

Chapter 11

Chemical Bonding II:

Valence Bond

and

Molecular Orbital

Theories

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. 😊

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!

- 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

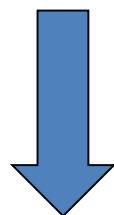
- It’s a “mathematically polite” way of getting our “blobs” of VSEPR 😊

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.

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



Number of hybrid orbitals needed

What is a skeletal bond?

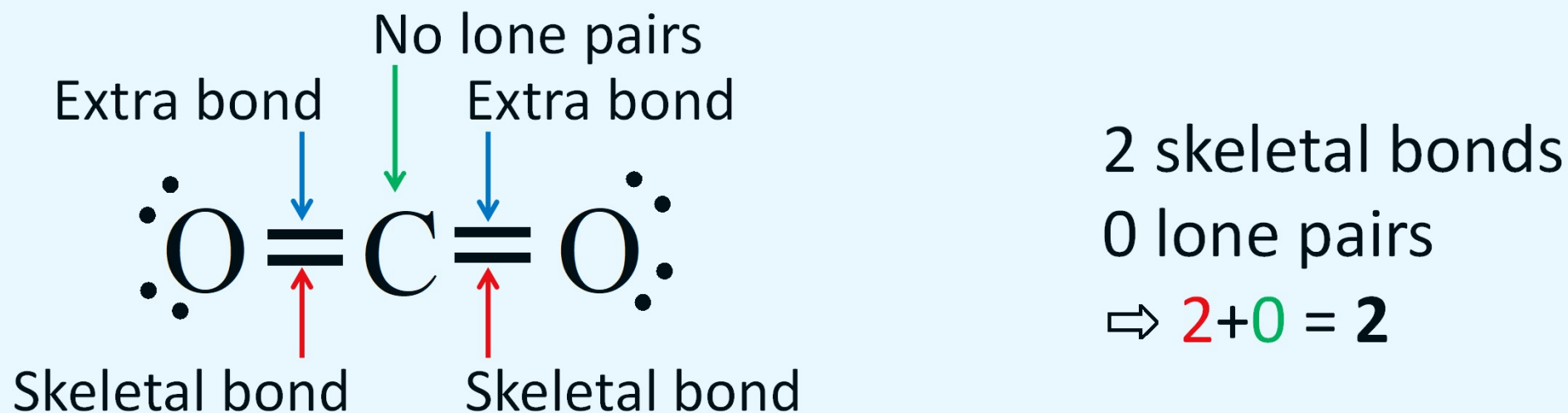
The first bond that forms between two atoms

The first bond in a double or triple bond

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

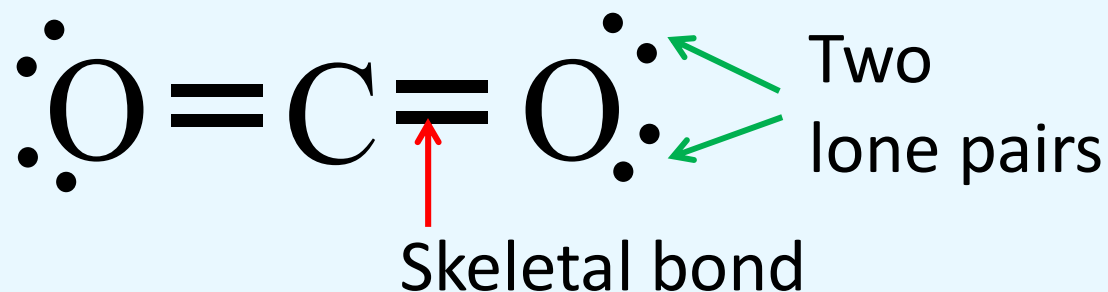
How many hybrid orbitals does an atom need?
 Same as “electron groups” we counted in VSEPR.
 Count the skeletal bonds and lone pairs around it

How many hybrid orbitals does C in CO₂ need?

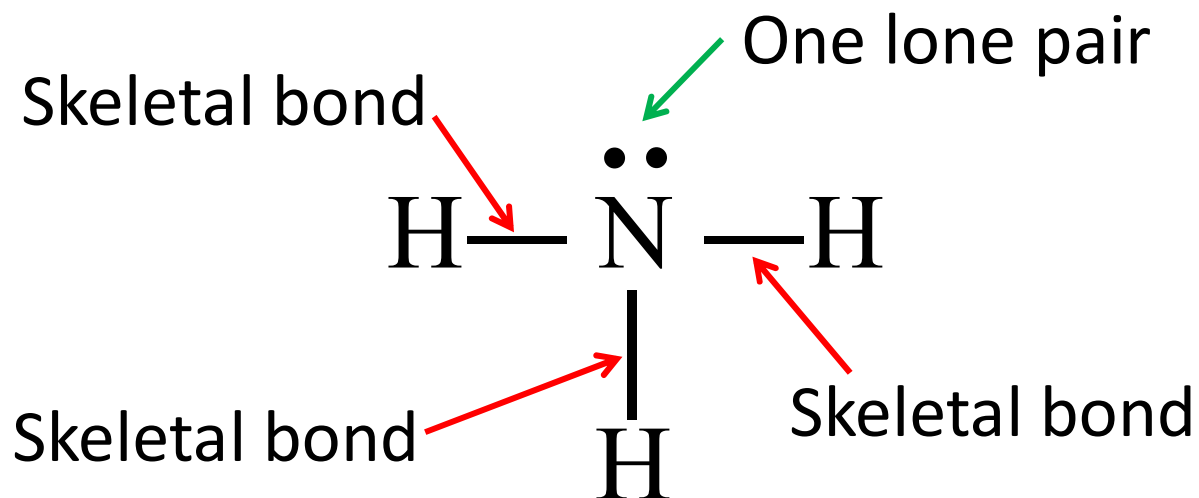


How many hybrid orbitals does each O in CO₂ need?

1 skeletal bond
 2 lone pairs
 $\Rightarrow 1 + 2 = 3$



How many hybrid orbitals does N in NH_3 need?



