

Simple Molecular Orbital Theory

Chapter 5

Wednesday, October 7, 2015

Using Symmetry: Molecular Orbitals

One approach to understanding the electronic structure of molecules is called Molecular Orbital Theory.

- MO theory assumes that the valence electrons of the atoms within a molecule become the valence electrons of the entire molecule.
- Molecular orbitals are constructed by taking *linear combinations* of the valence orbitals of atoms within the molecule. For example, consider H₂:



- Symmetry will allow us to treat more complex molecules by helping us to determine which AOs combine to make MOs

LCAO MO Theory

The most common approach to approximating MOs is the linear combination of atomic orbitals method

$$\psi_n = \sum_i c_{ni} \phi_i = c_{n1} \phi_1 + c_{n2} \phi_2 + c_{n3} \phi_3 + \dots$$

- ϕ s are the valence AOs of the atoms that make up the molecule
- c s are weighting coefficients that tell how much of each AO is in the MO

Three conditions must be met for AOs to interact and form MOs:

- The AOs must have the same symmetry
- The AOs must have similar energy
- The AOs must have spatial overlap

Like any model, LCAO MO theory provides only an approximation to the exact electronic structure of molecules.

MO Math for Diatomic Molecules

Consider two atoms A and B each carrying a single atomic orbital, ϕ_1 and ϕ_2 .



Each MO may be written as an LCAO: $\psi = c_1\phi_1 + c_2\phi_2$

Since the probability density is given by the square of the wavefunction:

$$\psi^2 = (c_1\phi_1 + c_2\phi_2)^2 = c_1^2\phi_1^2 + c_2^2\phi_2^2 + 2c_1c_2\phi_1\phi_2$$

$$\int \psi^2 d\tau = c_1^2 \int \phi_1^2 d\tau + c_2^2 \int \phi_2^2 d\tau + 2c_1c_2 \int \phi_1\phi_2 d\tau$$

probability of finding the
electron close to atom A

ditto atom B

overlap term, important
between the atoms

MO Math for Diatomic Molecules

$$\int \psi^2 d\tau = c_1^2 \int \phi_1^2 d\tau + c_2^2 \int \phi_2^2 d\tau + 2c_1c_2 \int \phi_1\phi_2 d\tau$$

(Note: In the original image, red arrows point from the integrands to the values 1, 1, and S respectively.)

$$\int \psi^2 d\tau = c_1^2 + c_2^2 + 2c_1c_2S$$

The individual AOs are *normalized*:

$$\int \phi_1^2 d\tau = 1$$

$$\int \phi_2^2 d\tau = 1$$

100% probability
of finding electron
somewhere for
each free atom

MO Math for Homonuclear Diatomic Molecules

For two identical AOs on identical atoms, the electrons are equally shared, so:

$$\psi = c_1\phi_1 + c_2\phi_2 \quad c_1^2 = c_2^2$$

In other words: $c_1 = \pm c_2$

So we have two MOs from the two AOs:

