

Molecules Module – Lecture 5: Valence Bond Theory

Learning Objective	Openstax 2e Chapter
Valence-Bond Theory	<u>8.1</u>
Hybridization of Atomic Orbitals	<u>8.2</u>

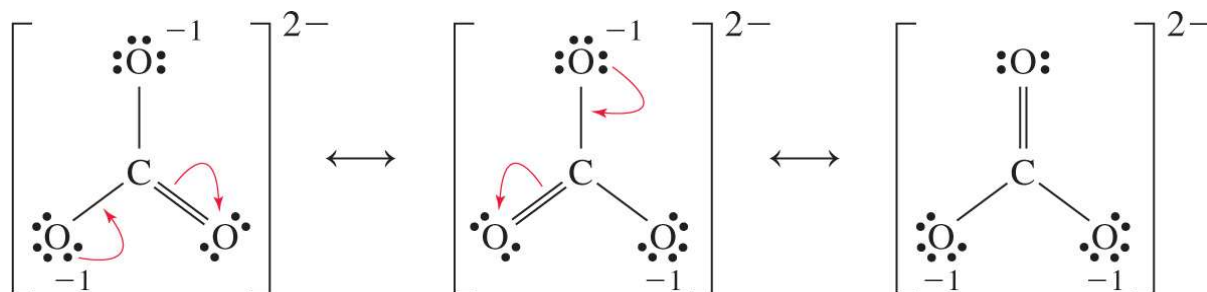
Suggested Practice Problems

[Chapter 8 Exercises](#) – Questions: 3, 5, 7, 11, 13, 17, 21

Answers can be found in the [Chapter 8 Answer Key](#)

Chemical Bond Theories

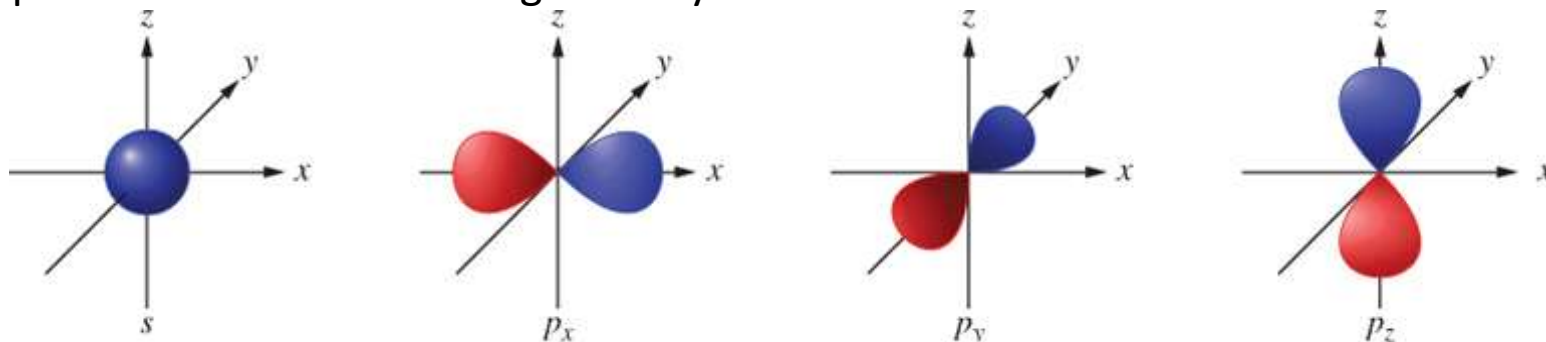
Lewis theory is useful for many purposes, including using **electronic configuration of atoms** and **valence electrons** to explain **chemical bonding** and **molecular shapes**.



What about **Atomic Orbitals**? Can we combine **Lewis theory** with **Atomic Orbital theory**?

Initial consideration of atomic orbital shapes and orientations does not seem to align with known molecular properties such as molecular geometry.