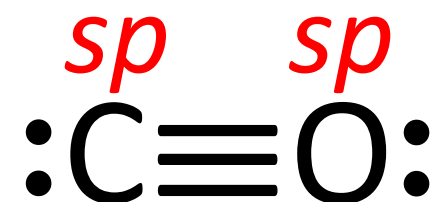
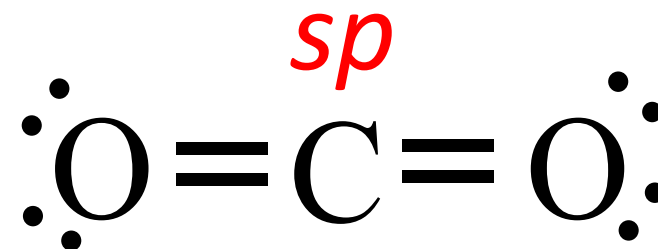
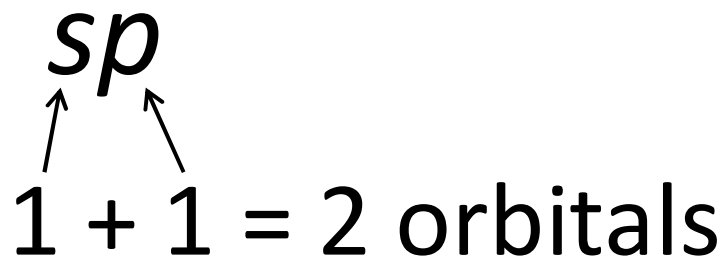
3 skeletal bonds
 1 lone pair
 $\Rightarrow 3 + 1 = 4$

How about the hydrogens?

They don't hybridize their orbitals.

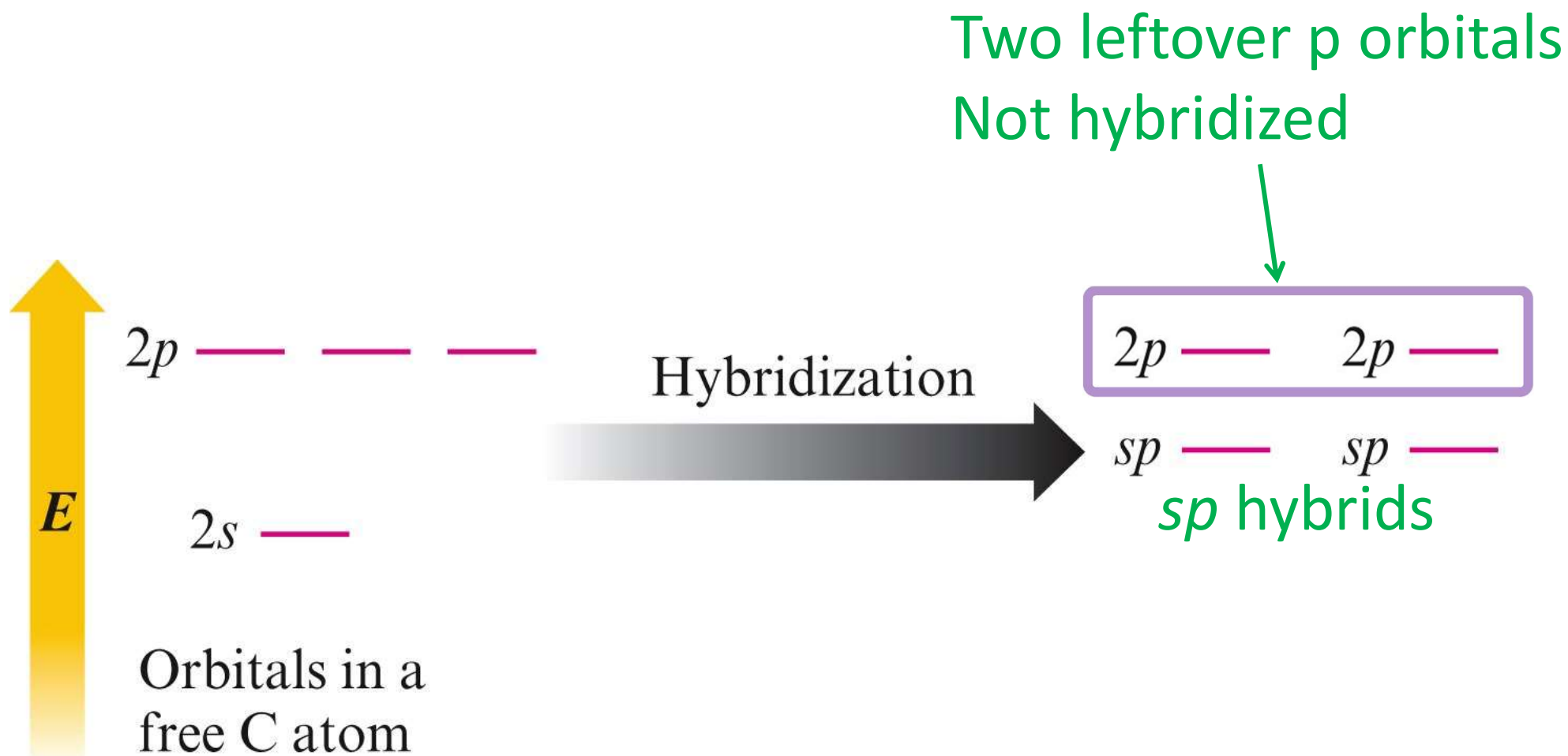
They keep their pure atomic 1s orbitals.

Two electron groups on the atom: *sp* Hybridization



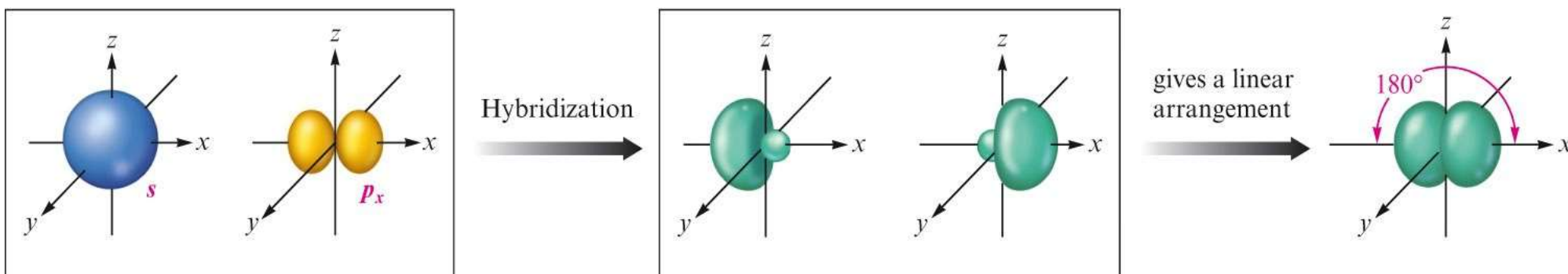
- Combination of **one s** and **one p** orbital.
- Gives a linear arrangement of atomic orbitals.
 - same as predicted by VSEPR
- The two unhybridized *p* orbitals form “extra” bonds that form two double bonds or a triple bond (so the extra bonds are added to an already existing “skeletal” bond made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