$$\psi_+ = c_{+,1}(\phi_1 + \phi_2) \quad \psi_- = c_{-,1}(\phi_1 - \phi_2)$$

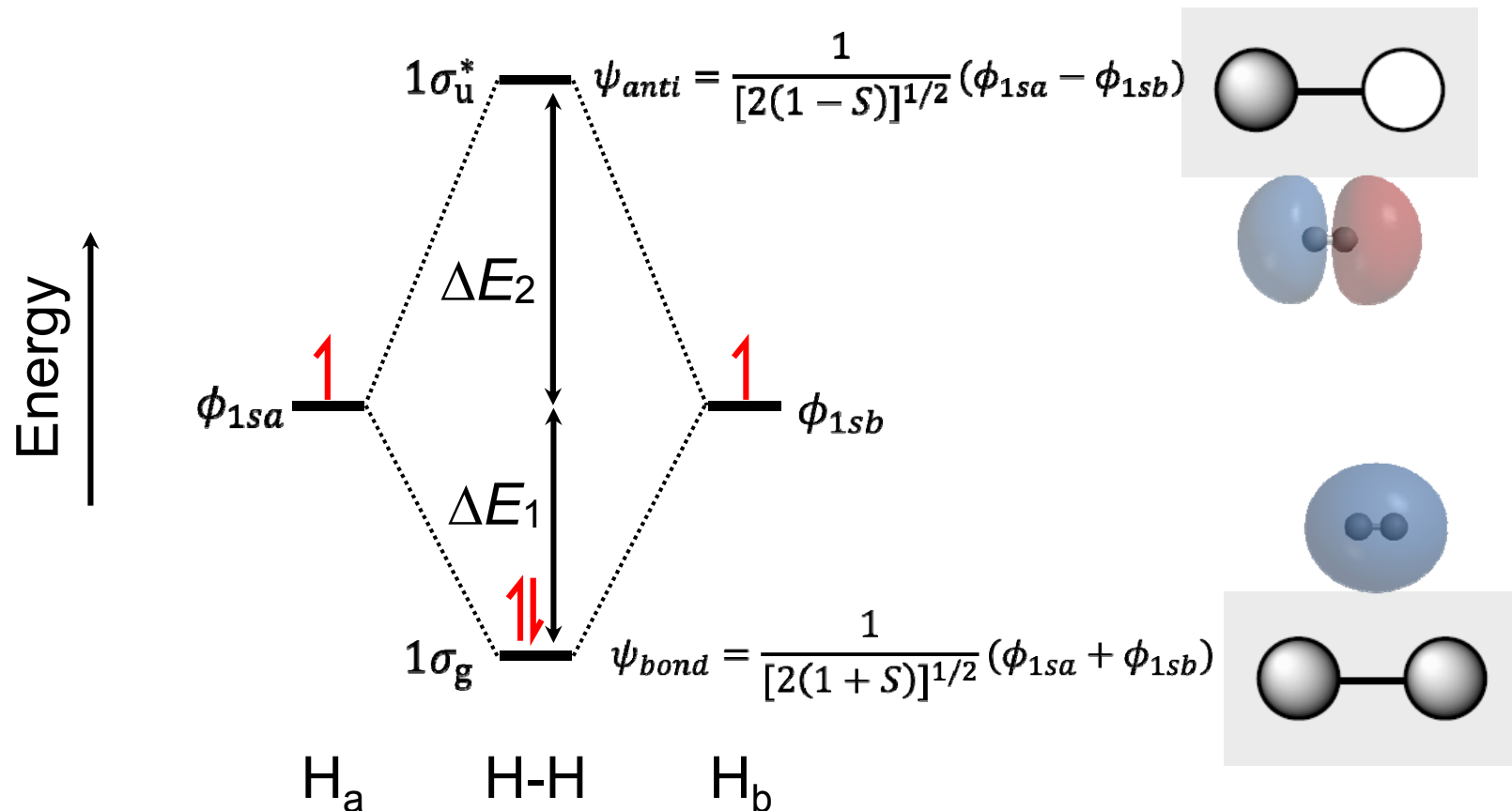
After normalization (setting $\int \psi_+^2 d\tau = 1$ and $\int \psi_-^2 d\tau = 1$):

$$\psi_+ = \frac{1}{[2(1+S)]^{1/2}} (\phi_1 + \phi_2) \quad \psi_- = \frac{1}{[2(1-S)]^{1/2}} (\phi_1 - \phi_2)$$

where S is the **overlap integral**: $S = \int_{\text{space}} \phi_1 \phi_2 d\tau \quad 0 \leq S \leq 1$

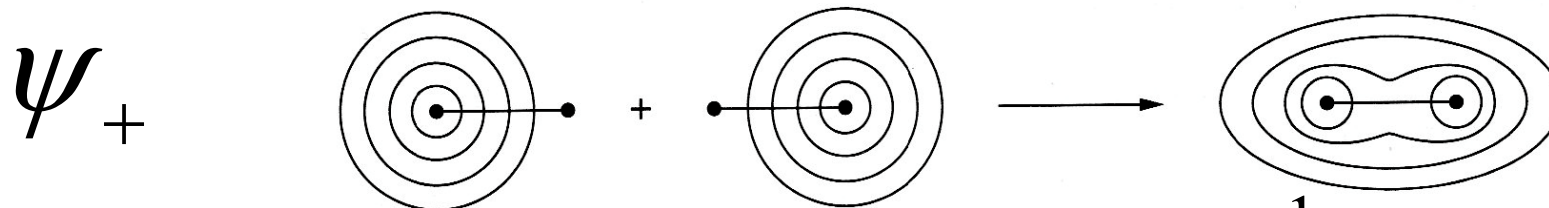
LCAO MO Energy Diagram for H₂

H₂ molecule: two 1s atomic orbitals combine to make one bonding and one antibonding molecular orbital.



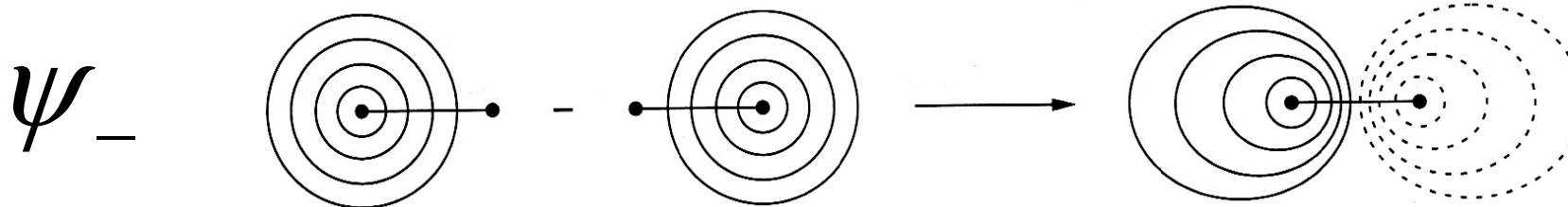
- $\Delta E_2 > \Delta E_1$, so the antibonding orbital is always more anti-bonding than the bonding orbital is bonding