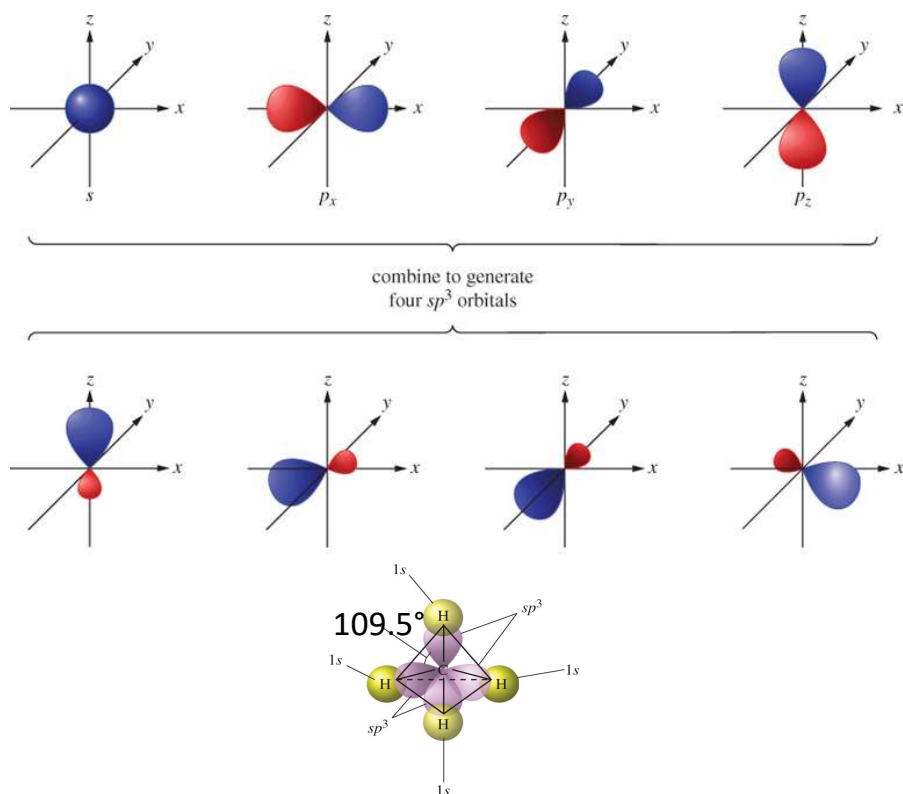
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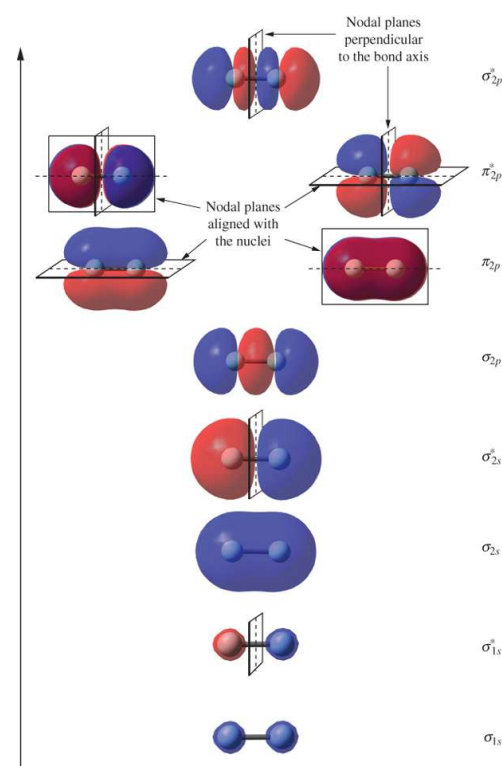
We need a better model!

Chemical Bond Theories

- Valence Bond (VB) Theory**
(this lecture)



- Molecular Orbital (MO) Theory**
(next lecture)



Bond Formation between two hydrogen atoms

What interactions occur as two hydrogen atoms approach from an infinite distance?

