

CHEM 115

Valence Bond Theory and Molecular Orbital Theory

Lecture 26
Prof. Sevian



1

Agenda for Lectures 25 and 26

- Using bond enthalpies to estimate enthalpy of reaction
 - Lewis structures when expanded octets are possible
 - Molecular dipoles
 - Valence shell electron pair repulsion theory (VSEPR)
 - Return Exam 3 at end of Lecture 25
-
- Valence bond theory
 - Hybridization of atomic orbitals to prepare for bonding
 - Single, double and triple bonding
 - σ and π bonding orbitals
 - Predicting bond angles
 - Refrain molecular dipoles
 - Molecular orbital theory
 - Give out “individualized academic prescriptions” at end of Lecture 26

Announcements

- If you weren't in class last Thursday, you can pick up your Exam 3 at my office (W-4-181) during normal business hours - someone there will get it for you.

Reminders:

- Final Exam has been scheduled for:
 - Tuesday, May 19
 - 3:00-6:00 PM
 - Lipke Auditorium (S-2-003A), which is our regular classroom
- Final exam is comprehensive (covers the whole semester)
- Official ACS exam
- 70 questions, all multiple-choice
- There will be some questions on topics that we haven't covered (e.g., gas laws) - these will be extra credit if you get them right, and no penalty₃ if you get them wrong, so it's to your advantage to guess

About the i>clickers

- There will not be any clicker questions today
- If you borrowed an i>clicker from me, you can return it either at the final exam, or to my office (W-4-181) during normal business hours, where someone will check it in
 - Hopefully the follow two things will not apply to anyone:
 - If you do not return your i>clicker, you will receive an INC and then an administrative F in the class
 - If you lost the i>clicker I loaned you, you can buy a new one and turn that in to me instead.

How do bond polarities sum to determine molecular polarity?

A molecule is a dipole:

1. If it has at least one bond in it that is polar covalent and
2. If the bond dipoles do not cancel each other out (cancellation happens when bond dipoles are symmetrically located)

Remember how to determine whether a bond is a dipole?

Difference in electronegativities of the two atoms in the bond

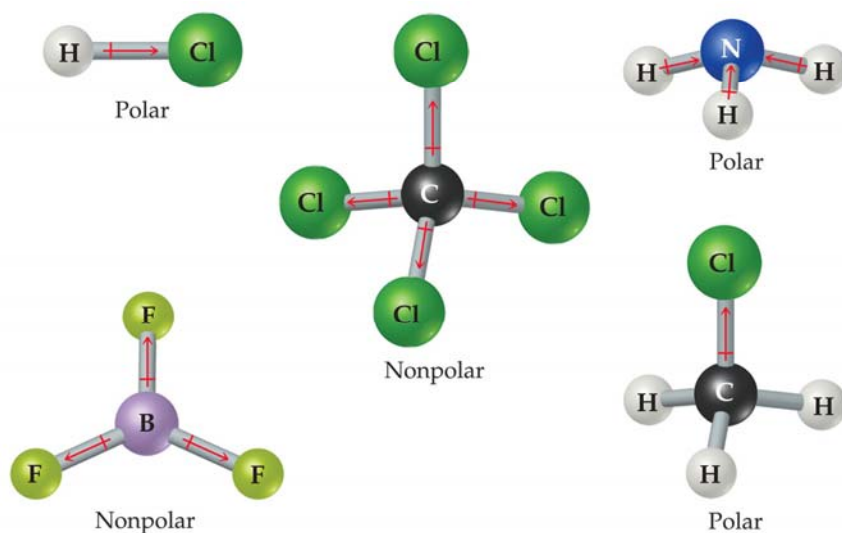
No difference: perfectly covalent

Some difference (as between non-metals): polar covalent

Very different (as between a metal and a non-metal): ionic

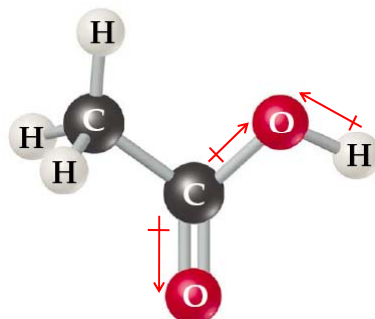
5

These are some molecules that contain polar bonds, but not all of the molecules are polar



Copyright © 2006 Pearson Prentice Hall, Inc.

Molecular dipole example



Dipole moment of the molecule is the vector sum of the three bond dipoles*

1.74 D*

*This is an average - the dipole moment fluctuates as the single bonds twist and vibrate

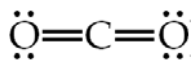
- The strength of a molecule's dipole explains many properties of the compound, such as:
 - How high (or low) the melting and boiling points are
 - How well the compound can dissolve in polar or nonpolar solvents
 - How reactive the compound is, and where its reactivity sites are

A question to go over

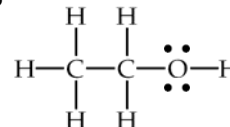
(would have been a clicker question)

Which of the following molecules would be expected to have the largest molecular dipole moment?