MOs for H₂



- in phase combination
- constructive interference
- large e⁻ density in the internuclear region (**bonding**)
- an electron in this MO lowers the molecule's energy

$$\psi_+^2 = \frac{1}{2(1+S)} (\phi_1^2 + \phi_2^2 + 2\phi_1\phi_2)$$

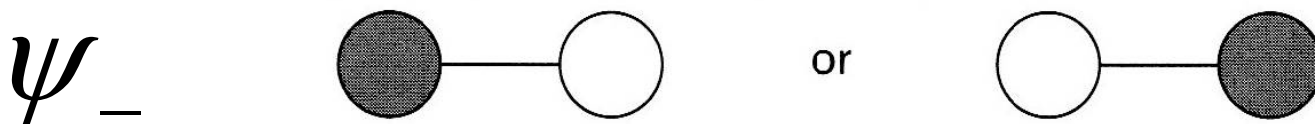


- out of phase combination
- destructive interference
- small e⁻ density in the internuclear region (**antibonding**)
- nodal plane between atoms
- an electron in this MO raises the molecule's energy

$$\psi_-^2 = \frac{1}{2(1-S)} (\phi_1^2 + \phi_2^2 - 2\phi_1\phi_2)$$

MO Notation

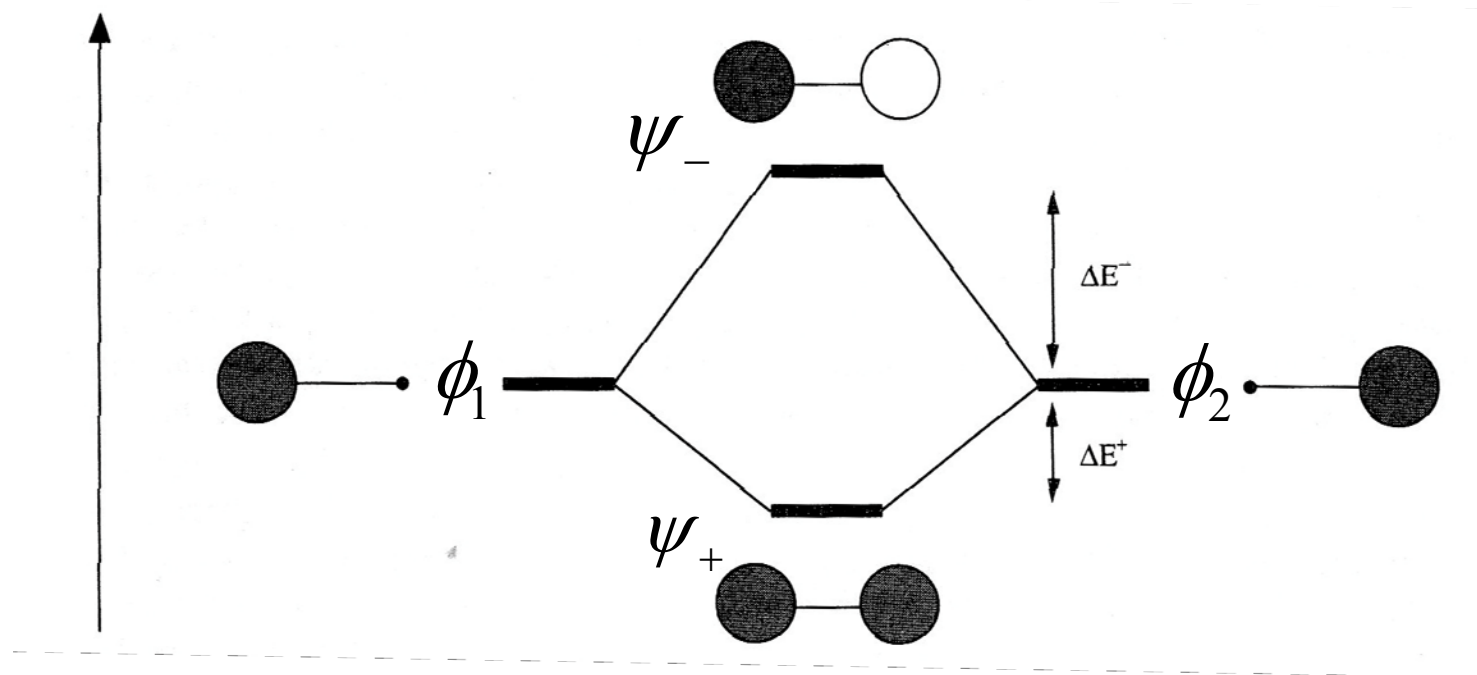
Schematic representations of the MOs:



- shading indicates sign of AO
- size of AO reflects the magnitude of its coefficient in the MO