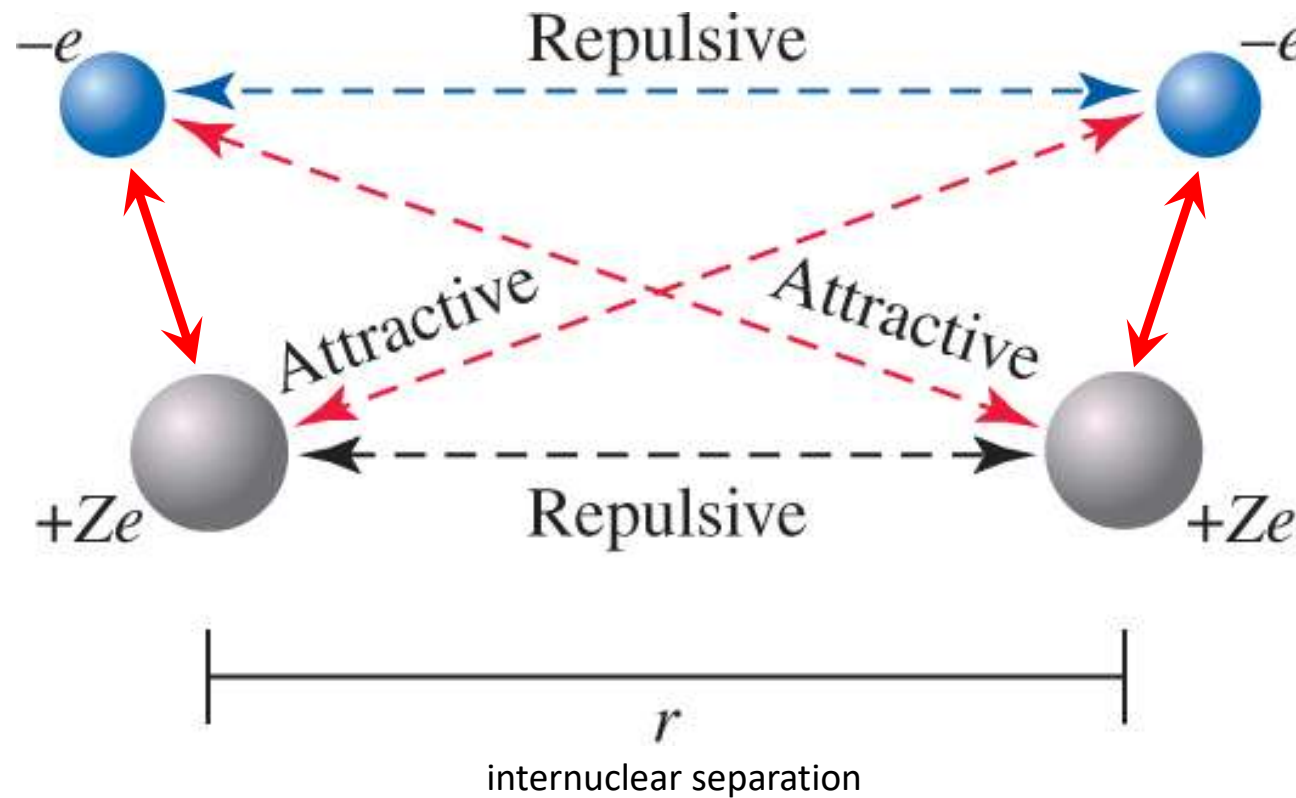
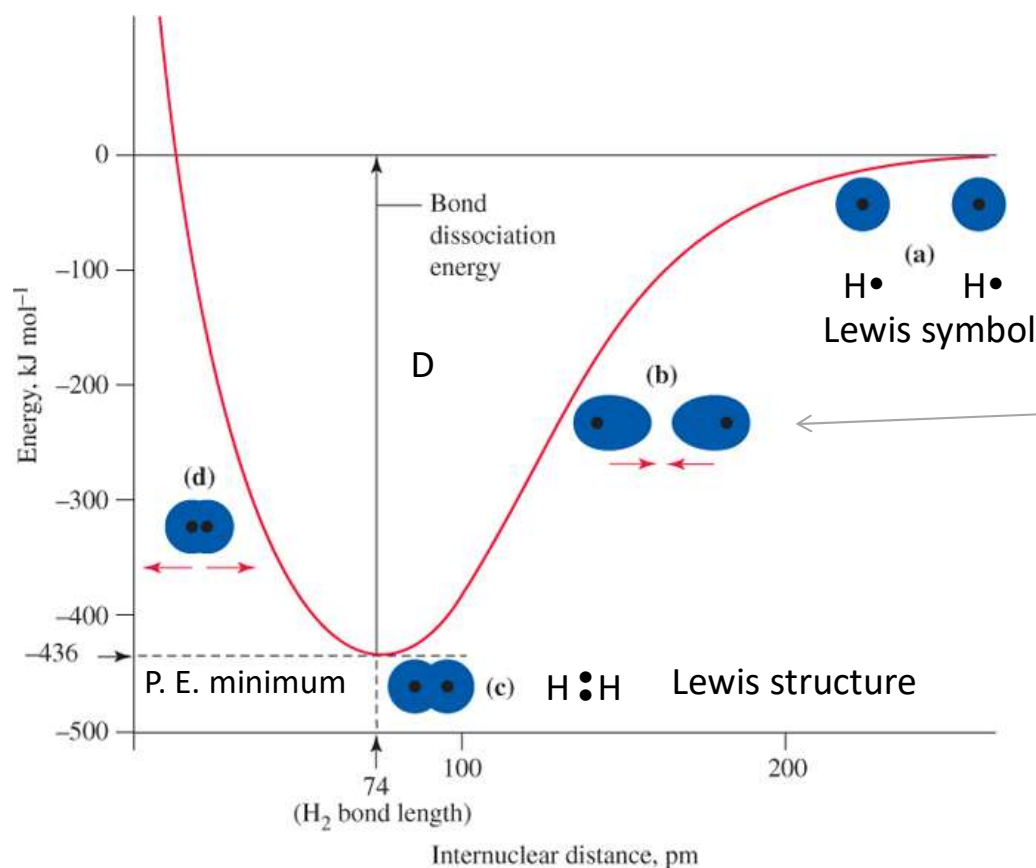


Figure 1: Type of interactions between two hydrogen atoms

Bond Formation between two hydrogen atoms



- When two H atoms are far apart, the potential energy (P.E.) is zero.
- As atoms approach each other, each electron is attracted to the nucleus of the other atom, while repulsions also occur between electrons and between nuclei.