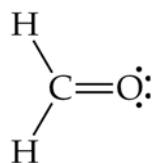
(A) CO₂



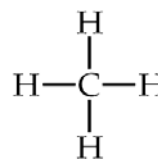
(C) C₂H₅OH



(B) CH₂O



(D) CH₄



Also review from last lecture: What are all the bond angles in these molecules?

Summary of today's class

- Valence bond theory
 - σ bonds are localized to existing between two atoms. π bonds can be localized also, or can be delocalized across molecule (e.g., benzene)
 - Hybridization of different combinations of s , p and d atomic orbitals accounts for electron pair geometry, i.e., explains how bond angles arise
 - Single bonds are always σ type, orbitals overlap directly on axis of bond
 - Second and third bonds are always π type, off axis by atomic p -orbital overlap (i.e., to make π bonds in molecules, must reserve some atomic p -orbitals and not hybridize them)
- Molecular orbital theory
 - All bonds are delocalized across entire molecule
 - Mix together all atomic orbitals of every atom and determine new molecular orbital energies, then populate with electrons according to same Aufbau, Pauli and Hund
 - No molecular geometry predictions, but paramagnetism predictions more accurate

9

Valence Bond Theory

A mathematical model that explains why the electron domain geometries are the way they are

Central ideas:

1. Atomic orbitals initially form hybrids to get ready for bonding to form molecules/ions (costs a little bit of energy – less stable)
2. Bonds in molecules/ions are formed by the overlap of atomic orbitals (win back a lot of energy – much more stable)

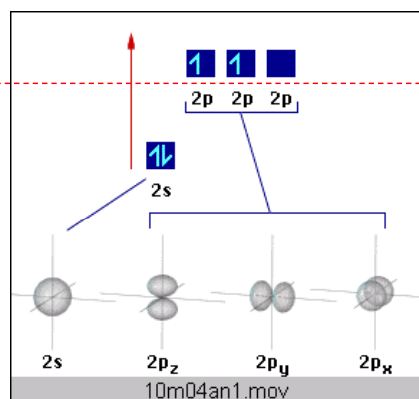
How VB theory explains molecular geometries and the inversely proportional bond order-bond length relationship:

1. Bond angles are determined by where the σ bonds are
2. π bonds, if present, add strength off axis, and also pull the atoms closer together so that the reserved p -orbitals can overlap better

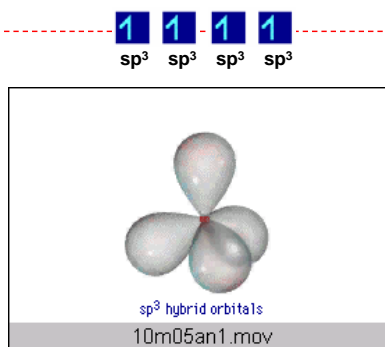
10

Why it costs a little energy, endothermic, to form hybrid orbitals (but more than that energy is won back when bonds, which are exothermic, form)

Carbon atom's valence with a 2s and three 2p orbitals



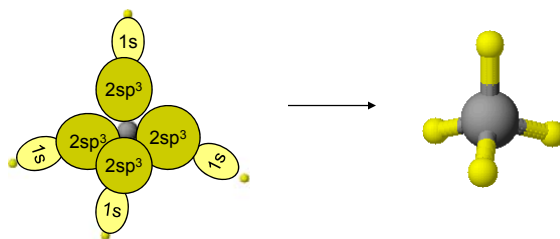
Carbon atom's valence with four sp^3 hybridized orbitals ready to make four σ bonds



Explains tetrahedral electron domain geometry

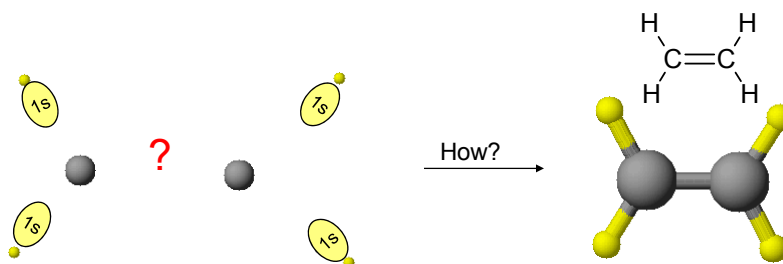
Four single bonds between one carbon and four hydrogens

- The first bond between two atoms: Overlap occurs on the axis of bond \Rightarrow σ orbital
 - Only one σ bonding orbital can form between two atoms
 - Bonds that form on the axis between two atoms are always σ type



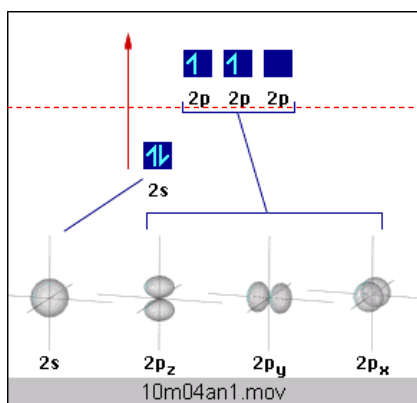
Double bond between two Carbons

- The second (and third) bond between two atoms (if a σ bond has already formed): Overlap occurs outside the axis of a bond \Rightarrow π orbital
 - It is possible to form either one or two π bonds between atoms
 - Bonds that occur off-axis are always π type