Basic Rule #1 of MO Theory

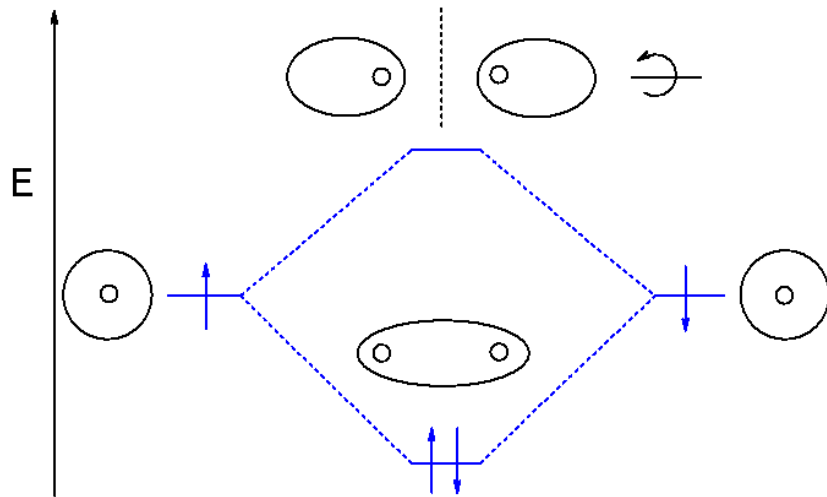
Rule #1: The interaction of n AOs leads to the formation of n MOs. If $n = 2$, one MO is bonding and one antibonding. The bonding orbital is more stable than the lower-energy AO. The antibonding orbital is less stable than the higher-energy AO. The bonding orbital is stabilized less than the antibonding orbital is destabilized.