Energy levels of sp hybrid orbitals



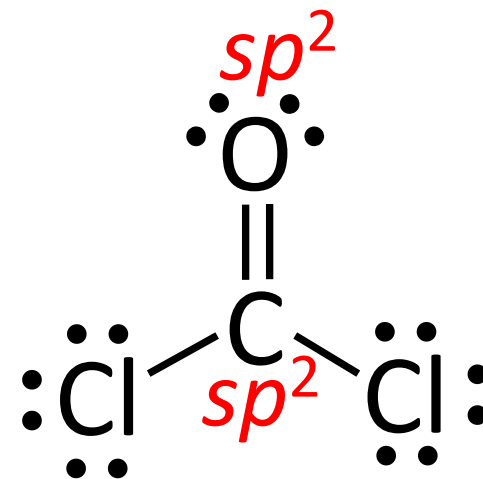
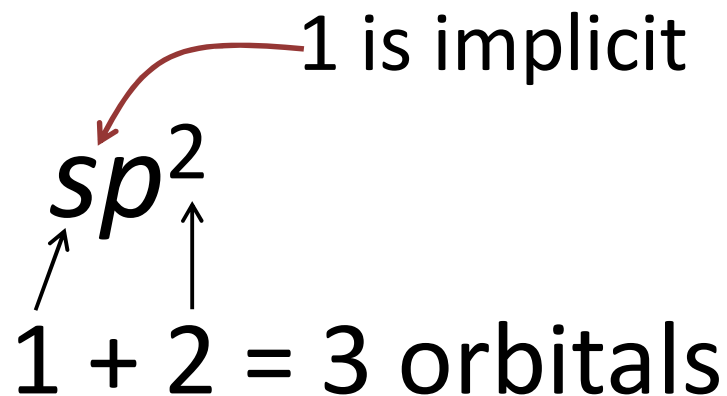
$$s + p \Rightarrow sp$$

Two sp orbitals oriented away from each other at 180°



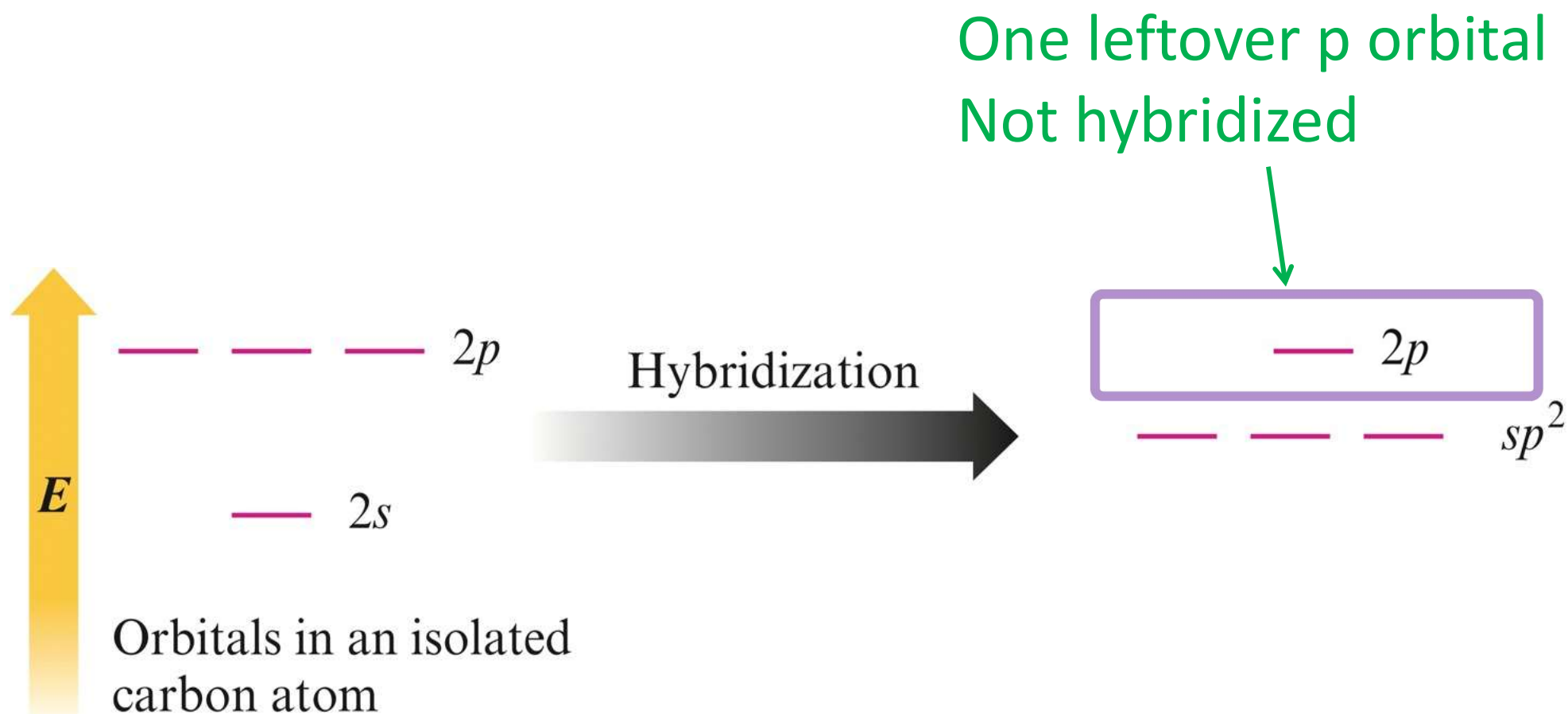
© Cengage Learning. All Rights Reserved.