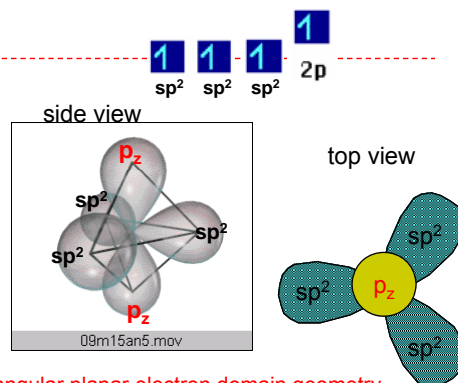


Reserving a p-orbital for making a π bond

Carbon atom with a 2s and three 2p orbitals



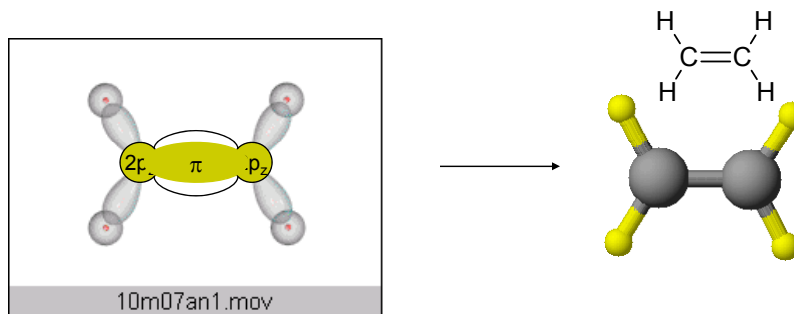
Carbon atom with three sp^2 hybridized orbitals and one 2p orbital left over, ready to make 3 σ bonds and 1 π bond



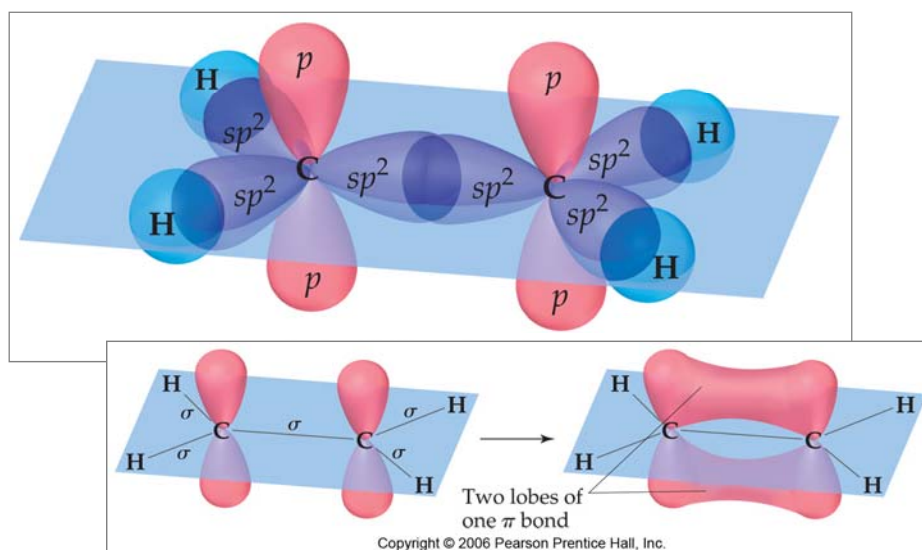
Explains triangular planar electron domain geometry

Double bond between two Carbons

- The second (and third) bond between two atoms (if a σ bond has already formed): Overlap occurs outside the axis of a bond \Rightarrow π orbital
 - It is possible to form one or two π bonds between atoms
 - What are the bond angles?