Figure 2: Energy of interaction of two hydrogen atoms plotted for internuclear separations from zero to infinity

Valence-Bond (VB) Theory

VB method is a description of covalent bond formation in terms of atomic orbital overlap.

- A covalent bond is *normally* created by the overlap of half-filled orbitals on two atoms (or *sometimes* overlap of a filled orbital on one atom and an empty orbital on another if coordinate covalent bonding).
- This is a localized electron model of bonding: Core electrons and lone-pair valence electrons stay in the same orbital locations as in the individual isolated atoms, but the bonding electrons do not.

Example: For each H atom, there is one electron in the 1s AO (half-filled).

Covalent bond between two H atoms is formed by overlap (interpenetration) of two 1s orbitals.

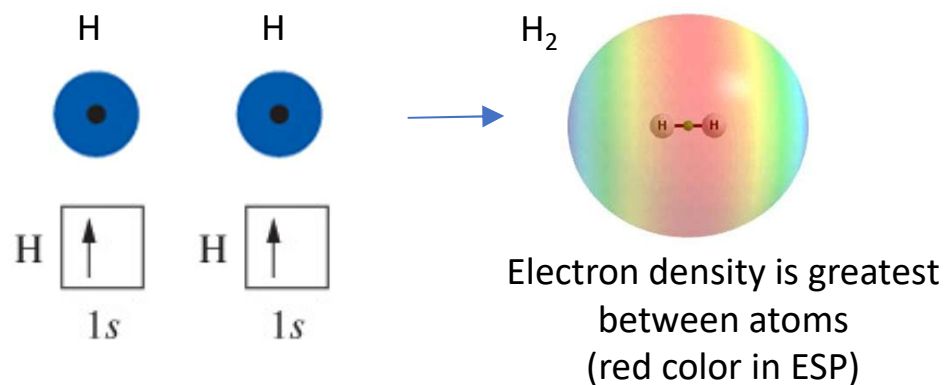
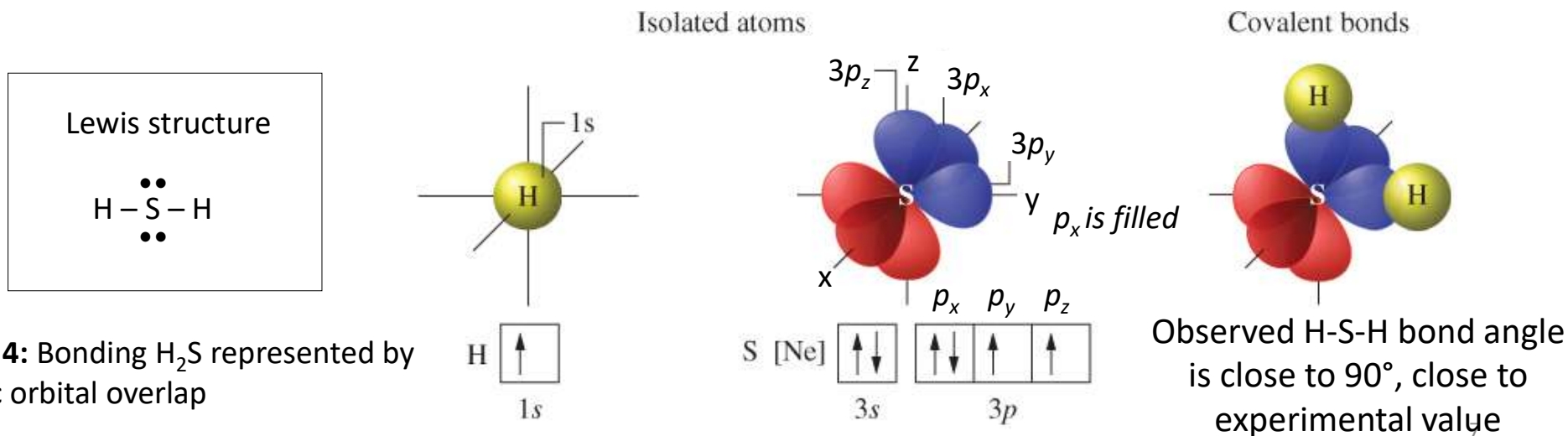


Figure 3: ESP map for H₂ 6

Using the VB method to describe a molecular structure

1. Identify the valence orbitals of the central atom
2. Sketch the valence orbitals
3. Bring in atoms to be bonded to the central atom & sketch orbital overlap
4. Describe the resulting structure

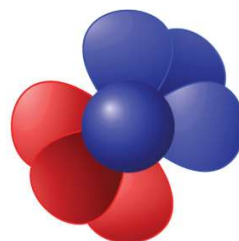
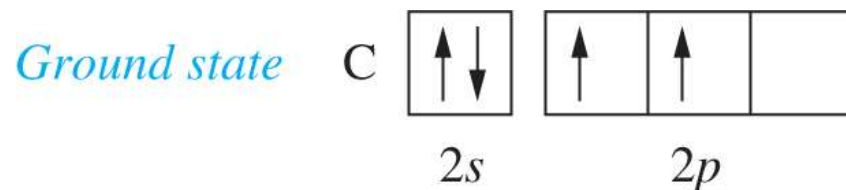


When simple VB theory breaks down...

