

Chapter 11

Chemical Bonding II:

Valence Bond and Molecular Orbital Theories

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We will start by continuing the Localized Electron Model of bonding (better known as “Valence Bond Theory”)

We will study “hybrid orbitals”, which just formalize the electron groups (or “featureless blobs” as I sometimes call them) of VSEPR.

- It’s like putting uniforms on the soldiers of a ragtag army and giving them ranks and titles. 😊

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Hybrid orbitals

Localized Electron Model (Valence Bond Theory) and VSEPR works well in predicting molecular geometries

- But ordinary atomic orbitals (s and p) do not!
- They would give the wrong bond angles and lengths
 - No predicted angle between the spherical s-orbitals and the any of the p-orbitals
 - Predicted angle between p-orbitals is 90°

Bottom line:

Atomic orbitals in the valence shell don’t seem to survive bond-making!

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Hybrid orbitals

- VSEPR works by treating electron pairs as indistinguishable “blobs”
- We can obtain indistinguishable atomic orbitals by mixing pure atomic orbitals: **hybridization**

Hybrid orbitals \longleftrightarrow “blobs”
(electron groups)
of VSEPR

- It’s a “mathematically polite” way of getting our “blobs” of VSEPR 😊

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Hybrid orbitals

When an atom starts bonding, its original atomic orbitals are mixed (hybridized) in such a way that minimizes repulsion between electron pairs in **skeletal bonds as well as lone pairs**.

- To achieve the same result predicted by VSEPR

Skeletal bonding pairs and the lone pairs have the same hybridization.

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Hybrid orbitals

Number of electron groups in Lewis structure
(*no. of skeletal bonds and lone pairs*)



Number of hybrid orbitals needed

What is a skeletal bond?

The first bond that forms between two atoms

The first bond in a double or triple bond

- Second and third bonds are not skeletal (so, not made from hybrid orbitals)

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Hybrid orbitals

How many hybrid orbitals does an atom need?
Same as "electron groups" we counted in VSEPR.
Count the skeletal bonds and lone pairs around it

How many hybrid orbitals does C in CO₂ need?

2 skeletal bonds
0 lone pairs
⇒ 2+0 = 2

How many hybrid orbitals does each O in CO₂ need?

1 skeletal bond
2 lone pairs
⇒ 1+2 = 3

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Hybrid orbitals

How many hybrid orbitals does N in NH₃ need?

3 skeletal bonds
1 lone pair
⇒ 3+1 = 4

How about the hydrogens?

They don't hybridize their orbitals.
They keep their pure atomic 1s orbitals.

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Hybrid orbitals

Two electron groups on the atom:
sp Hybridization

sp

1 + 1 = 2 orbitals

- Combination of **one s** and **one p** orbital.
- Gives a linear arrangement of atomic orbitals.
➤ same as predicted by VSEPR
- The two unhybridized p orbitals form "extra" bonds that form two double bonds or a triple bond (so the extra bonds are added to an already existing "skeletal" bond made by hybridized orbitals)

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Hybrid orbitals

Energy levels of **sp hybrid orbitals**

2p — — —

2s — — —

Orbitals in a free C atom

Hybridization

Two leftover p orbitals
Not hybridized

sp — — — sp — — —
sp hybrids

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Hybrid orbitals

$s + p \Rightarrow sp$
Two sp orbitals oriented away from each other at 180°

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Hybrid orbitals

Three electron groups on the atom:
sp² Hybridization

1 is implicit

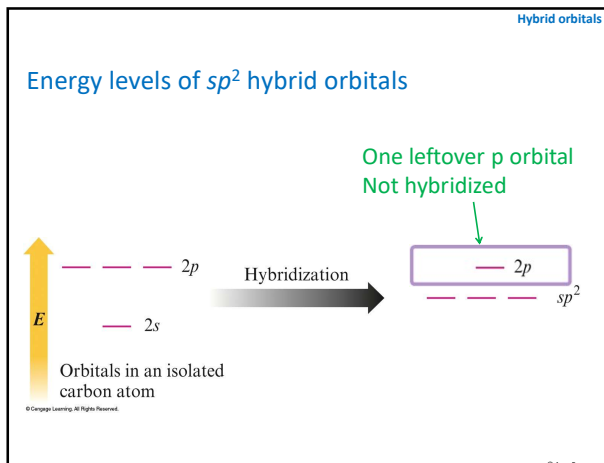
sp^2

1 + 2 = 3 orbitals

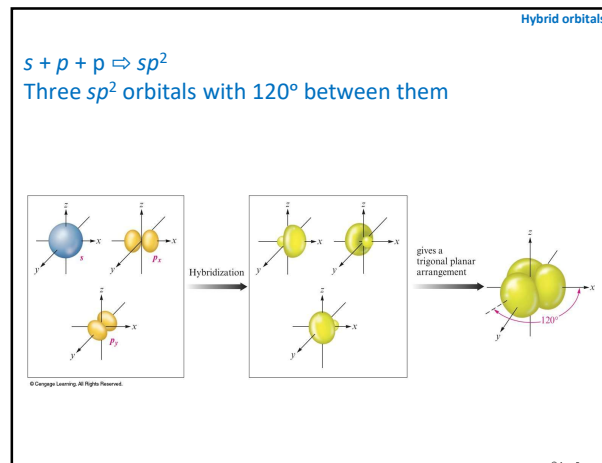
- Three electron groups needed
- Combination of **one s** and **two p** orbitals.
- Gives a trigonal planar arrangement of atomic orbitals
➤ same as predicted by VSEPR
- The unhybridized p orbital forms an "extra" bond with the unhybridized p orbital of a neighboring atom
➤ Leads to a "double bond"