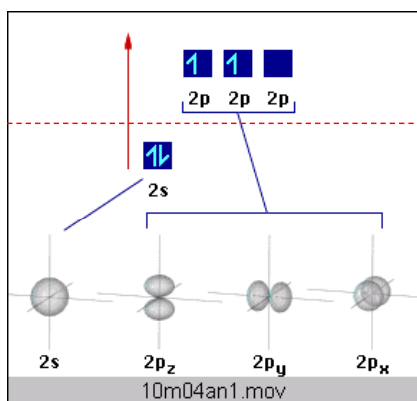


Another view of forming C_2H_4

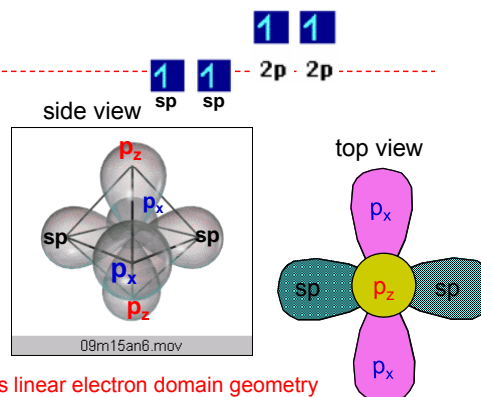


Reserving two p-orbitals for making two π bonds

Carbon atom with a 2s and three 2p orbitals



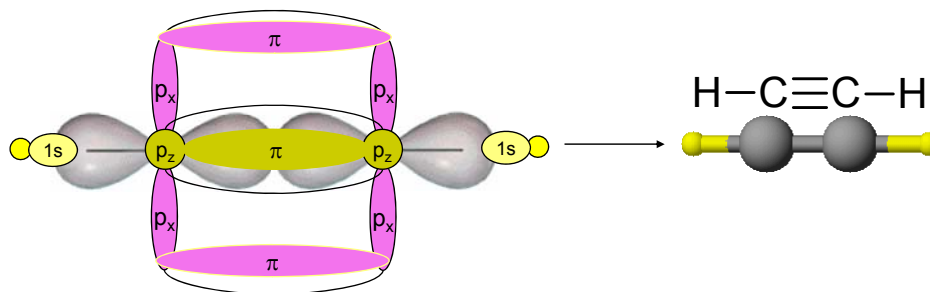
Carbon atom with two sp hybridized orbitals and two 2p orbitals left over, ready to make 2 σ bonds and 2 π bonds



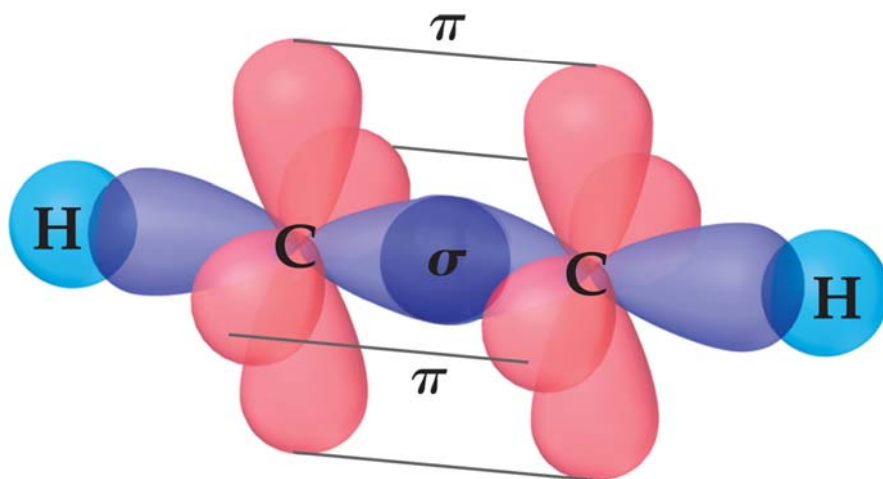
Explains linear electron domain geometry

Triple bond between two Carbons

- The second (and third) bond between two atoms (if a σ bond has already formed): Overlap occurs outside the axis of a bond \Rightarrow π orbital
 - It is possible to form one or two π bonds between atoms
 - What are the bond angles?

