General Chemistry I
Tutorial 08

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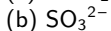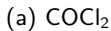
CHEM1103 - Tutorial 08 - **Nov. 21, 2022**

Outline

Quiz 9.1

Sketch and name the shape of the following molecules and ions: (central atom = red)
(a) COCl$_2$
(b) SO$_3{}^{2-}$
(c) ICl$_3$
(d) PCl$_4{}^+$

Problem 5.1

(a) The ionization energy of molecular hydrogen (H$_2$) is greater than that of atomic hydrogen (H), but that of molecular oxygen (O$_2$) is lower than that of atomic oxygen (O). Explain. (Hint: Think about the stability of the molecular ion that forms in relation to bonding and antibonding electrons.)

(b) What prediction would you make for the relative ionization energies of atomic and molecular fluorine (F and F$_2$)?

Problem 5.2

An sp^2 hybrid orbital that lies in the xy-plane has the form:

$$\psi_{sp^2} = -\frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_x} + \frac{1}{\sqrt{2}}\psi_{2p_y}$$

(1) Show that ψ_{sp^2} is normalized, provided that $\psi_{2s}, \psi_{2p_x}, \psi_{2p_y}$ are all normalized.

(2) Write the explicit form of this hybrid orbital ψ_{sp^2} and find out the ϕ angle such that ψ_{sp^2} is maximized.

Problem 5.3

Mixing SbCl$_3$ and GaCl$_3$ in a 1:1 molar ratio (using liquid sulfur dioxide as a solvent) gives a solid ionic compound of empirical formula GaSbCl$_6$. A controversy arises over whether this compound is (SbCl$_2$$^+$)(GaCl$_4$$^-$) or (GaCl$_2$$^+$)(SbCl$_4$$^-$).

(a) Using the VSEPR theory, predict the molecular structures of the two anions.

(b) It is learned that the cation in the compound has a bent structure. Based on this fact, which formulation is more likely to be correct?

Problem 5.4

The molecular $S_3N_3^-$ has the cyclic structure and all S-N bonds are equivalent.

(a) Give six equivalent resonance Lewis diagrams for this molecular ion.

(b) Compute the formal charges on all atoms in the molecular ion in each of the six Lewis diagrams.

(c) Determine the charge on each atom in the polyatomic ion, assuming that the true distribution of electrons is the average of the six Lewis diagrams arrived at in parts (a) and (b).

(d) An advanced calculation suggests that the actual charge resident on each N atom is -0.375 and on each S atom is $+0.041$. Show that this result is consistent with the overall -1 charge on the molecular ion.

$$\begin{bmatrix} \begin{smallmatrix} & & S & & \\ N & & & & N \\ | & & & & | \\ S & & & & S \\ & & N & & \end{smallmatrix} \end{bmatrix}^-$$

Figure 1: Cyclic structure of $S_3N_3^-$

Problem 5.5

$AlCl_3$ and BH_3 form dimer molecules in the gas phase. In the dimer molecules Al_2Cl_6 and B_2H_6, Al and B are located in tetrahedral centers and are 'bridged' by two Cl and H atoms, respectively. In the following, complete the bridging Al–Cl and B–H bonds and calculate their bond orders. Draw additional resonant structures when necessary.

(a)
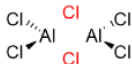
Bond order of bridging Al–Cl = ?

(b)
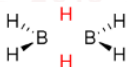
(b) Bond order of bridging B-H = ?

Valence Bond Theory

Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy directed orbitals localized on a particular atom. The directionality of the orbitals is determined by the geometry around the atom which is obtained from the predictions of VSEPR theory.

Remark 2.1

Valence bond theory is all about promoting electron and hybridizing orbitals into the shape required by experiments!