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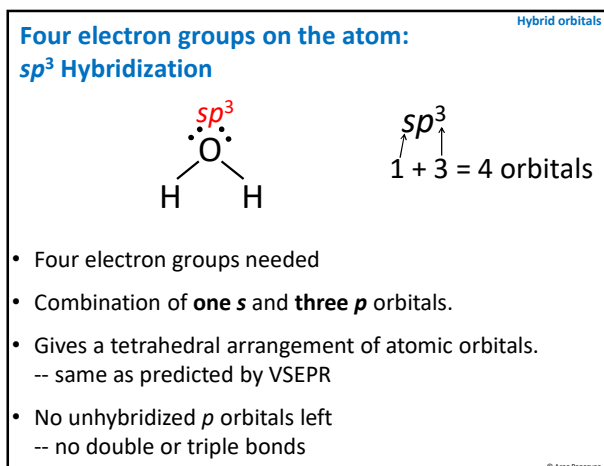
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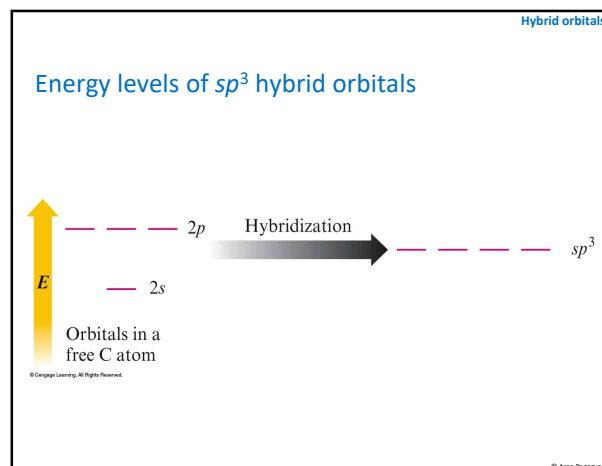
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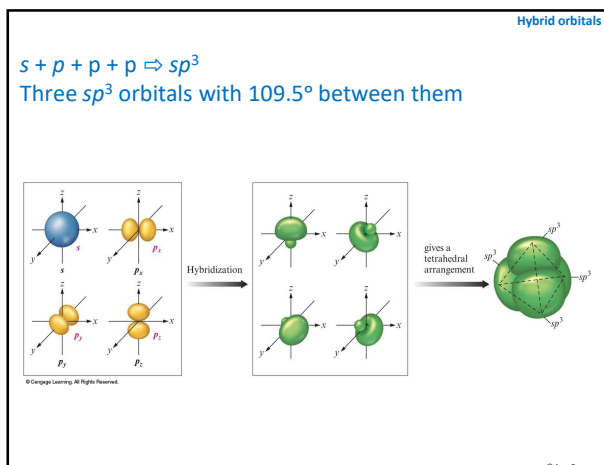
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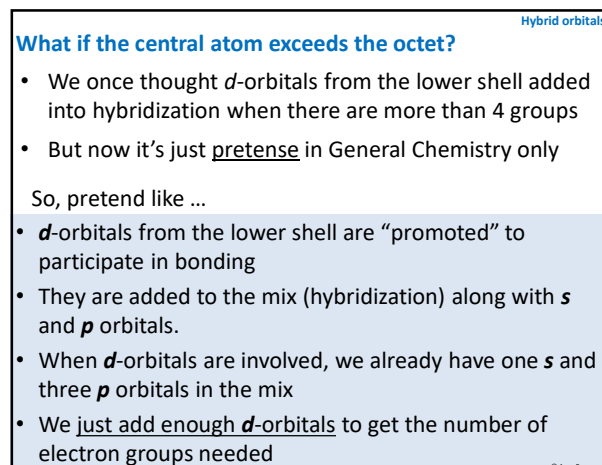
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So, if we are not recruiting the d orbitals of the lower shell, how is it that the central atom can seem to have 5 or 6 electron groups, like we saw in VSEPR?

There is a reasonable way to describe those situations with resonance in unconventional Lewis structures involving ionic bonds, but we're not going to do that.

General Chemistry curriculum nationwide has not yet mustered the boldness to discard what's wrong and replace it with something that's not that hard to explain. I might start including it, but not yet.

So ...

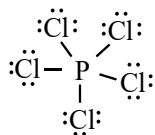
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Pretend hybridization #1 dsp^3 Hybridization

- Because 5 electron groups are needed
- Combination of **one d** , **one s** , and **three p** orbitals.
- Gives a trigonal bipyramidal arrangement of 5 equivalent hybrid orbitals.