Three electron groups on the atom: sp^2 Hybridization



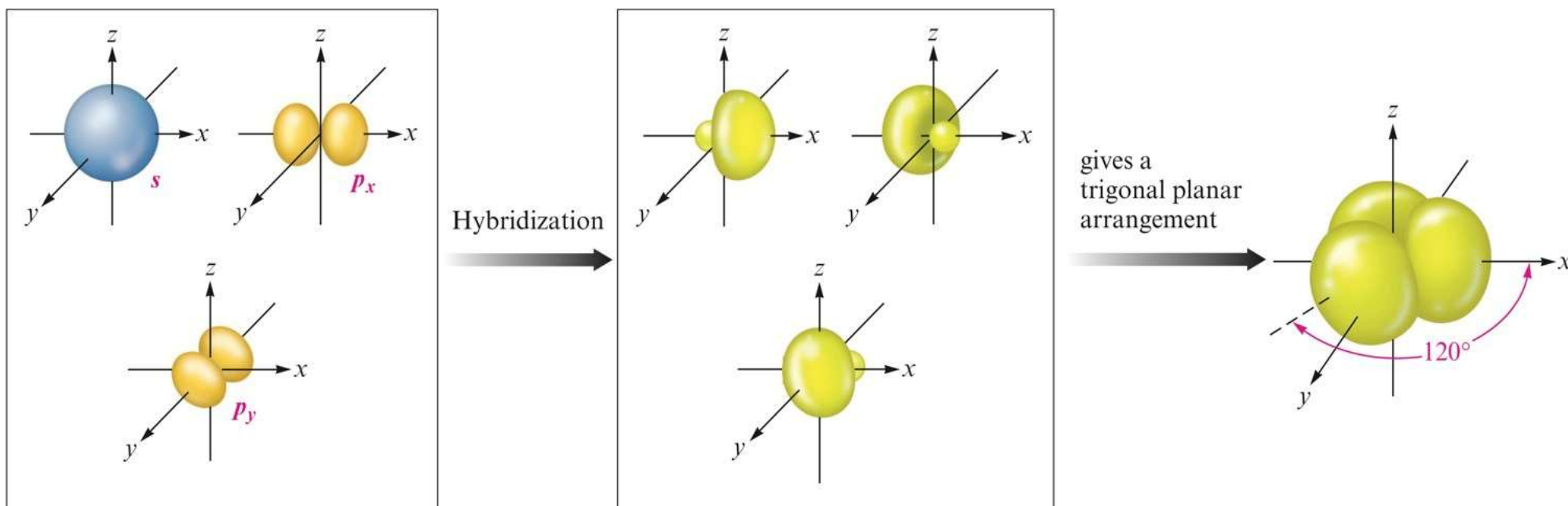
- Three electron groups needed
- Combination of **one s** and **two p** orbitals.
- Gives a trigonal planar arrangement of atomic orbitals
 - same as predicted by VSEPR
- The unhybridized p orbital forms an “extra” bond with the unhybridized p orbital of a neighboring atom
 - Leads to a “double bond”

Energy levels of sp^2 hybrid orbitals

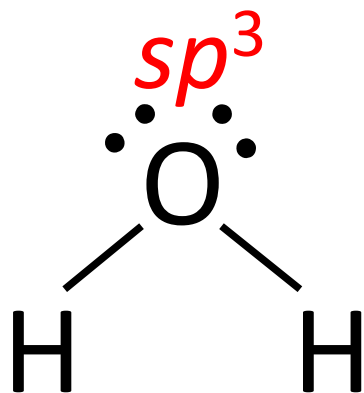




Three sp^2 orbitals with 120° between them



Four electron groups on the atom: sp^3 Hybridization

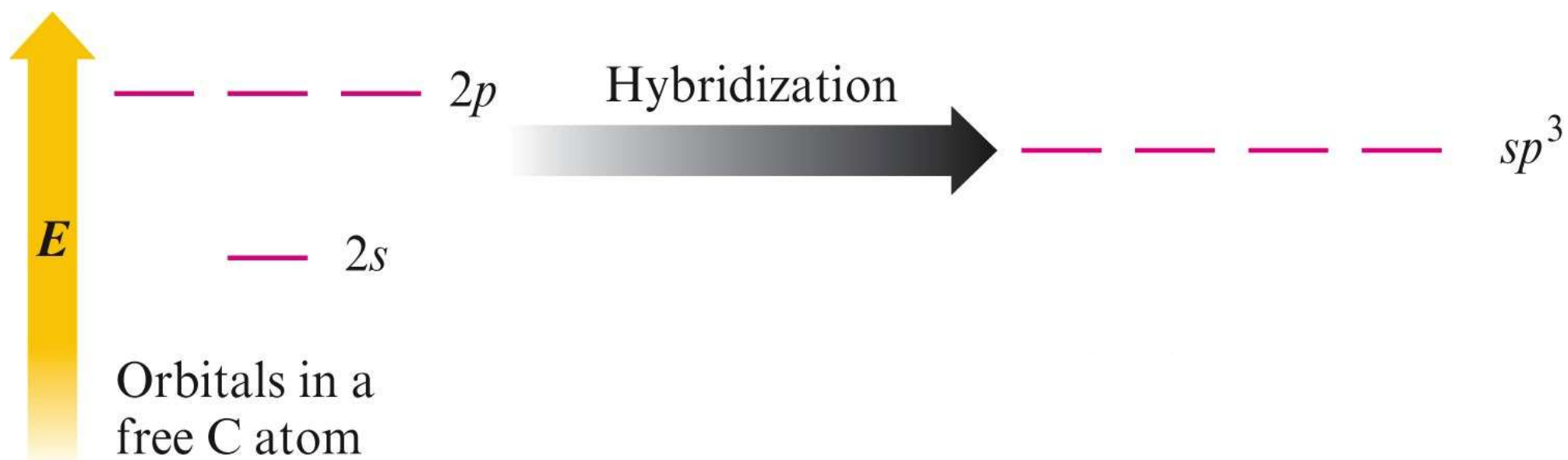


$$1 + 3 = 4 \text{ orbitals}$$

The diagram shows the calculation of the number of hybrid orbitals. An arrow points from the number '1' to the 's' in sp^3 , and another arrow points from the number '3' to the 'p' in sp^3 . The result is '4 orbitals'.