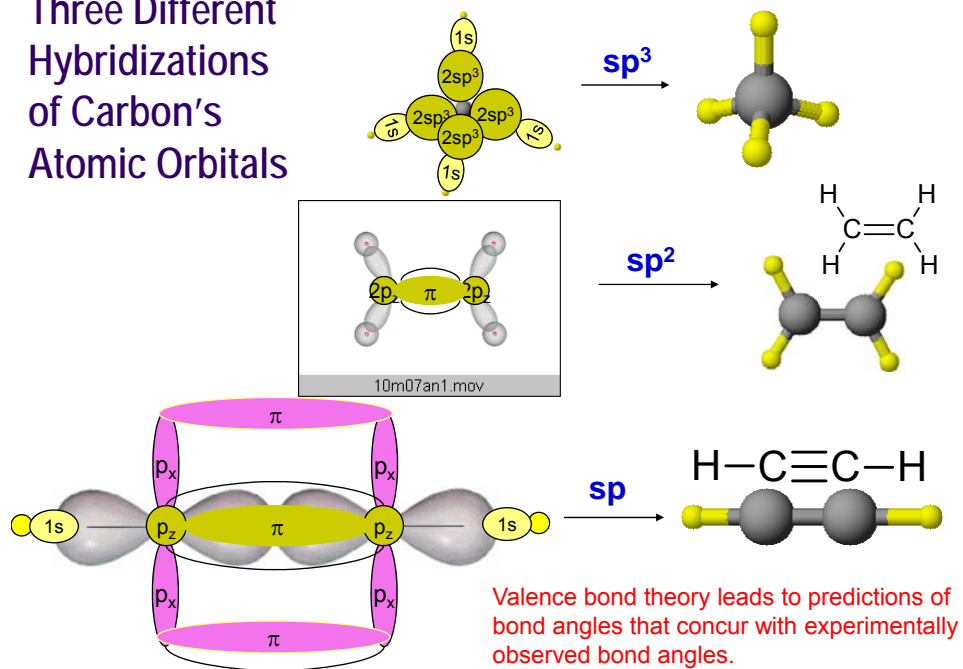


Another view of forming C₂H₂

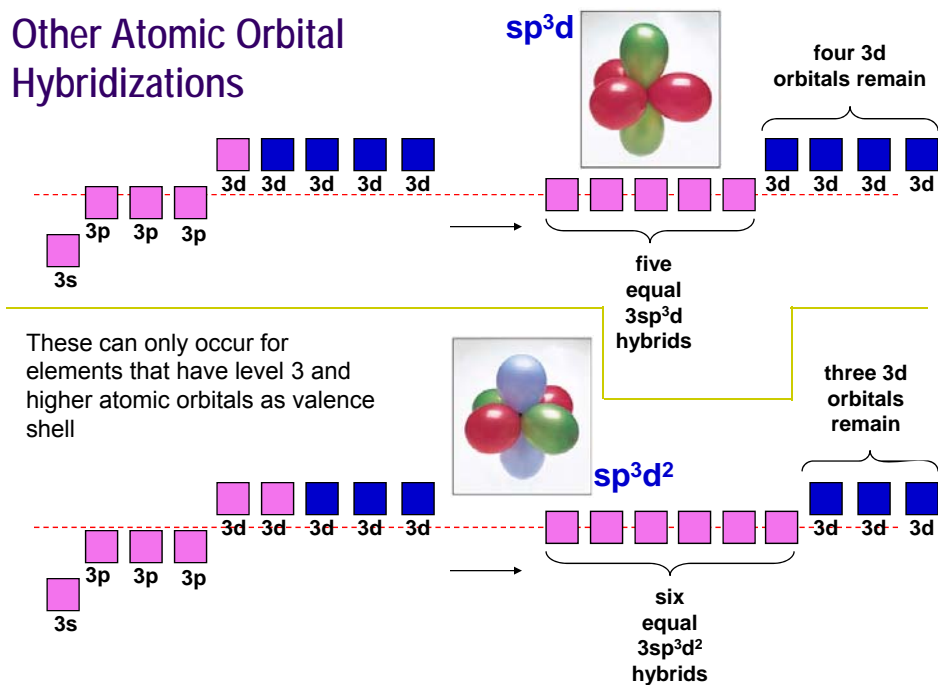


Copyright © 2006 Pearson Prentice Hall, Inc.

Three Different Hybridizations of Carbon's Atomic Orbitals

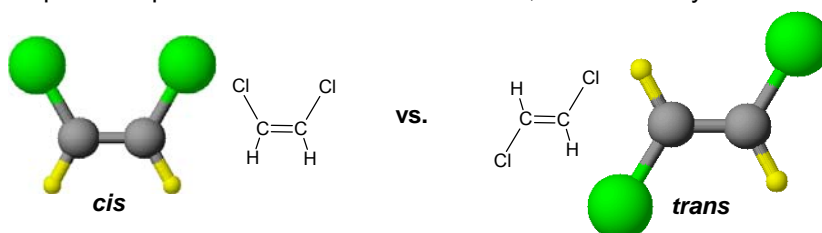


Other Atomic Orbital Hybridizations



Consequences of π Bonding

- Atoms can twist around σ bond
- When π bonds are present in addition to a σ bond, the π bond(s) locks the atoms in a specific orientation (molecule is restricted to no twisting around the σ bond)
- Isomer (= same parts) can result
- Simple example: cis- and trans- versions of 1,2-dichloroethylene



- Much of nature works by recognizing specific isomers to the exclusion of others
- What are the bond angles?

Resonance and Delocalization of Electrons in π Bonds (example: benzene)

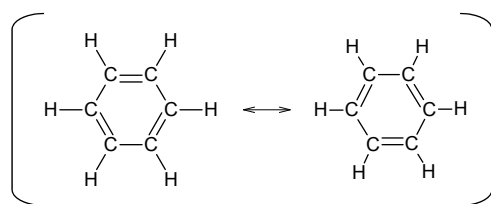
Macroscopic evidence

- Laboratory data indicate that benzene has a planar, symmetrical structure

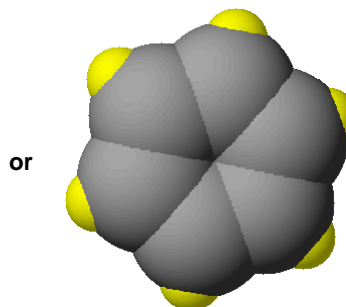
Particle level – valence bond theory prediction

- Delocalized means not localized to a specific location, but instead spread out over many locations
- For example, in benzene, delocalization occurs with bonding electrons in π bonds

Symbolic representation



two resonance forms



Two competing theories that predict various properties of molecules

Valence bond theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Lewis structure's electron pairs translated into quantum mechanics
- Electrons in a particular bond are localized to specific valence bond orbitals

Molecular orbital theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Wave functions (molecular orbitals) are formed from all bonding electrons in molecule
- Electrons in all bonds are spread out (delocalized) over all molecular bonding orbitals in molecule

Mathematically, the approaches are different.