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Consider the Lewis structure for PCl_5



What is the **shape** of the molecule?

trigonal bipyramidal

What are the ideal **bond angles**?

90° and 120°

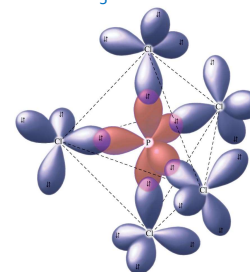
What is the hybridization of P?

dsp^3

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The Orbitals Used to Form the Bonds in PCl_5

Notice how the sigma bonds are formed by head-to-head overlap of hybrid orbitals on P and Cl



The central **P** atom is dsp^3 hybridized

Cl atoms each have just one skeletal bond and three lone pairs, all sp^3 hybridized. But the **hybridization of peripheral atoms doesn't affect the geometry around the central atom.**

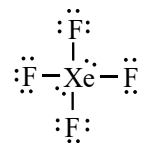
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Pretend hybridization #2 d^2sp^3 Hybridization

- Because 6 electron groups are needed
- Combination of **two d** , **one s** , and **three p** orbitals.
- Gives an octahedral arrangement of 6 equivalent hybrid orbitals.

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Consider the Lewis structure for XeF_4 .



What is the **shape** of the molecule?

square planar

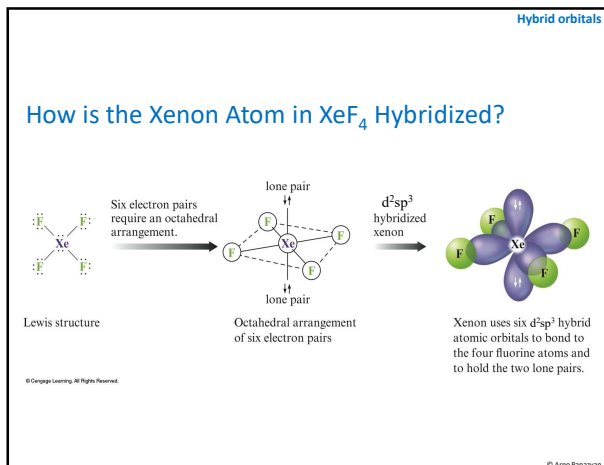
What are the ideal **bond angles**?

90° and 180°

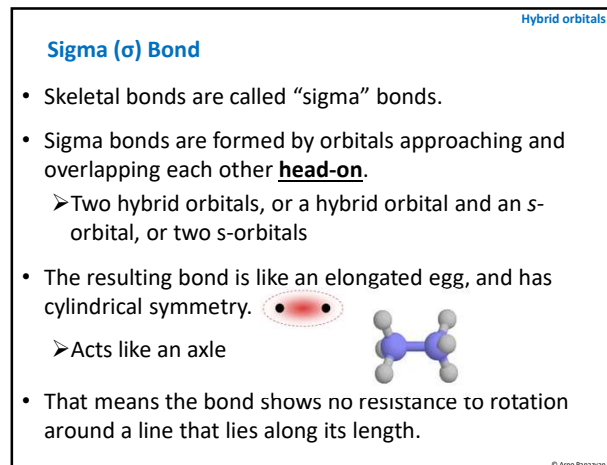
What is the **hybridization of Xe**?