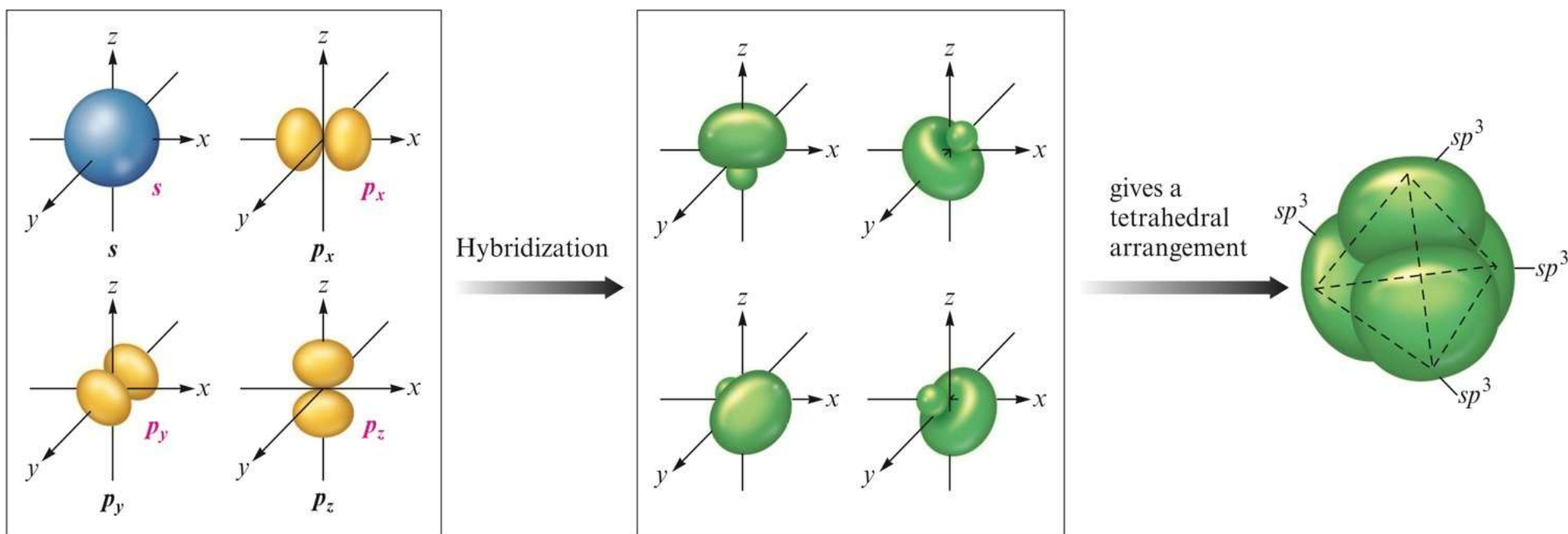
- Four electron groups needed
- Combination of **one s** and **three p** orbitals.
- Gives a tetrahedral arrangement of atomic orbitals.
-- same as predicted by VSEPR
- No unhybridized p orbitals left
-- no double or triple bonds

Energy levels of sp^3 hybrid orbitals





Three sp^3 orbitals with 109.5° between them



What if the central atom exceeds the octet?

- We once thought *d*-orbitals from the lower shell added into hybridization when there are more than 4 groups
- But now it's just pretense in General Chemistry only

So, pretend like ...

- *d*-orbitals from the lower shell are “promoted” to participate in bonding
- They are added to the mix (hybridization) along with *s* and *p* orbitals.
- When *d*-orbitals are involved, we already have one *s* and three *p* orbitals in the mix
- We just add enough *d*-orbitals to get the number of electron groups needed

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.

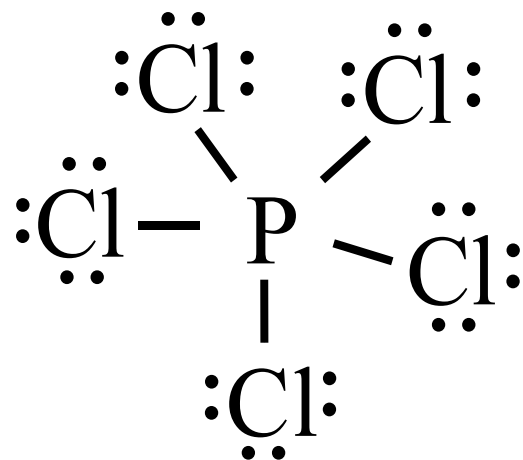
So ...

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.

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°

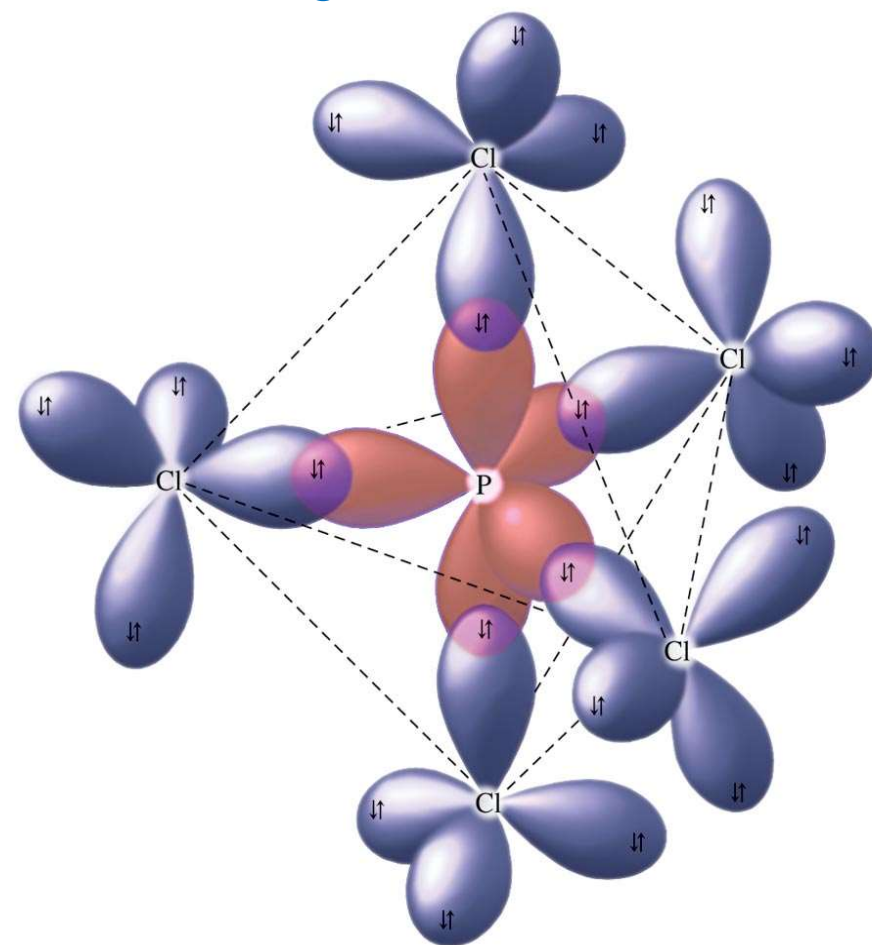
What is the hybridization of P?

dsp^3

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



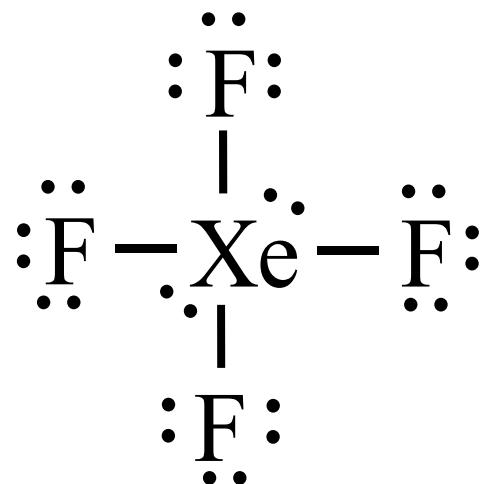
Cl atoms each have just one skeletal bond and three lone pairs, all sp^3 hybridized. But the **hybridization of peripheral atoms doesn't affect the geometry around the central atom.**

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.