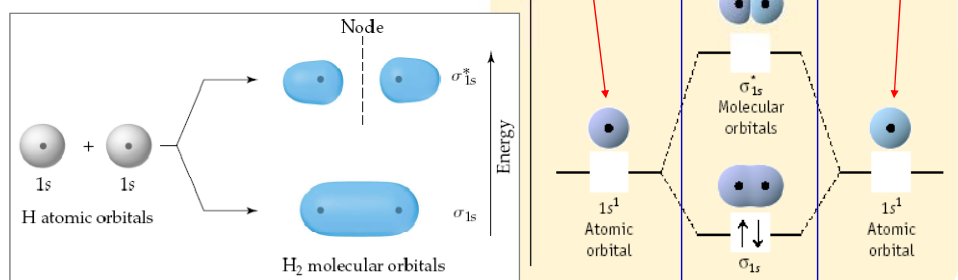
Results (predictions) are often the same.

Molecular Orbital Theory

Central ideas:

- Atomic orbitals on all atoms mathematically combine to form molecular orbitals.
- Electrons then populate the molecular orbitals and are delocalized across entire molecule.

Mathematical combination of the 1s wavefunctions on two individual hydrogen atoms to form two molecular orbitals

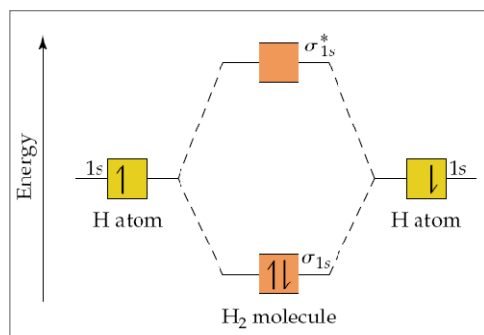


Molecular Orbital Theory Principles

1. Orbitals are conserved. The total number of molecular orbitals equals the total number of atomic orbitals that contributed.
2. Conservation of energy is obeyed. Bonding molecular orbitals have lower energy than the average of the contributing atomic orbitals. Antibonding molecular orbitals have higher energy.
3. When assigning electrons to molecular orbitals for ground state electron configuration prediction, the Aufbau rule, Pauli exclusion principle and Hund's rule still apply.
 - Bond order can be predicted by comparing how many bonding orbitals are filled vs. how many antibonding orbitals are filled.
 - Paramagnetism can be predicted as with electronic configurations of atoms.
4. The more similar the atoms are, the more effective the bonding can be. (Molecular orbitals form most effectively when the atoms that contribute the atomic orbitals are most similar.)

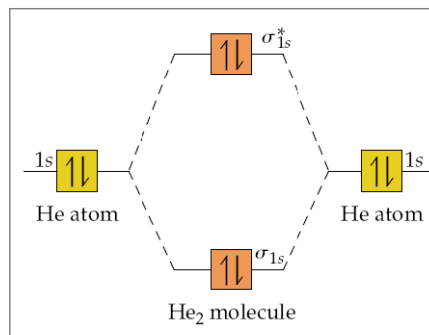
26

Compare and Learn



Molecular orbital theory prediction for H₂ molecule forming from two isolated H atoms

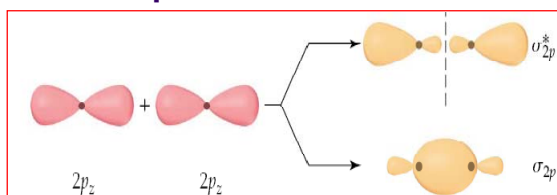
Net 1 bond because 1 pair of electrons in a bonding orbital



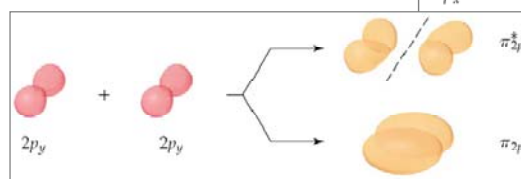
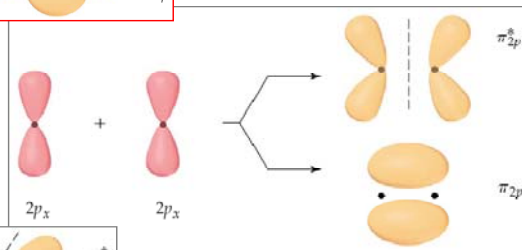
Molecular orbital theory prediction for He₂ molecule forming from two isolated He atoms

Net 0 bonds because equal pairs of electrons in bonding and antibonding orbitals

Molecular Orbitals Also Form from Atomic p-Orbitals

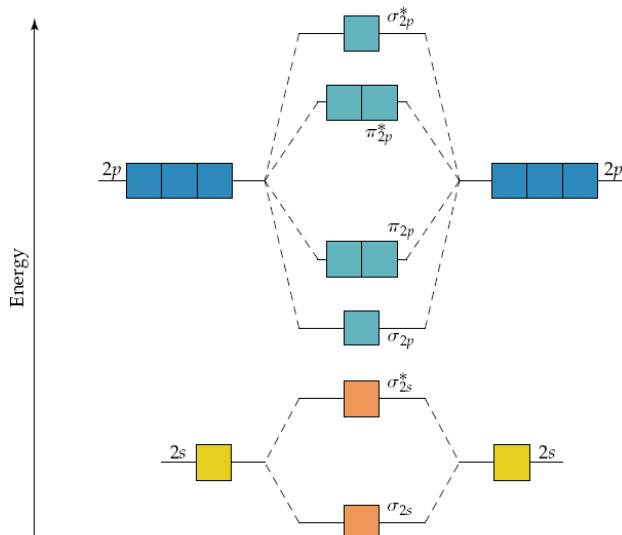


σ molecular orbitals (bonding and antibonding) form from the atomic p-orbitals (one on each atom) that are along axis of bonding