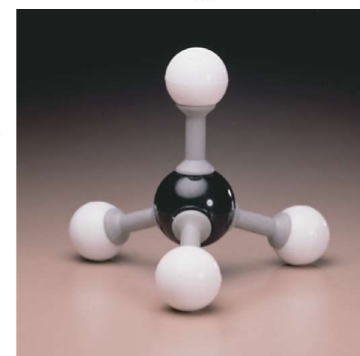
Our description of molecules based on overlap of unmodified AOs does not always conform to observed measurements.

- **Example 1: geometry of CH_4**

- C forms 4 bonds with H atoms, VSEPR gives tetrahedral geometry.
- p-orbitals don't give tetrahedral bond angles.

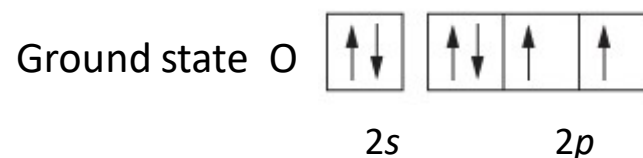


Valence orbitals of an isolated C atom

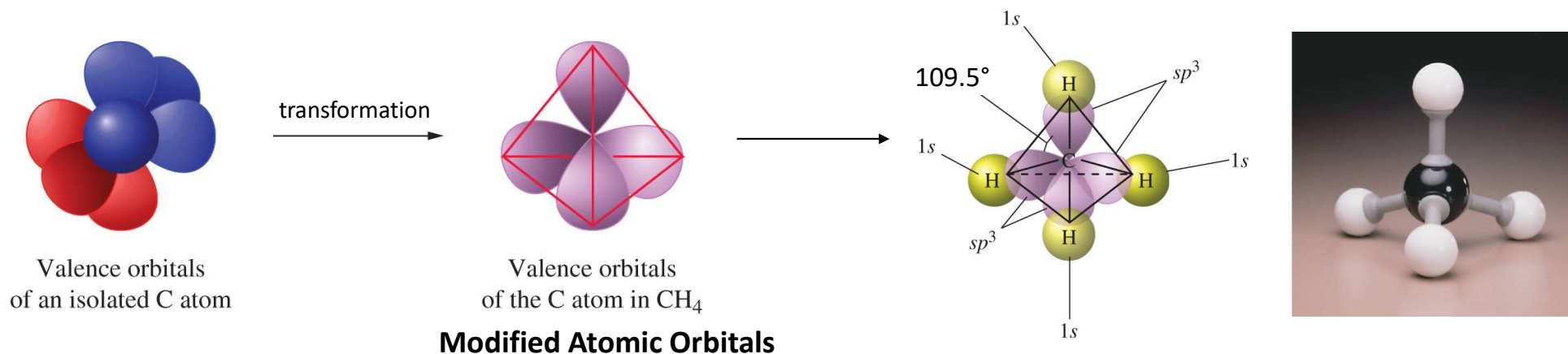


- **Example 2: paramagnetic O_2**

- VB should match unpaired electrons of one O atom with those of the other
- How can O_2 have unpaired electrons (be paramagnetic)?



Modify VB Theory: Hybridization of Atomic Orbitals



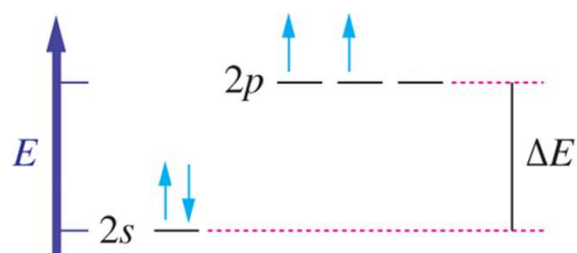
- Hybridization is the (mathematical) process of transforming pure atomic orbitals into reformulated atomic orbitals for bonded atoms. The new orbitals are called hybrid orbitals, which are still atomic orbitals. The number of hybrid orbitals equals the number of pure atomic orbitals reformulated.
- Hybrid orbitals are an after-the-fact rationalization of the experimentally observed molecular shape (can we force the orbitals to match the known geometry).
- Extended VB theory: covalent bonds are formed by overlap of pure or hybrid atomic orbitals, which ever gives the correct shape.

sp^3 hybridization

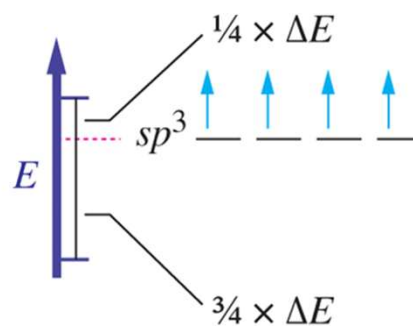
Example: Carbon atom in CH_4

- 1 s + 3 p orbitals give 4 sp^3 hybrid orbitals.
- Each sp^3 hybrid orbital has 25% s character and 75% p character, so its energy is intermediate between those.