Consider the **Lewis structure** for XeF_4 .



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

square planar

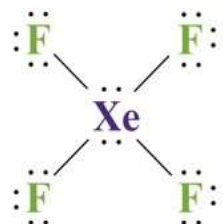
What are the ideal **bond angles**?

90° and 180°

What is the **hybridization of Xe**?

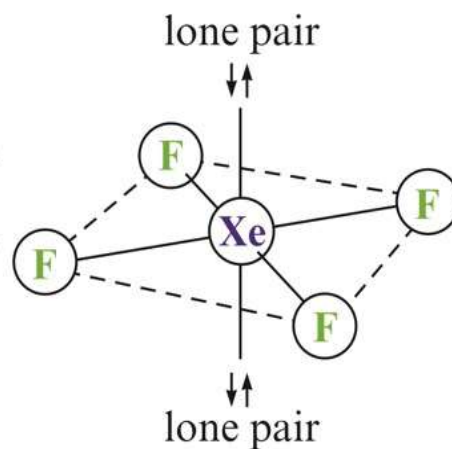
d^2sp^3

How is the Xenon Atom in XeF_4 Hybridized?

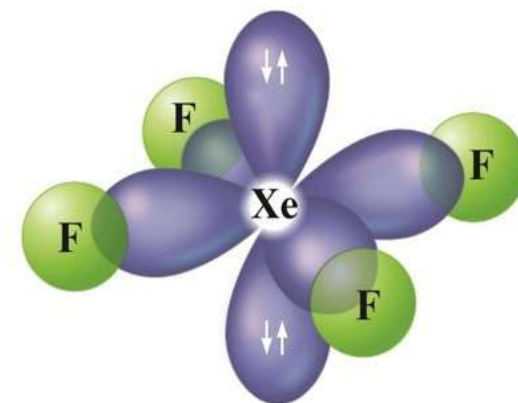


Lewis structure

Six electron pairs
require an octahedral
arrangement.

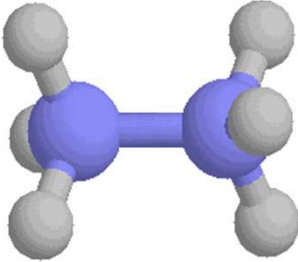
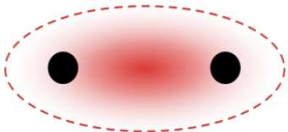
Octahedral arrangement
of six electron pairs

d^2sp^3
hybridized
xenon



Xenon uses six d^2sp^3 hybrid
atomic orbitals to bond to
the four fluorine atoms and
to hold the two lone pairs.

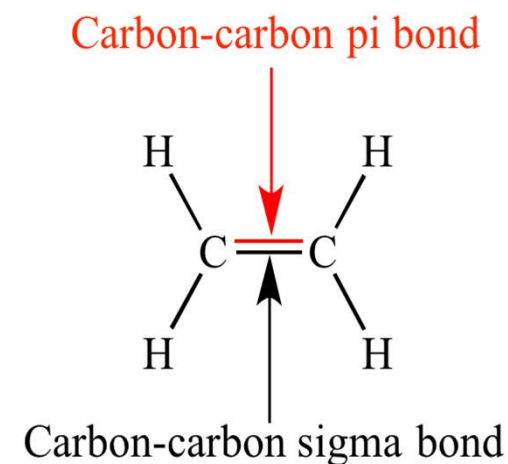
Sigma (σ) Bond

- Skeletal bonds are called “sigma” bonds.
- Sigma bonds are formed by orbitals approaching and overlapping each other **head-on**.
 - Two hybrid orbitals, or a hybrid orbital and an s-orbital, or two s-orbitals
- The resulting bond is like an elongated egg, and has cylindrical symmetry.
 - Acts like an axle
- That means the bond shows no resistance to rotation around a line that lies along its length.

Pi (π) Bond

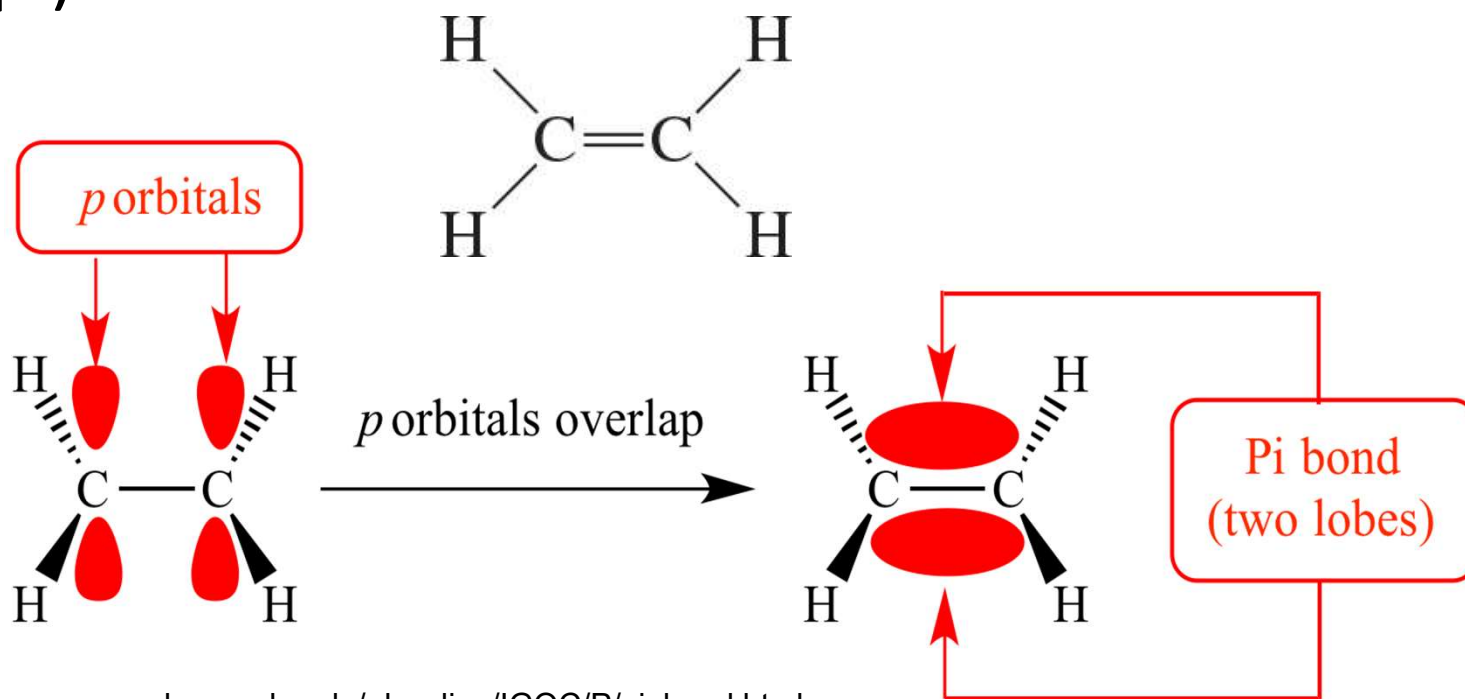
- The “leftover” p-orbitals that are **not used in forming hybrid** orbitals are used in making the “extra” bonds we saw in Lewis structures.