π molecular orbitals (bonding and antibonding) form from the atomic p-orbitals (two on each atom) that are perpendicular to the axis of bonding

Diatomics Formed from Elements in Second Period of Periodic Table



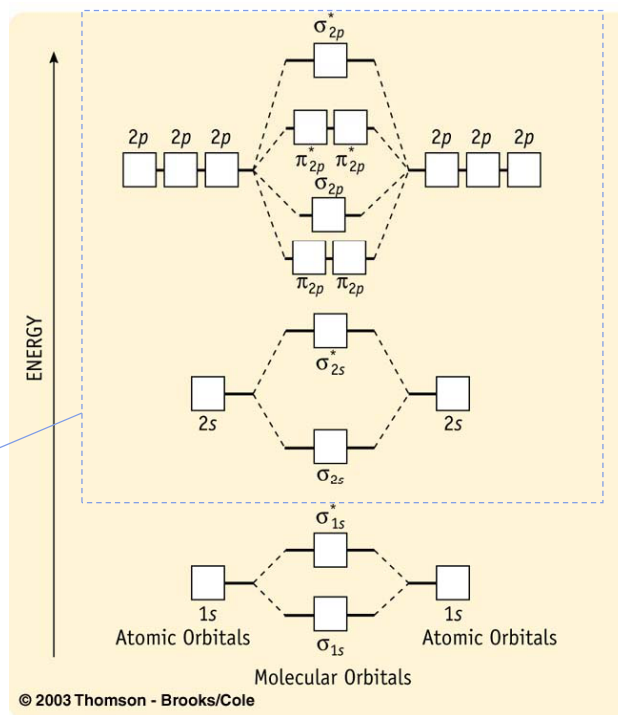
Note: only the valence level ($n=2$) is shown here

29

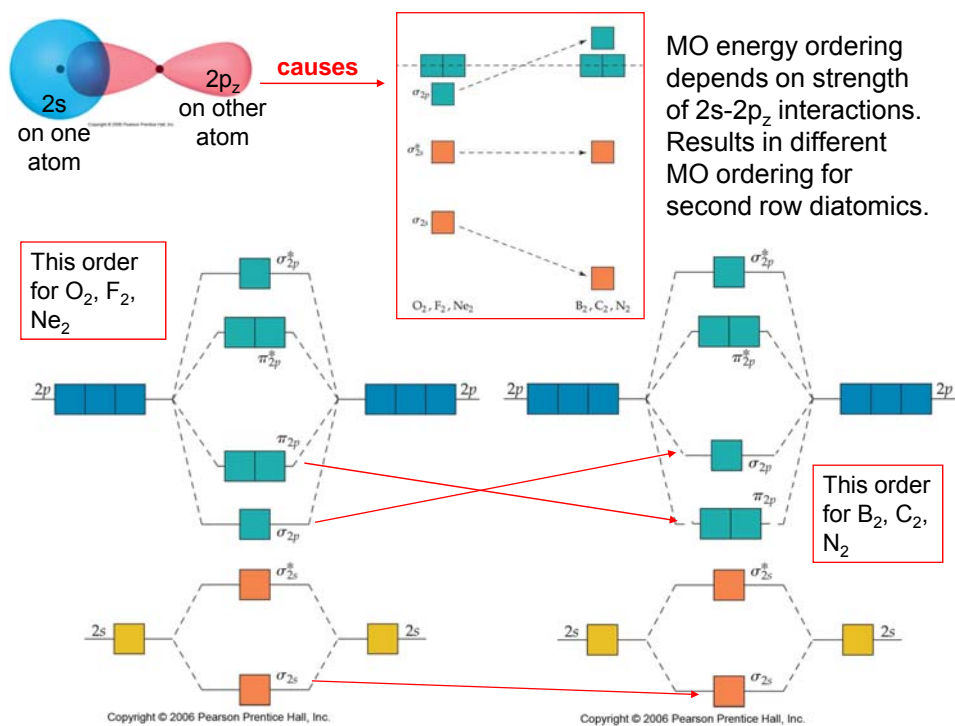
Entire Molecular Orbital Energy Level Diagram for some of the Second-Period Diatomics

Now let's take a closer look at this part

From Chemistry: A Chemical Approach, 4th edition by Victor J. Stoltz, © 2003. Reprinted with permission of Brooks/Cole, a division of Thomson Learning. www.thomsonlearning.com Fax: 800-730-2215.



© 2003 Thomson - Brooks/Cole



Compare

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
π_{2p}^*	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
σ_{2p}	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
π_{2p}	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
σ_{2s}^*	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
σ_{2s}	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

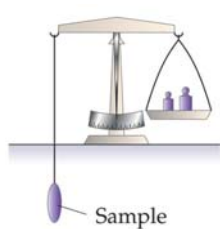
Note these are the MO's that are switched in energy order

Copyright © 2006 Pearson Prentice Hall, Inc.