$$\Delta E^- > \Delta E^+$$

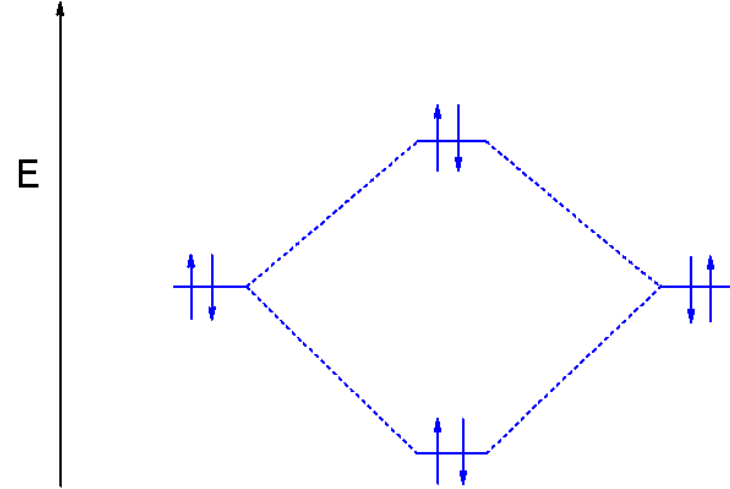
H₂ vs. He₂

dihydrogen



bond order: 1
stable molecule

dihelium

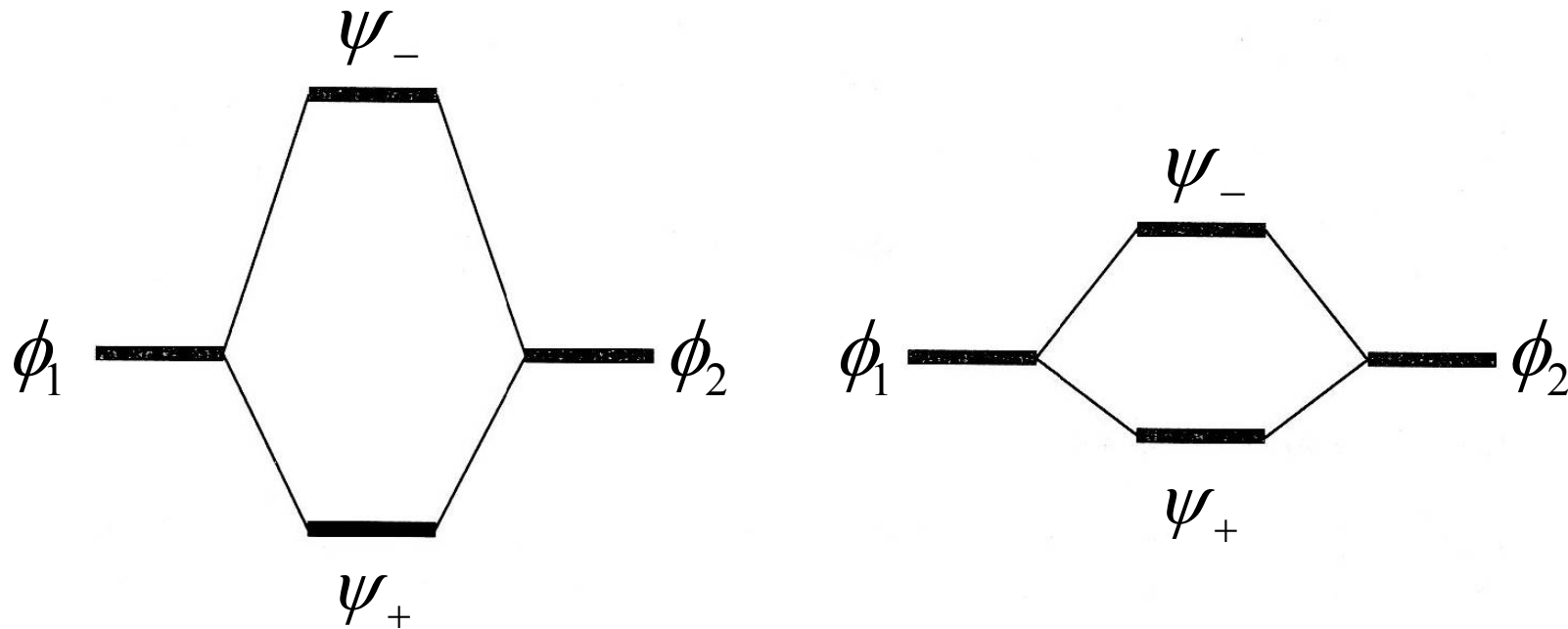


bond order: 0
unstable molecule

$$BO = \frac{1}{2} [(\# \text{ bonding } e) - (\# \text{ anti-bonding } e)]$$

Basic Rule #2 of MO Theory

Rule #2: If the AOs are degenerate, their interaction is proportional to their overlap integral, S .



large overlap

small overlap

$$S = \int_{\text{space}} \phi_1 \phi_2 d\tau$$

The greater the degree of overlap, the stronger the bonding/antibonding.

Basic Rule #3 of MO Theory

Rule #3: Orbitals must have the same symmetry (same irreducible representation) to have non-zero overlap.

$$S = \int_{space} \phi_1 \phi_2 d\tau$$

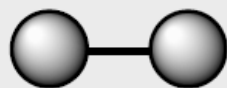
- **$S = 0$ if orbitals have different *irreducible representations*.**
- **If $S \neq 0$, then bonding and antibonding MOs result.**

If the overlap integral between two orbitals centered on different atoms is zero, then there is no interaction between them.

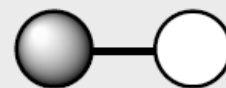
- **If an orbital has $S = 0$ with all other orbitals in the molecule, then it is a 100% non-bonding orbital.**

Overlap and Bond Type

The bonding nature of an orbital interaction is defined by the relative orbital phasing



bonding

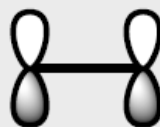


anti-bonding

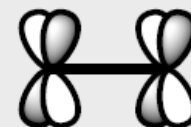
The type of bonding is defined by the number of nodes parallel to the bond



σ or σ -bonding



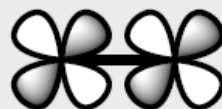
π



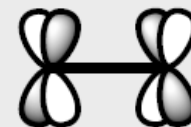
δ



σ^* or σ -anti-bonding

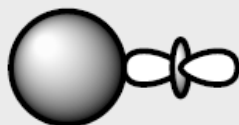


π^*

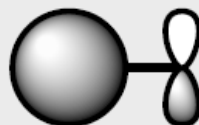


δ^*

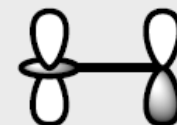
Interactions between different types of orbitals is okay as long as there is net overlap



σ



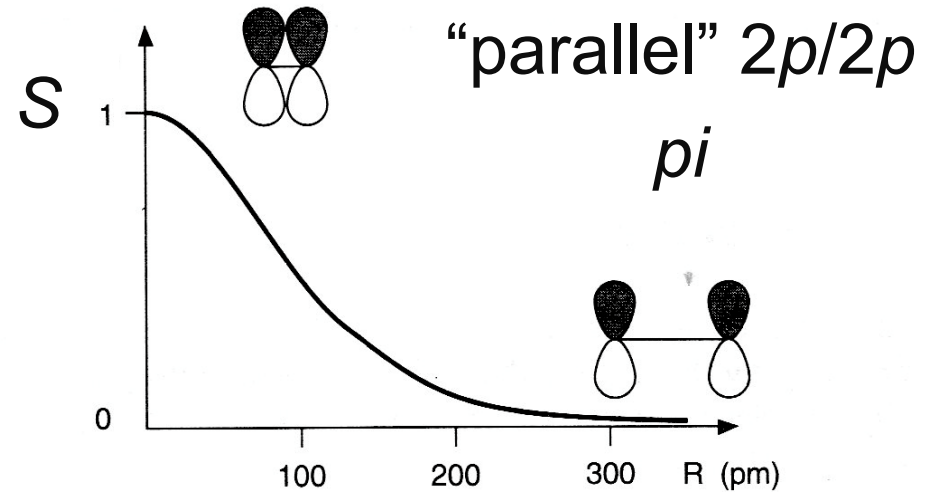
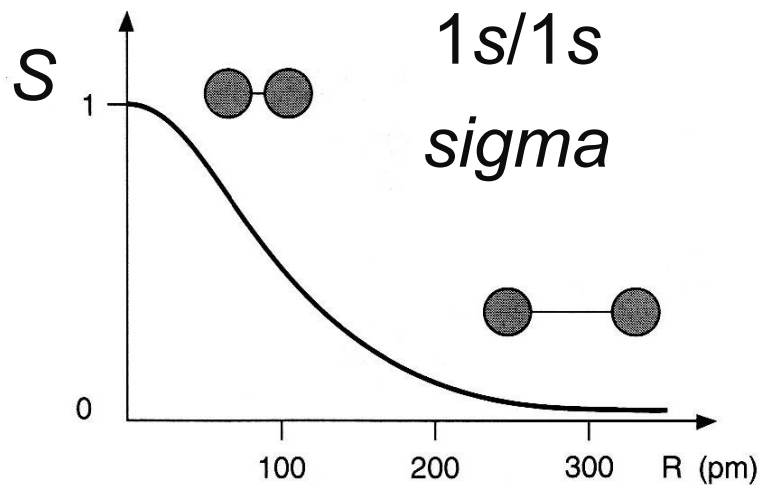
non-bonding