d^2sp^3

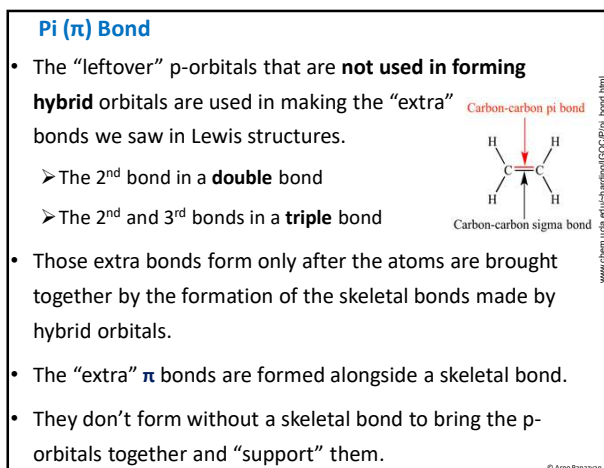
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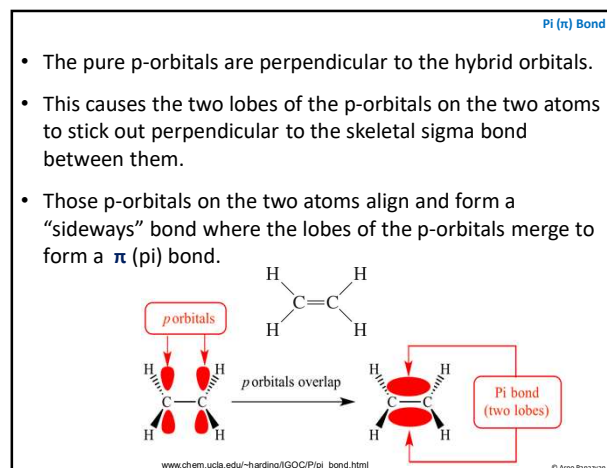
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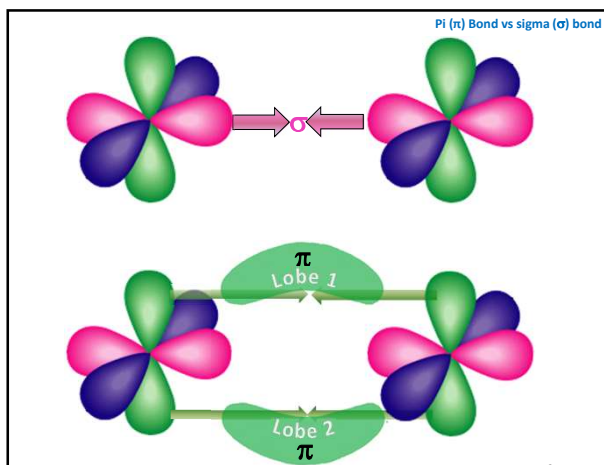
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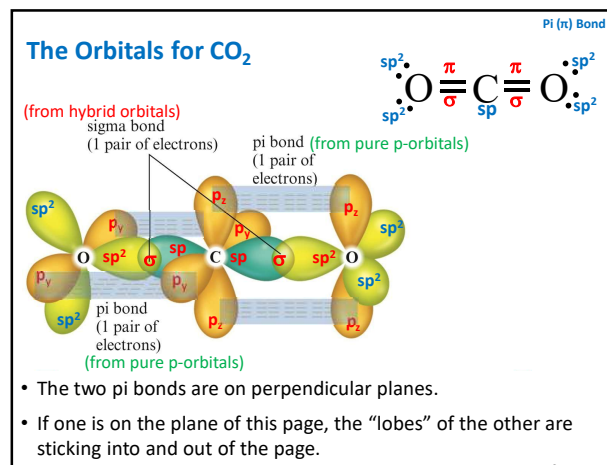
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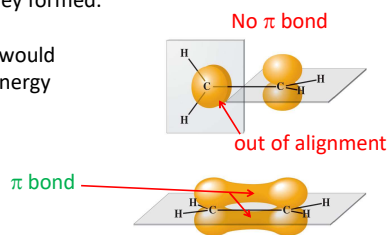


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Pi bonds don't allow rotation

Pi (π) Bond

- Since a π bond relies on the alignment of the p-orbitals on two atoms, rotation around the skeletal bond would mean breaking the π bond.
- That means π bonds prevent rotation around the skeletal bond over which they formed.
- Breaking a pi bond would require too much energy



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Exercise:

Hybrid orbitals

- Draw the Lewis structure for HCN.
- Show all bonds between atoms.
- Label each bond as σ or π .
- Which hybrid orbitals are used?

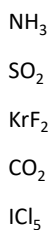
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Exercise:

Hybrid orbitals

Determine the **ideal bond angle(s)** and the **hybridization** (real or pretend) of the **central atom** for each of the following molecules:



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Recap: Using the Localized Electron (also known as "Valence Bond") Model

1. Draw the Lewis structure(s).
 - Or we can use the "Papazyan shortcut" 😊 to find the number of lone pairs, when the peripheral atoms are hydrogens or halogens
2. Determine the arrangement of electron pairs using the VSEPR model
3. Specify the hybrid orbitals containing the electron pairs

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The Molecular Orbital (MO) model of bonding i.e. "the other model" of bonding

Molecular Orbital Theory

- Electrons are assumed to occupy orbitals just like in atoms (2 e⁻ per orbital)
 - But the orbitals extend over the entire molecule
- Formed from **pure** atomic orbitals like s and p
 - No hybrid orbitals in this picture!
- Atomic orbitals are replaced by molecular orbitals (MOs)
- Unlike the localized electron model, as well as bonds, it can also produce anti-bonds!

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- Molecular electron configurations can be written in much the same way as atomic electron configurations.
- Each molecular orbital can hold 2 electrons with opposite spins.
- The **number of orbitals is conserved**.
 - The total number of atomic orbitals coming from different atoms is equal to the number of molecular orbitals created

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Molecular Orbital Theory

Sigma (σ) molecular orbitals (MOs)

- Same shape and name as sigma (s) bonds
- The electron density of σ molecular orbitals is centered along the line passing through the two nuclei.
 - It has the same “symmetry” as a stick (or a cigar, or an egg)
 - If you spin it along its length, you won’t see a change.
- Formed by “head-on” approach of atomic orbitals
- Spherical s atomic orbitals have no choice but approach each other head-on and form sigma molecular orbitals

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Molecular Orbital Theory

Sigma (σ) molecular orbitals (MOs)

We will first use the case of **sigma** molecular orbitals formed by s atomic orbitals to talk about “bonding” and “anti-bonding” molecular orbitals

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Molecular Orbital Theory

Example: Combination of Hydrogen 1s Atomic Orbitals to form MOs

Atomic orbitals: s, s

Combine atomic orbitals

Molecular orbitals:

- Antibonding orbital, σ_g^*
- Bonding orbital, σ_g

Subtract

Add

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Two atomic orbitals create two molecular orbitals

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Molecular Orbital Theory

Again, the number of orbitals are conserved

Remember?