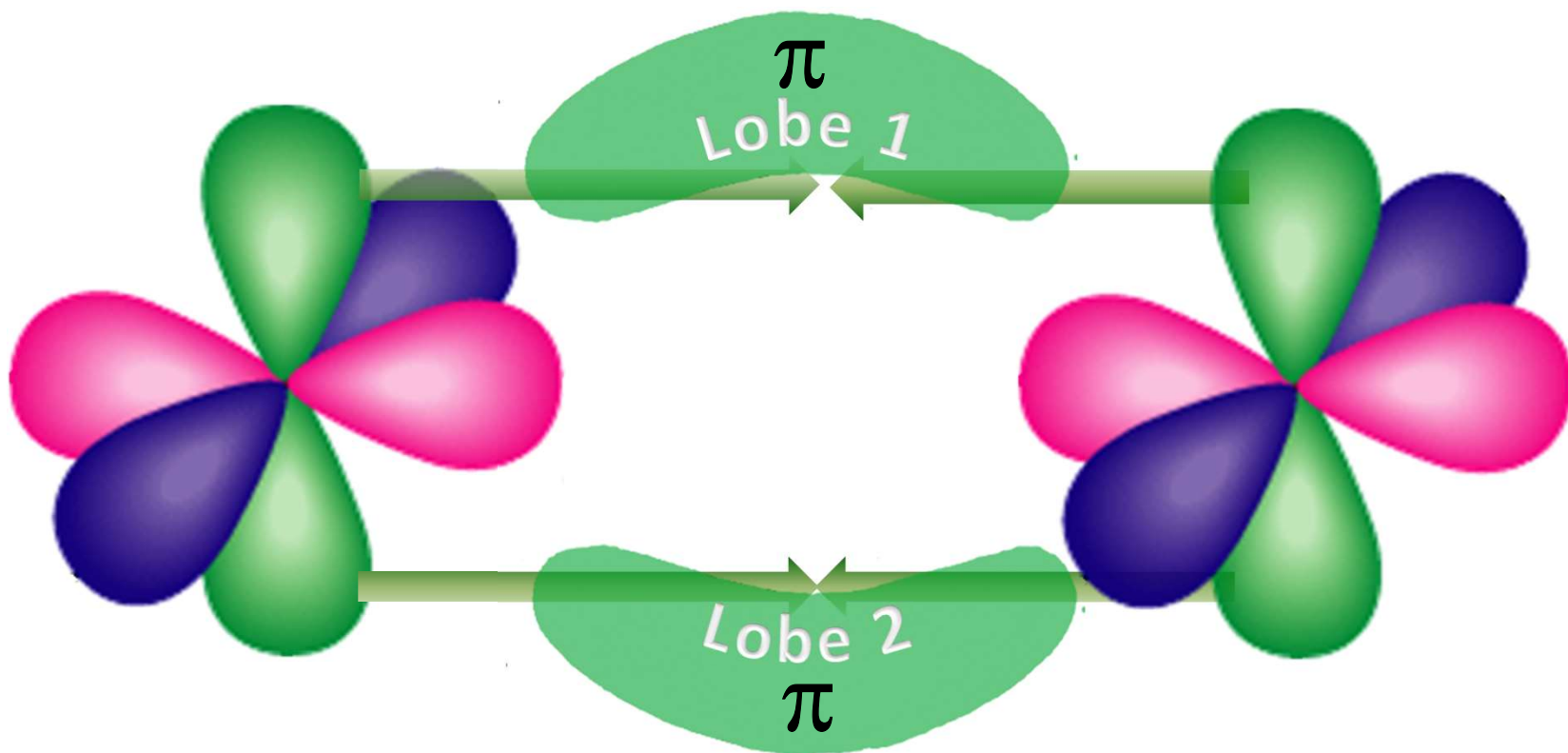
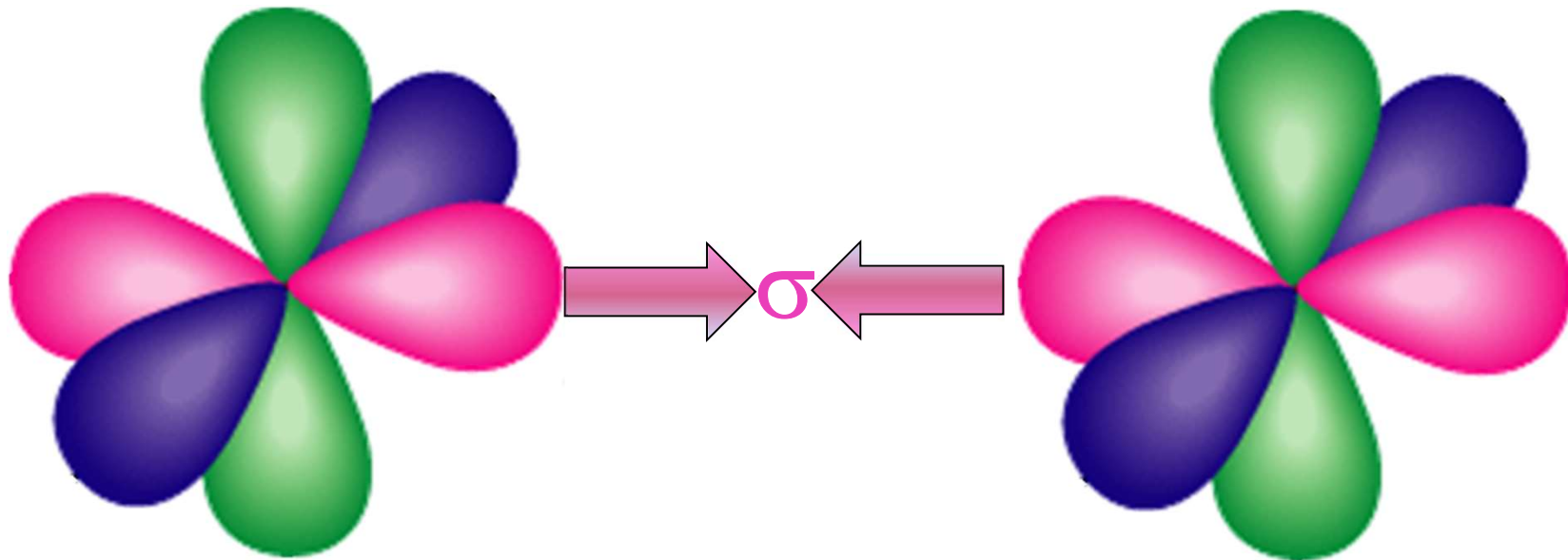
- The 2nd bond in a **double** bond
- The 2nd and 3rd bonds in a **triple** bond