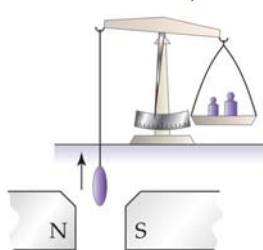
Paramagnetic vs. diamagnetic

As before, results from one or more spin-unpaired electrons

As before, when all electrons are spin-paired

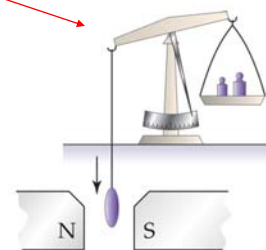


(a) The sample is first weighed in the absence of a magnetic field.



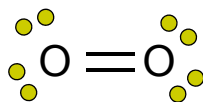
(b) When a field is applied, a diamagnetic sample moves out of the field and thus appears to have a lower mass.

Copyright © 2006 Pearson Prentice Hall, Inc.

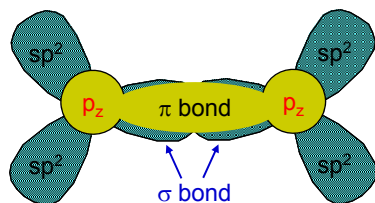


(c) A paramagnetic sample is drawn into the field and thus appears to gain mass.

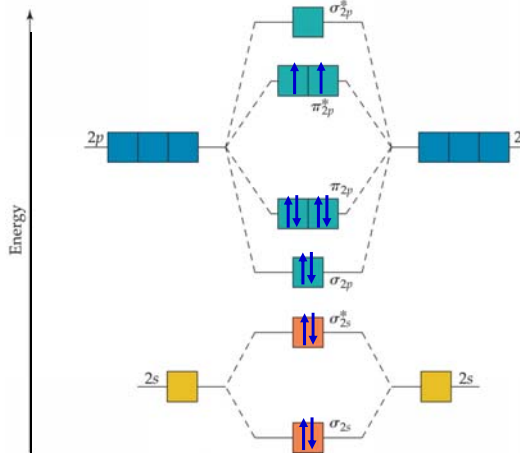
Valence Bond Theory vs. Molecular Orbital Theory for O₂



Lewis diagram predicts sp² hybridization on O atoms



1. Molecular shape predicted to be flat
2. Correct bond order 2 predicted
3. All orbitals are occupied by pairs of electrons – not paramagnetic



Copyright © 2006 Pearson Prentice Hall, Inc.

1. No prediction about molecular shape
2. Correct bond order predicted (net pairs of electrons in bonding orbitals)
3. Some unpaired electrons – paramagnetic

Summary of today's class

- Valence bond theory
 - σ bonds are localized to existing between two atoms. π bonds can be localized also, or can be delocalized across molecule (e.g., benzene)
 - Hybridization of different combinations of s , p and d atomic orbitals accounts for electron pair geometry, i.e., explains how bond angles arise
 - Single bonds are always σ type, orbitals overlap directly on axis of bond
 - Second and third bonds are always π type, off axis by atomic p -orbital overlap (i.e., to make π bonds in molecules, must reserve some atomic p -orbitals and not hybridize them)
- Molecular orbital theory
 - All bonds are delocalized across entire molecule
 - Mix together all atomic orbitals of every atom and determine new molecular orbital energies, then populate with electrons according to same Aufbau, Pauli and Hund
 - No molecular geometry predictions, but paramagnetism predictions more accurate

35

What you'll see on your *Individualized Academic Prescription*
This is an example

Individualized "Academic Prescription" for Chem 115 Final Exam Prepared for
00xxxxxx "LastName" "FirstName"

Extra credit (maximum 5 pts) calculated as

$$XC = \left(\frac{\text{Overall change}}{100 - \text{Pretest score}} \right) \times 5 = +2$$

Chapter(s) and Major Topics*	Q # on test	Your scores			Class average		
		Pre	Post	Change	Pre	Post	Change
1 and 2: Matter, formulas, and names	1, 2, 4, 6	50%	75%	25%	61%	74%	13%
3 (1st half): Chemical equations, balancing	21, 23, 24, 28	25%	100%	75%	37%	55%	18%
3 (2nd half): Quantitative calculations such as moles ↔ masses and % composition ↔ empirical formula	3, 8, 21, 22, 24, 25, 26, 27, 29, 30	10%	30%	20%	26%	47%	20%
4: Solutions, solubility and reactions in aqueous solutions	16, 17, 19, 20, 21, 32	33%	67%	33%	34%	51%	18%
5: Temperature, heat energy, and calorimetry	10, 11, 14, 15, 18	20%	40%	20%	34%	46%	12%
7: Explaining periodicity	31, 38	50%	50%	0%	25%	41%	16%
8 and 9: Lewis structures, valence bond & MO theories, molecular shapes, bond order and bond angles	33, 34, 35, 36, 39	0%	60%	60%	35%	39%	5%
All together (except questions on topics not covered in Chem 115)	maximum possible = 33 questions**	24%	52%	27%	36%	51%	15%

*More detailed lists of topics in each chapter are included separately