When we considered the hybrid atomic orbitals, the number of pure atomic orbitals going into the mix was equal to the number of hybrid atomic orbitals created.

Same here:
Two atomic orbitals create two molecular orbitals.

of atomic orbitals used = # of MOs created

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Molecular Orbital Theory

We will consider only the MOs formed by valence shell atomic orbitals. MOs made by core orbitals don’t contribute significantly to bonding and chemistry.

Also, we consider only the molecular orbitals formed by atomic orbitals of similar (or same) energy; otherwise the resulting MO would be essentially the same as the atomic orbital with the much lower energy, and not be useful as a “molecular orbital” description.

We will mostly deal with homonuclear (same element) diatomic species, where MOs are formed by valence orbitals of equal energy, coming from each atom.

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Molecular Orbital Theory

Energies of MOs:

Anti-bonding MO > parent atomic orbitals

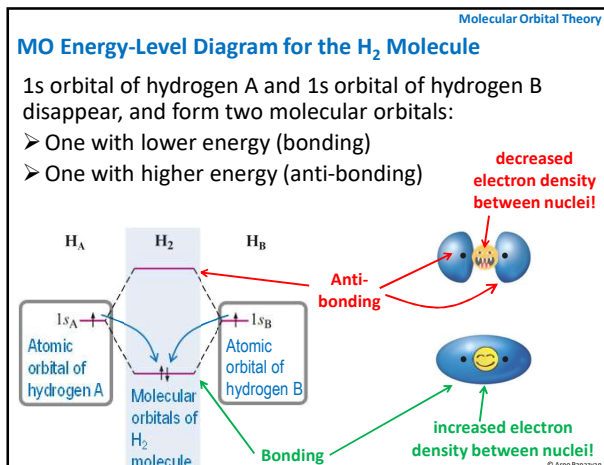
Bonding MO < parent atomic orbitals

Antibonding molecular orbital: higher in energy **bad!** 😬

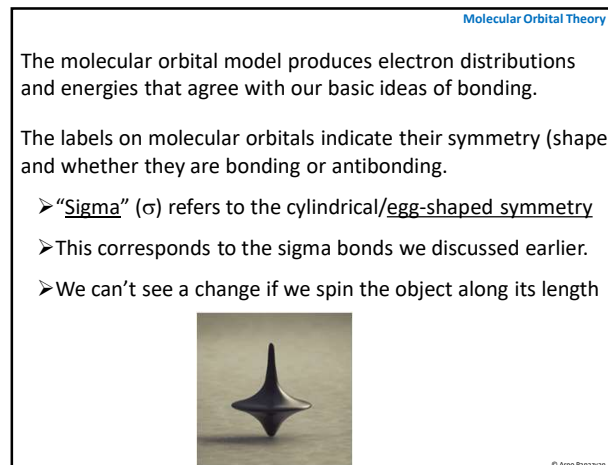
Bonding molecular orbital: lower in energy **good** 😊