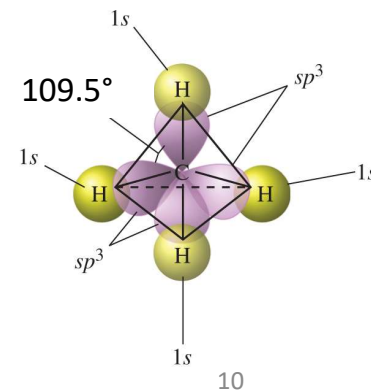
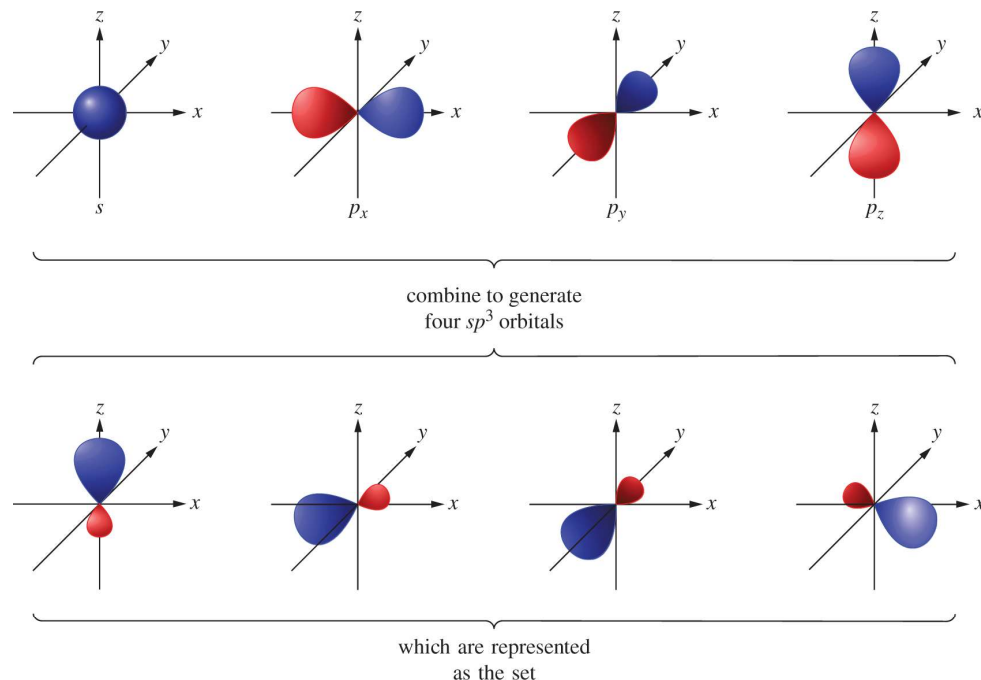
$$\Psi(sp^3) = \Psi(s) + a\Psi(p_x) + b\Psi(p_y) + c\Psi(p_z)$$



Pure AO



Hybrid AO



sp^3 hybridization

Example: Nitrogen in NH_3 and Oxygen in H_2O

Hund's rule also applies for hybrid orbitals

sp^3 Hybridization in nitrogen

(5 valence electrons):

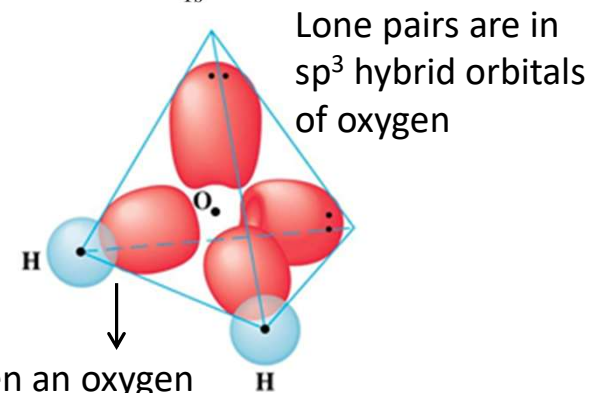
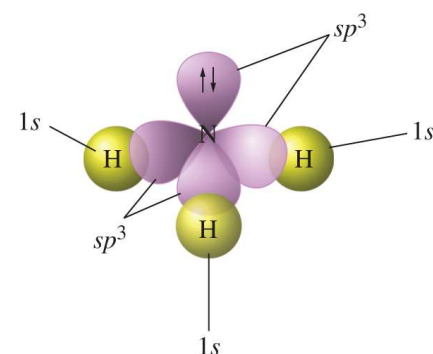


sp^3 Hybridization in oxygen

(6 valence electrons):