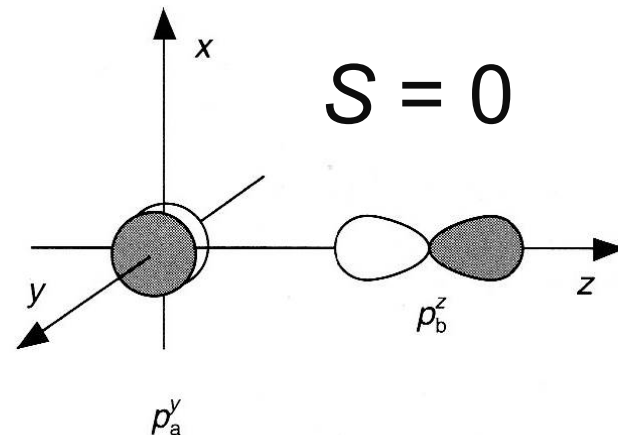
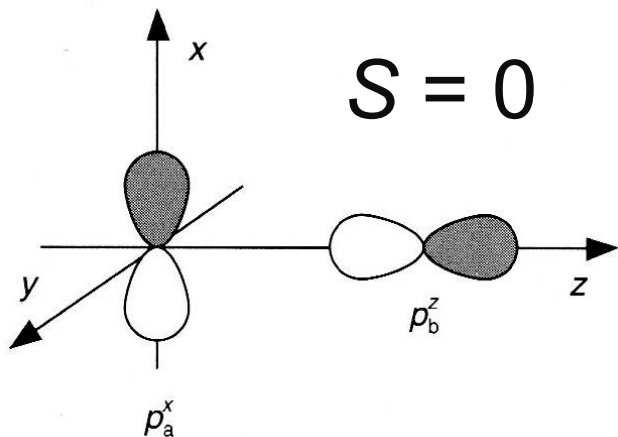
non-bonding

Overlap and Symmetry

The extent of overlap depends on the internuclear separation, the nature of the orbitals involved (s, p, or d), and their relative orientation.

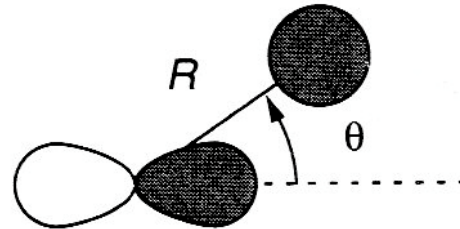


"perpendicular" $2p/2p$ have zero overlap by symmetry



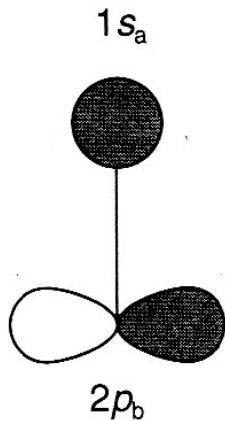
Overlap and Symmetry

$1s/2p$ overlap depends on the angle θ :



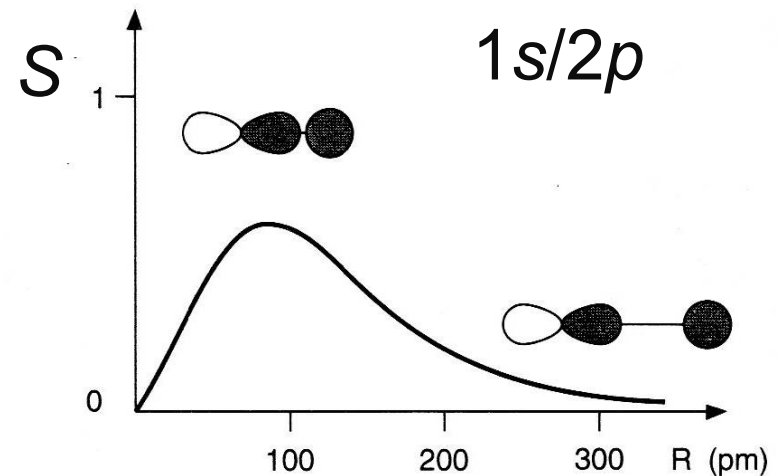
overlap goes as $\cos\theta$:

$$\theta = 90^\circ$$



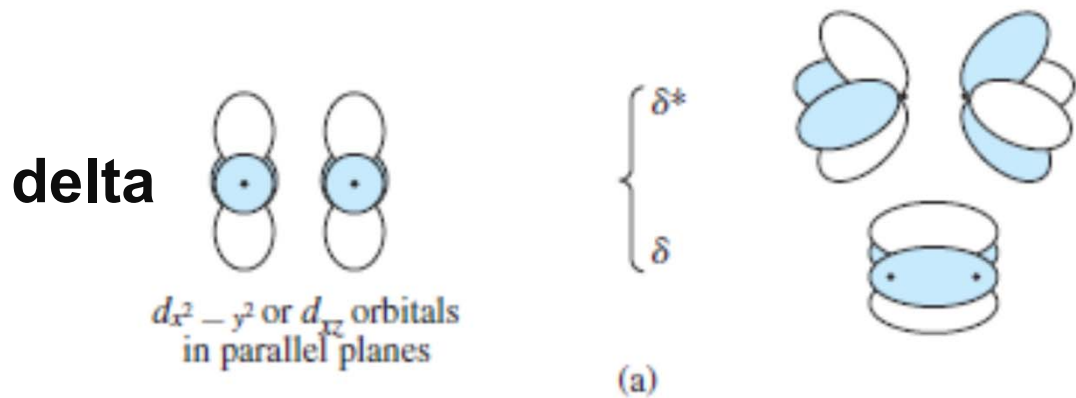
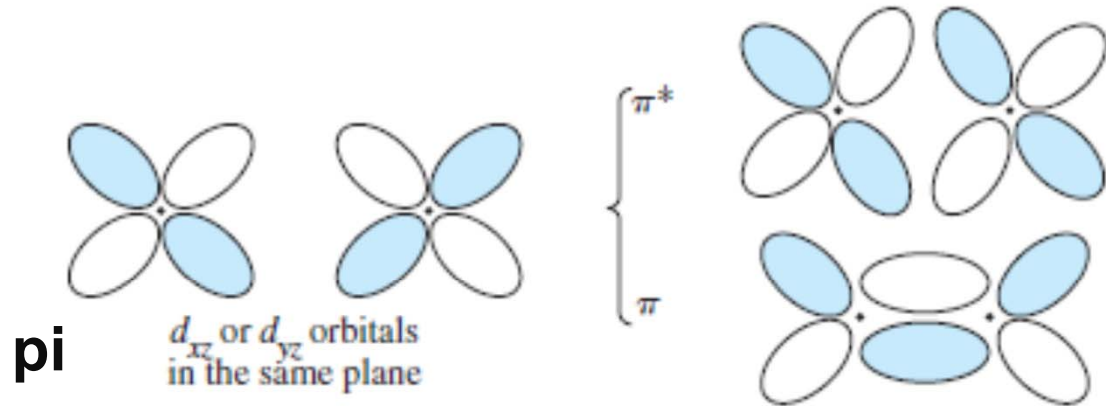
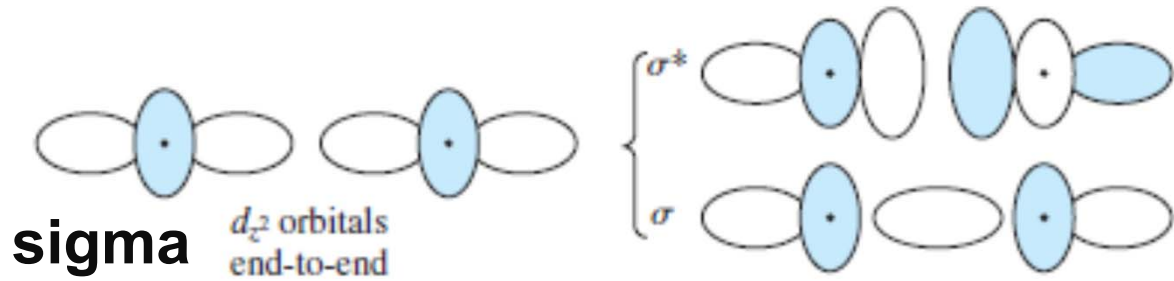
$$S = 0$$

$$\theta = 0^\circ$$



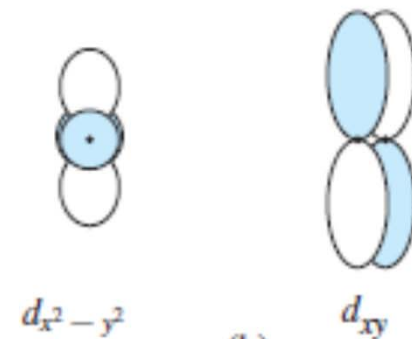
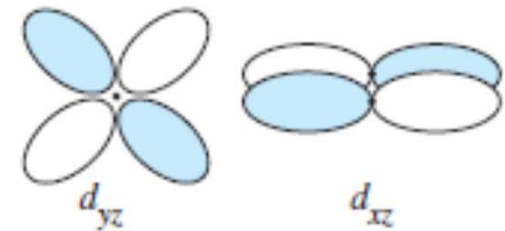
Overlap and Symmetry

d orbitals



(a)

