6, two C_3, three σ_v, 3 σ_d
C_{7v}	E, two C_7, two C_7^2, two C_7^3, 7 σ_v

D_{nh} family point groups	Symmetry elements:
D_{2h}	E, C_2(z), C_2(y), C_2(x), i, σ_v(xy), σ_v(xz), σ_v(yz)
D_{3h}	E, two C_3, three C_2, σ_h two S_3, three σ_v
D_{4h}	E, two C_4, C_2(z-axis), two C_2', two C_2'', i, two S_4, σ_h, two σ_v, and two σ_d
D_{5h}	E, two C_5, two C_5^2, 5 C_2 (perpendicular to C_5) 5 σ_v, σ_h

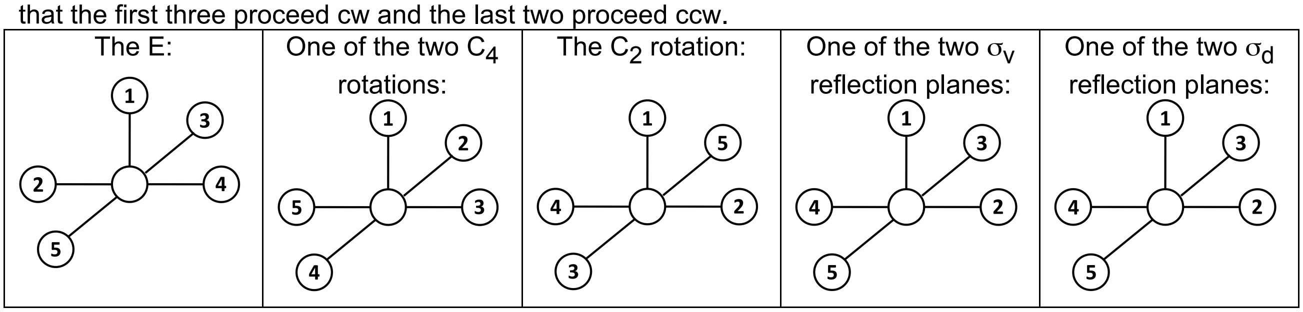
OH_2:



NH_3:



Square pyramid: Your answer may be different for the three instances where I ask for "One of the…" In order to determine if your is the same, there are really only two outcomes to these operations: either the numbers 2 – 5 proceed clockwise when viewed from Atom 1, or counterclockwise. The correct answer is that the first three proceed cw and the last two proceed ccw.

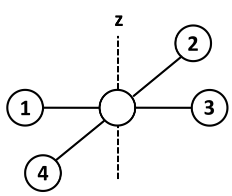
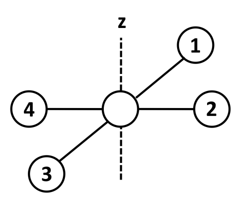
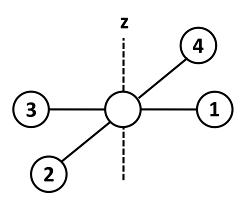
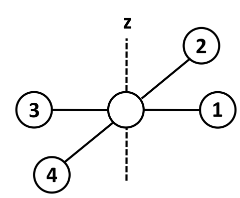
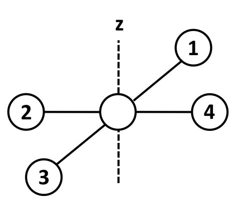
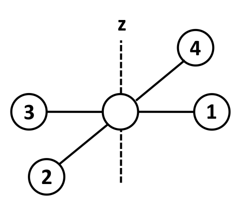
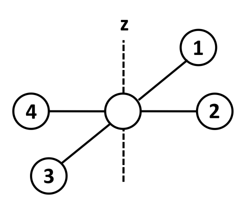
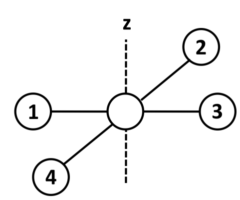
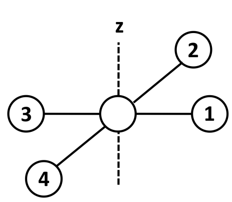
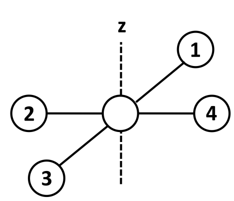


3. Points groups and ABE formulas.

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
2	AB_2	$D_{inf\text{-}h}$
3	AB_3	D_{3h}
3	AB_2E	C_{2v}
4	AB_4	T_d
4	AB_3E	C_{3v}
4	AB_2E_2	C_{2v}
5	AB_5	D_{3h}
5	AB_4E	C_{2v}
5	AB_3E_2	C_{2v}
5	AB_2E_3	$D_{inf\text{-}h}$
6	AB_6	O_h
6	AB_5E	C_{4v}
6	AB_4E_2	D_{4h}

A. The D_{nh} groups. Your answer may be different for the instances where I ask for "One of the…" In order to determine if your is the same, there are really only two outcomes to these operations: either the numbers 1 – 4 proceed clockwise when viewed from the position labeled "z", or counterclockwise. The correct answer is given below each drawing.

E  cw	clockwise C_4  cw	C_2 (rotation z-axis):  cw	C_2' rotation y-axis:  ccw
C_2'' (between x- and y)  ccw	i  cw	S_4  cw	σ_h  cw
either one of the two σ_v:  ccw	either one of the two σ_d  ccw	Doodle space	

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
3	AB_3	D_{3h}
5	AB_5	D_{3h}
6	AB_4E_2	D_{4h}

4. Point groups with very high or low symmetry.

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
2	AB_2	D_{inf-h}
4	AB_4	T_d
5	AB_2E_3	D_{inf-h}
6	AB_6	O_h

The octahedron. There are so many ways to perform each of these operations, an answer would not likely match yours and would make you uncertain about your work. Bring your questions in and we can discuss them.