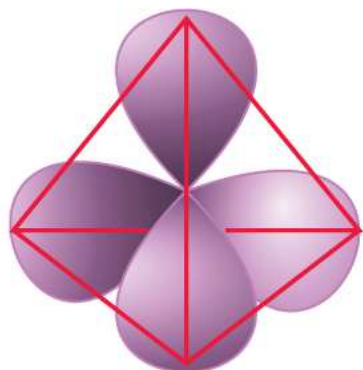
Tetrahedral electron-group geometry



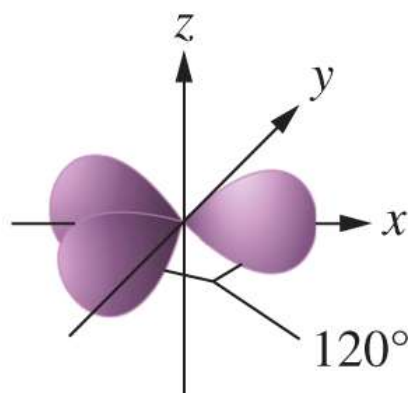
O-H bond is formed between an oxygen sp^3 hybrid orbital and an H $1s$ orbital

Do all *p* orbitals have to hybridize?

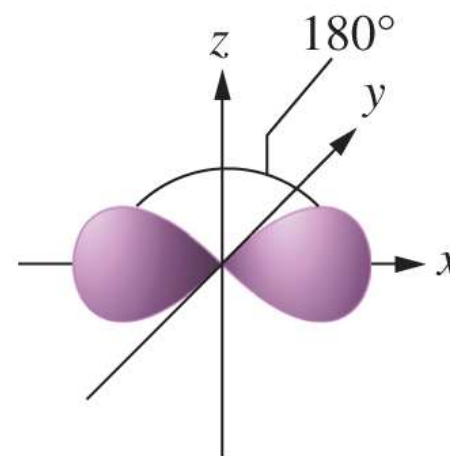
- Hybridization can occur using an *s* orbital and either 1, 2, or 3 *p* orbitals.



sp^3



sp^2

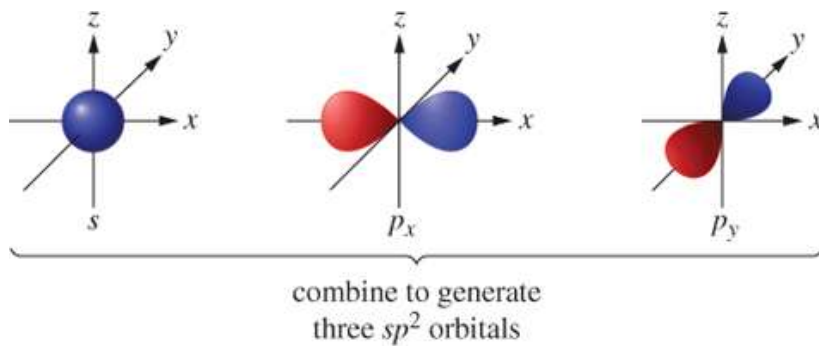


sp

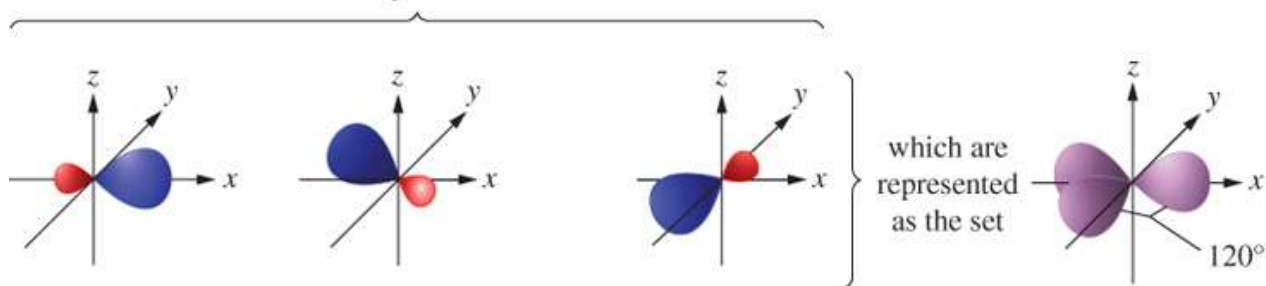
sp^2 hybridization

Example: Boron atom in BF_3

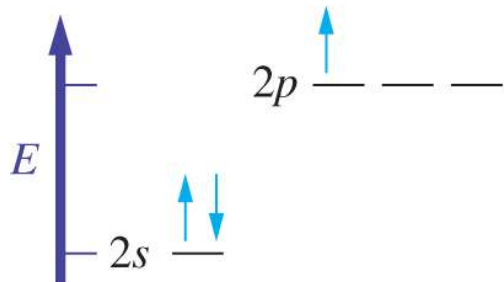
- 1 s + 2 p gives 3 sp^2 orbitals.
- Each sp^2 orbital has 33% s character and 66% p character.