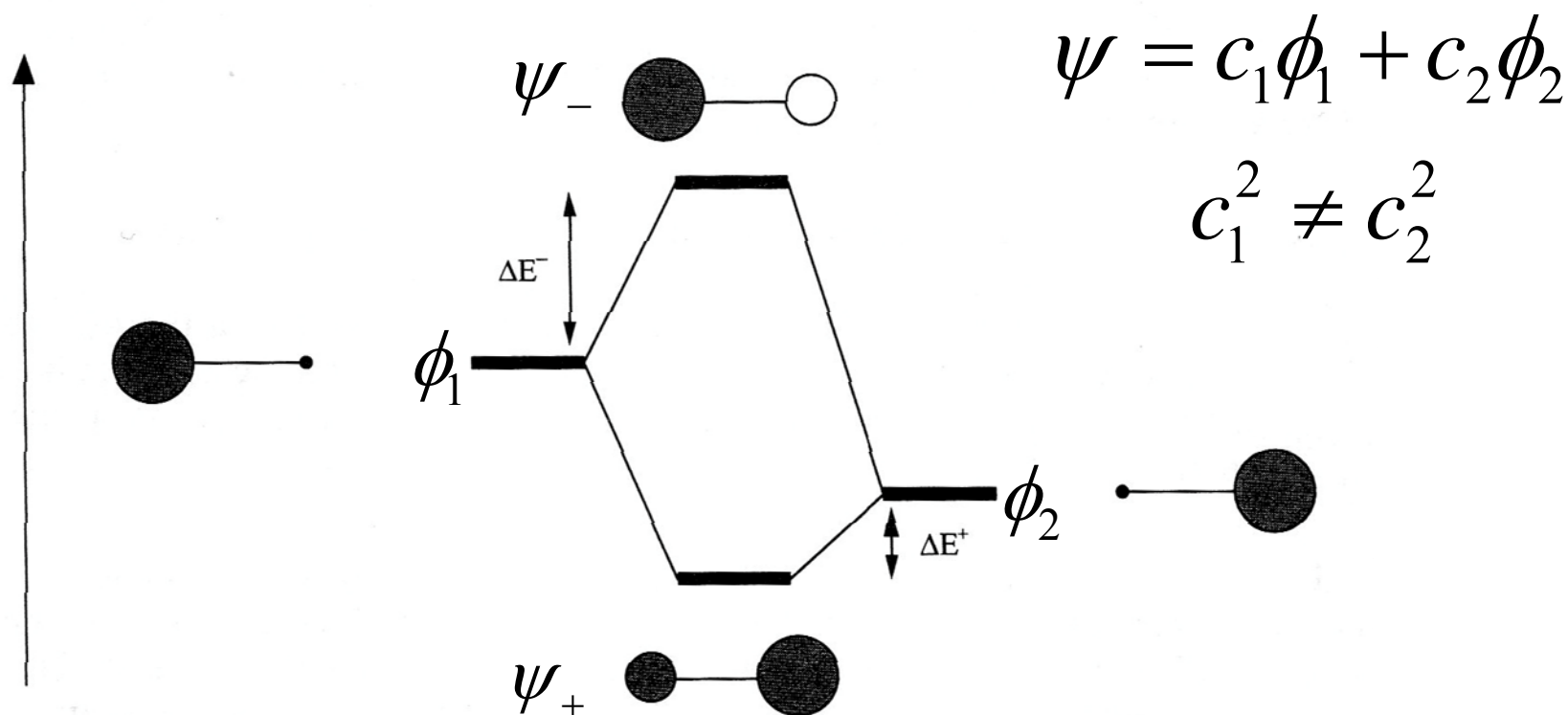
zero overlap by symmetry



(b)

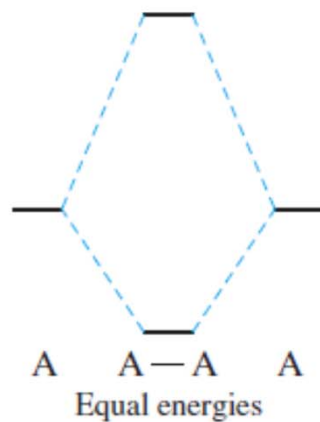
Basic Rule #4 of MO Theory

Rule #4: If the AOs are non-degenerate, their interaction is proportional to $S^2/\Delta E$, where ΔE is the energy separation between the AOs. In this case the bonding orbital is mostly localized on the atom with the deeper lying AO, usually the more electronegative atom. The antibonding orbital is mostly localized on the atom with the higher AO.

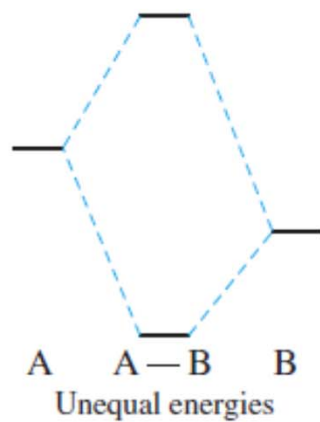


Orbitals with $\Delta E > 12-14$ eV have essentially zero interaction.

Basic Rule #4 of MO Theory



**strong
interaction
*bonding and
antibonding***



**weak
interaction
*almost
nonbonding***