How to predict shape? VSEPR Theory

From the very start, VSEPR is based on Lewis structures. Please revise it if you've forgotten key concepts concerning Lewis structures. 😊

Remark 2.2

Key concepts of VSEPR

- *Only valence electrons count.*
- *Repulsions no more than $90°$ are considered.*
- *Repulsion energy: lp-lp >lp-bp >bp-bp.*

Steric Number(SN):

$$SN = \#\text{Lone pairs} + \#\text{Ligands}$$

How to predict molecular shape? VSEPR Theory

SN	Shape	Hybridization
2	Linear	sp
3	Trigonal	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^{3}d
6	Octahedral	sp^{3}d^2

Table 1: Relation between SN, molecular shape and hybridization

Remark 2.3

*Shape in **Table 1** $\neq$ shape of molecules.*

In sp^{3}d hybridization, equatorial and axial positions are not equivalent. Lone pairs prefer equatorial positions.
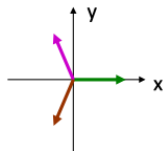
From VSEPR to hybridization (FYI)

Suppose that we know the geometry of molecules, then we derive mathematical interpretations of their hybridized orbitals.

According to VSEPR theory, BH$_3$ is sp^2 hybridized. Now, we're gonna derive mathematical interpretations of 3 hybridized sp^2 orbitals.

$$\psi_1 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{2}\phi_{p_y}$$

$$\psi_2 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{2}\phi_{p_y}$$

$$\psi_3 = \frac{1}{\sqrt{3}}\phi_s + \frac{2}{\sqrt{6}}\phi_{p_x}$$

**Figure 2:** Orientation of orbitals

A Patch of VBT: Resonance Structures

LCAO theory is most often used to describe the electronic states of molecules in contexts that require knowledge of energy levels. VB theory is more widely used to describe molecular structure, especially in pictorial ways. Here we combine the advantages of these two theories: σ bonds are described by VB and delocalized π bonds are described by LCAO.

Key concepts of resonance:

- Canonical form (Positions of atoms conserve while electrons change their locations)
- Electron pairs are share by more than 2 atoms

Several examples of resonance:
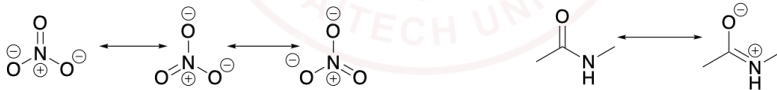
A Patch of VBT: Resonance Structures

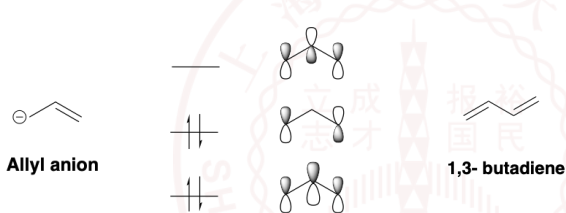- LCAO and delocalized π orbitals
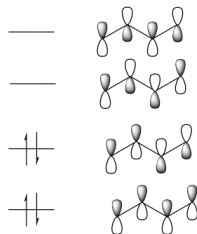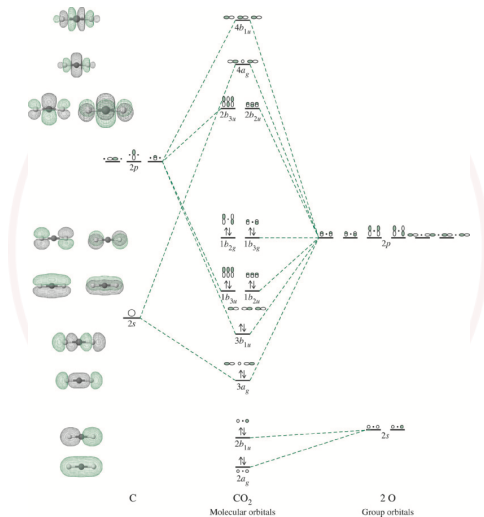

Figure 3: LCAO of allyl anion

Figure 4: LCAO of 1,3-butadiene

Remark 2.4

- *Orbital energy increases with increasing number of nodes.*
- *Bonding difference = # bonding - # antibonding*

A seemingly complicated molecular orbital: CO_2

Figure 5: Molecular orbital of CO_2