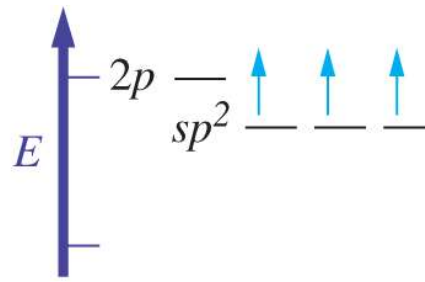
Carey B. Van Loon



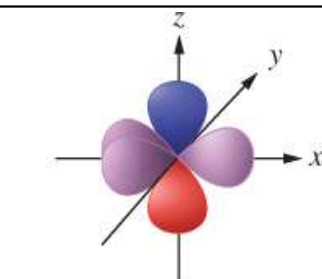
The $2p_z$ remains unhybridized



Pure AO



Hybrid AO

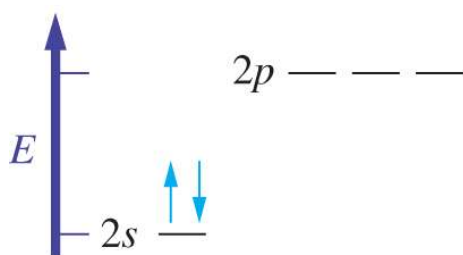
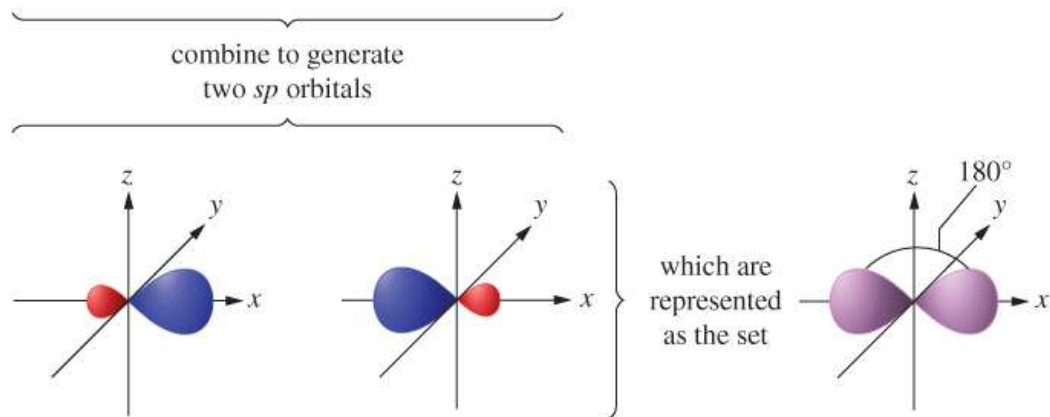
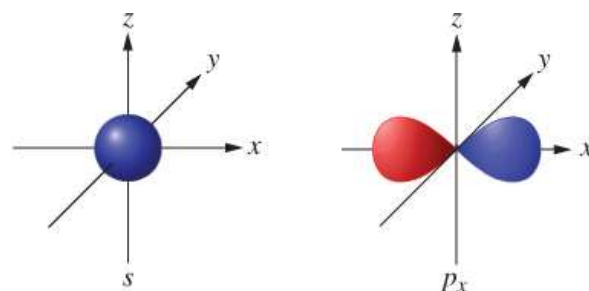


The set of orbitals $sp^2 + p$

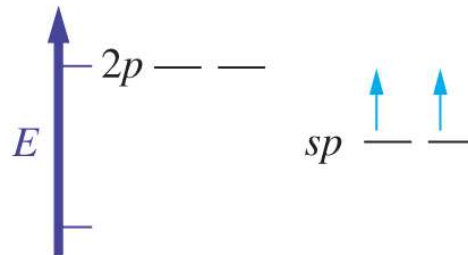
sp hybridization

Example: Beryllium atom in BeCl_2

- 1 s + 1 p gives 2 sp orbitals.
- Each sp orbital has 50% s character and 50% p character.



Hybridize



The $2p_z$ and $2p_y$ remain unhybridized