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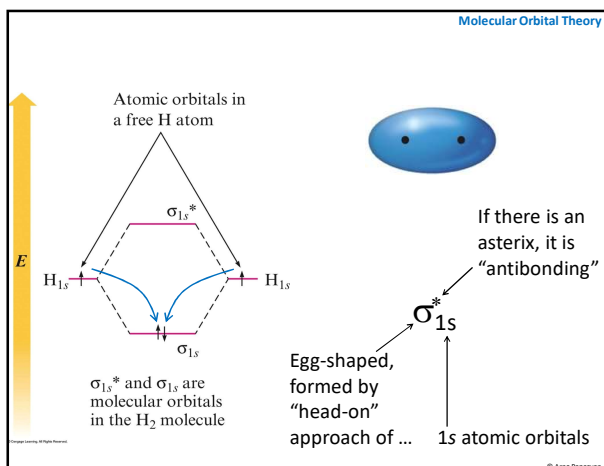
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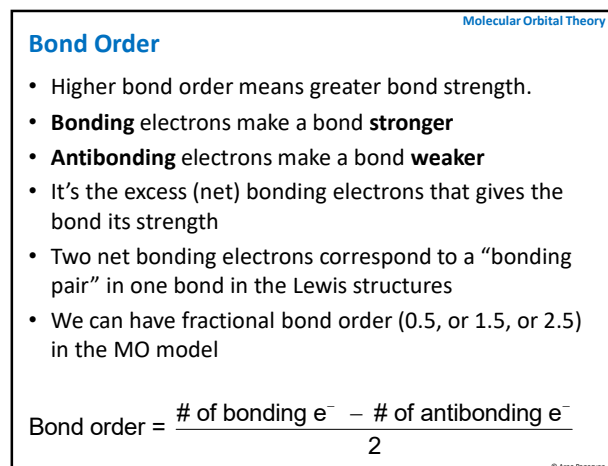
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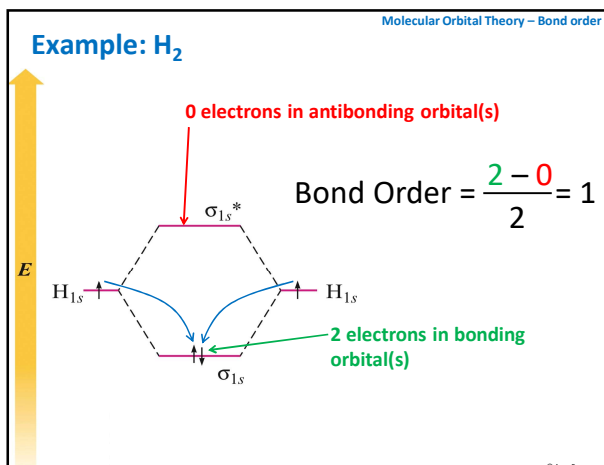
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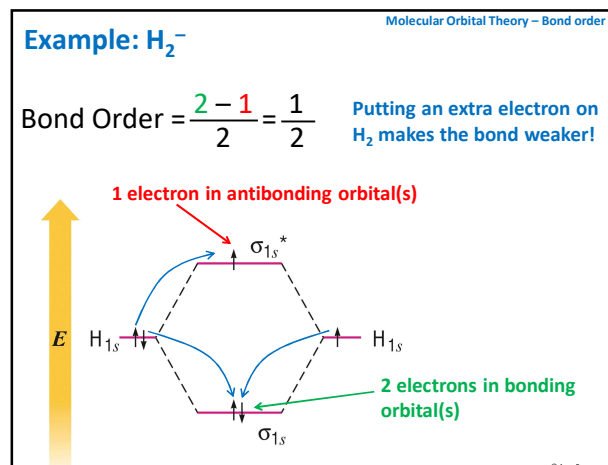
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Molecular Orbital Theory

Populating molecular orbitals

There is no good reason to keep writing the atomic orbitals, once we learn the energy order of the molecular orbitals formed by the valence orbitals of the atoms.

We then simply populate the MOs with the valence electrons in the order of increasing energy, from lower to higher.

The number of electrons in those MOs is the total number of valence electrons brought by the individual atoms, minus the charge on the species.

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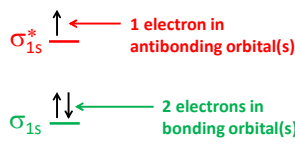
Molecular Orbital Theory

Example: H_2^-

We just populate molecular orbitals with the valence electrons.

H_2^- has 3 valence electrons: $(2)(1) - (-1) = 3$

Easy enough to list and order the MOs when we only have s-orbitals making molecular orbitals



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Molecular Orbital Theory

Sigma and Pi orbitals

Sigma (σ) MO (when it is the “bonding” kind) corresponds to the σ bond we created using **head-on** overlap of hybrid atomic orbitals.

- **But no hybrid orbitals here!**
- Just **pure atomic orbitals forming MOs.**

Pi (π) MO (when it is the “bonding” kind) corresponds to the π bond we created using sideways overlap of the **atomic pure p-orbitals.**

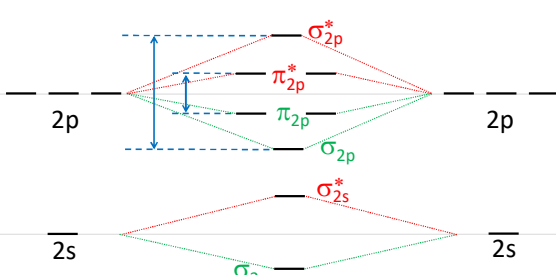
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Molecular Orbital Theory

Expected energy diagram for Molecular Orbitals

π orbitals from the sideways-overlap of p-orbitals are expected to have smaller “reward” (lowering of energy) and “penalty” (raising of energy) for being bonding and “anti-bonding” than the corresponding σ orbitals



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Molecular Orbital Theory -- Energy Diagrams

The expected energy diagram for MOs can predict the bond orders for the diatomic species just fine

	B_2 6 val. e ⁻ B.O. = $\frac{4-2}{2} = 1$	C_2 8 val. e ⁻ B.O. = $\frac{6-2}{2} = 2$	N_2 10 val. e ⁻ B.O. = $\frac{8-2}{2} = 3$	O_2 12 val. e ⁻ B.O. = $\frac{8-4}{2} = 2$	F_2 14 val. e ⁻ B.O. = $\frac{8-6}{2} = 1$
σ_{2p}^*	—	—	—	↑ ↑	↑ ↓
π_{2p}^*	—	—	—	↑ ↑	↑ ↓
π_{2p}	—	↑ ↑	↑ ↓	↑ ↓	↑ ↓
σ_{2p}	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ_{2s}^*	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ_{2s}	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓

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Molecular Orbital Theory -- Energy Diagrams

The expected energy diagram for MOs can predict the bond orders for the diatomic species just fine

	C_2^+ 7 val. e ⁻ B.O. = $\frac{5-2}{2} = 1.5$	C_2^- 9 val. e ⁻ B.O. = $\frac{7-2}{2} = 2.5$	N_2^{2-} 12 val. e ⁻ B.O. = $\frac{8-4}{2} = 2$	O_2^{2+} 10 val. e ⁻ B.O. = $\frac{8-2}{2} = 3$
σ_{2p}^*	—	—	—	—
π_{2p}^*	—	—	↑ ↑	↑ ↓
π_{2p}	↑	↑ ↓	↑ ↓	↑ ↓
σ_{2p}	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ_{2s}^*	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ_{2s}	↑ ↓	↑ ↓	↑ ↓	↑ ↓

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But ... The expected energy diagram for MOs can predict the magnetism of dimers made of **F, O, Ne only!**

It fails for any dimer that has **Li, Be, B, C, N!**

That's because, for the first 5 elements in a period, the actual MO energy diagram has an "unexpected" switch in the energy order!

The expected energy diagram places the electrons in the wrong orbitals and **gets the pairing of electron spins wrong!**

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Quick reminder

Paramagnetism:

- Substance is **attracted** to a magnetic field
- One or more unpaired electrons

Diamagnetism:

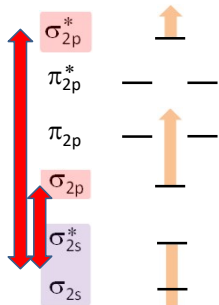
- Substance is **repelled** by a magnetic field
- All electrons paired

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Don't worry if you don't follow this.

For 2nd period atoms other than O, F, Ne:



Lower energy σ_{2s} and σ_{2s}^* orbitals, together, mix with both of the higher energy σ_{2p} and σ_{2p}^* orbitals

and are replaced with even higher-energy σ_{2p} and σ_{2p}^* , and even lower energy σ_{2s} and σ_{2s}^* orbitals

when at least one of the atoms is Li, Be, B, C, N

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Don't worry if you don't follow this.

Why don't O, F, Ne have the "switched" diagram?

O, F, Ne are at the end of the 2nd period.

The increasing nuclear charge affects the 2s electrons (and the σ_{2s} MOs they make) more than the 2p electrons (and the σ_{2p} MOs they make) because 2s electrons are closer to the nucleus.

When the energy levels of the σ_{2s} and σ_{2p} MOs are less similar, their interaction is less relevant.

The modification of the σ_{2s} and σ_{2p} energy levels is less.

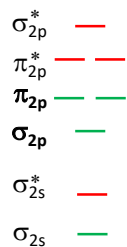
The energy order of the MOs is as expected.

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"Expected" Diagram

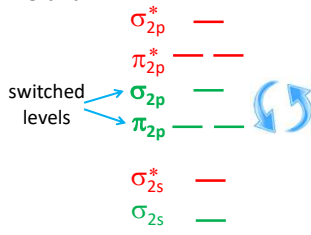
Applies only to O, F



"Switched" Diagram

π_{2p} is lower than σ_{2p}

Applies to dimers of 2nd period elements other than O and F



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"Expected" energy diagram predicts the bond order just fine because the switch is between bonding MOs

Even when the expected energy diagram incorrectly puts the electrons in σ_{2p} before π_{2p} , that doesn't affect the bond order because both are bonding orbitals.

Number of electrons in bonding orbitals is still correct.

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Molecular Orbital Theory -- Energy Diagrams

Example:
Predict whether C₂ is paramagnetic or diamagnetic

“Expected diagram” predicts **paramagnetic**

“Switched diagram” predicts **diamagnetic** ✓

C₂ is actually **diamagnetic**

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Molecular Orbital Theory -- Energy Diagrams

The correct energy diagrams can predict magnetism correctly

Switched energy diagrams

	B ₂ 6 val. e ⁻ paramagnetic	C ₂ 8 val. e ⁻ diamagnetic	N ₂ 10 val. e ⁻ diamagnetic	O ₂ 12 val. e ⁻ paramagnetic	F ₂ 14 val. e ⁻ diamagnetic
σ _{2p} [*]	—	—	—	—	—
π _{2p} [*]	—	—	—	↑ ↑	↑ ↓
σ _{2p}	—	—	↑ ↓	↑ ↓	↑ ↓
π _{2p}	↑ ↑	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ _{2s} [*]	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ _{2s}	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓

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Molecular orbital populations can be described similar to the electron configurations of atoms
 We just use the MO symbols instead

σ_{2p}^{*} ↑ ↓
 π_{2p}^{*} ↑ ↓ ↑ ↓
 π_{2p} ↑ ↓ ↑ ↓
 σ_{2p} ↑ ↓
 σ_{2s}^{*} ↑ ↓
 σ_{2s} ↑ ↓

$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4 (\sigma_{2p}^*)^2$

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σ_{2p}^{*} —
 π_{2p}^{*} — —
 σ_{2p} ↑
 π_{2p} ↑ ↓ ↑ ↓
 σ_{2s}^{*} ↑ ↓
 σ_{2s} ↑ ↓

$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^1$

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Molecular Orbital Theory -- Energy Diagrams

The correct energy diagrams can predict magnetism correctly

Switched energy diagrams

	B ₂ ²⁻ 8 val. e ⁻ diamagnetic	C ₂ ²⁺ 6 val. e ⁻ paramagnetic	N ₂ ²⁺ 8 val. e ⁻ diamagnetic	O ₂ ⁴⁺ 8 val. e ⁻ paramagnetic
σ _{2p} [*]	—	—	—	—
π _{2p} [*]	—	—	—	—
σ _{2p}	—	—	—	↑ ↑
π _{2p}	↑ ↓	↑ ↑	↑ ↓	↑ ↓
σ _{2s} [*]	↑ ↓	↑ ↓	↑ ↓	↑ ↓
σ _{2s}	↑ ↓	↑ ↓	↑ ↓	↑ ↓

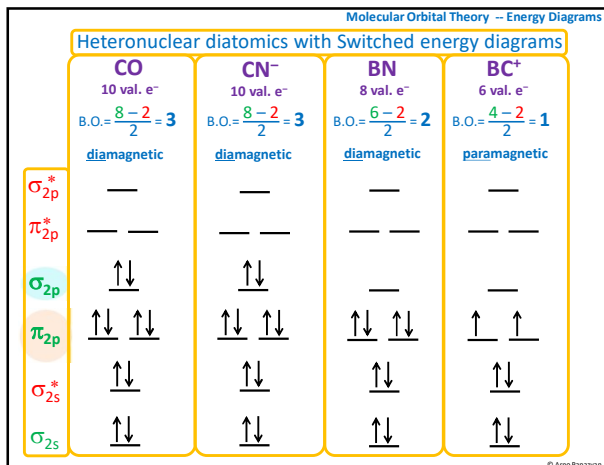
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Molecular Orbital Theory -- Energy Diagrams

Heteronuclear Diatomic Species (OF, CN, BC, CO, etc.)

- Composed of 2 different elements.
- If one of the atoms has the “switched” diagram in its homonuclear diatomic species, its heteronuclear species also does.
- So, all heteronuclear species other than OF (and its ions) have the “switched” diagram
- Again, important only when considering magnetic properties

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Delocalization revisited

- Describes molecules that have “resonance.”
- In molecules that have resonance, it is the π bonds that are delocalized, the σ bonds are still localized.
- p orbitals perpendicular to the plane of the molecule are used to form π molecular orbitals, with “lobes” above and below the plane of the atoms involved.
- So the electrons in the delocalized π molecular orbitals are delocalized above and below the plane of the molecule.

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Delocalization revisited

Delocalized bond electrons are truly molecular, and belong to many atoms, but we won't describe them using the MO diagrams (too difficult for General Chemistry)

We will think more in terms of “resonance” of Lewis structures.

➤ Ironic, since Lewis structures use localized bonding model.

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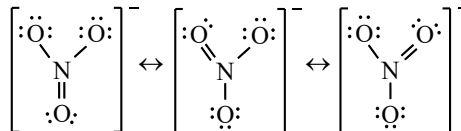
Delocalization revisited

Remember “resonance structures” when we learned Lewis structures?

About the nitrate ion, we said:

More than one valid Lewis structure can be written for a particular molecule.

Sometimes alternative Lewis structures are equivalent.



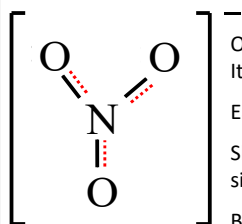
Each structure has 2 N-O single bonds and 1 N=O double bond, but the double bond is with a different O in each.

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Delocalization revisited

Delocalized electrons in the nitrate ion



One extra bond is spread over 3 bonds
It adds 1/3 bond to each bond

Each N-O bond is $1 + \frac{1}{3} = 1.33$ bond

Slightly stronger and shorter than a single bond

But not quite a double bond

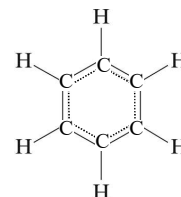
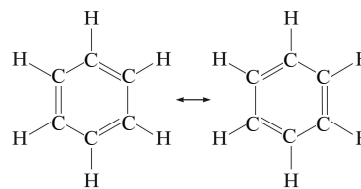
- Actual structure is an average of the resonance structures.
- Electrons are really **delocalized** – they can move around the entire molecule.

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Delocalization revisited

Resonance in Benzene

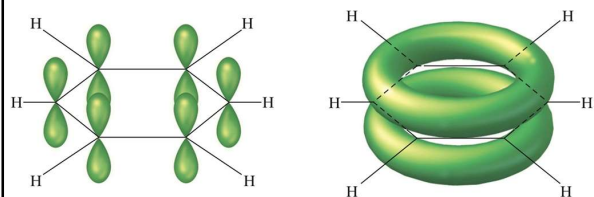


Actual bonding pattern is an average of the two equivalent resonance forms

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The Pi System for Benzene



The π electrons are delocalized around the benzene molecule.

The π orbitals formed by the p-orbitals are truly molecular.

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