- Those extra bonds form only after the atoms are brought together by the formation of the skeletal bonds made by hybrid orbitals.
- The “extra” π bonds are formed alongside a skeletal bond.
- They don't form without a skeletal bond to bring the p-orbitals together and “support” them.

- The pure p-orbitals are perpendicular to the hybrid orbitals.
- This causes the two lobes of the p-orbitals on the two atoms to stick out perpendicular to the skeletal sigma bond between them.
- Those p-orbitals on the two atoms align and form a “sideways” bond where the lobes of the p-orbitals merge to form a π (pi) bond.



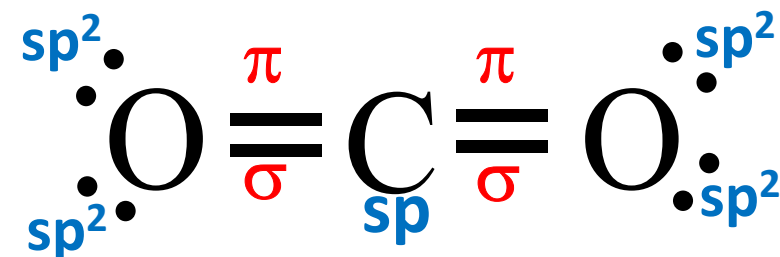
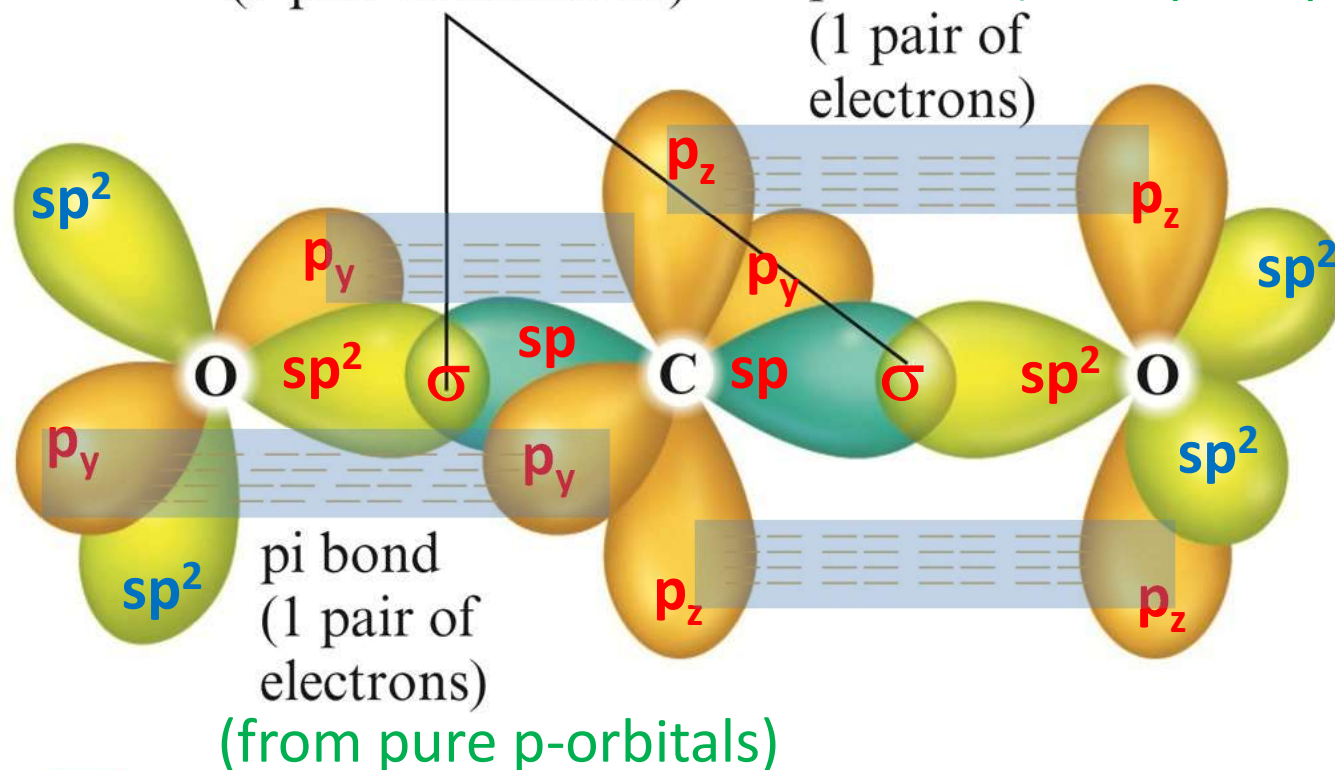


The Orbitals for CO₂

(from hybrid orbitals)

sigma bond
(1 pair of electrons)

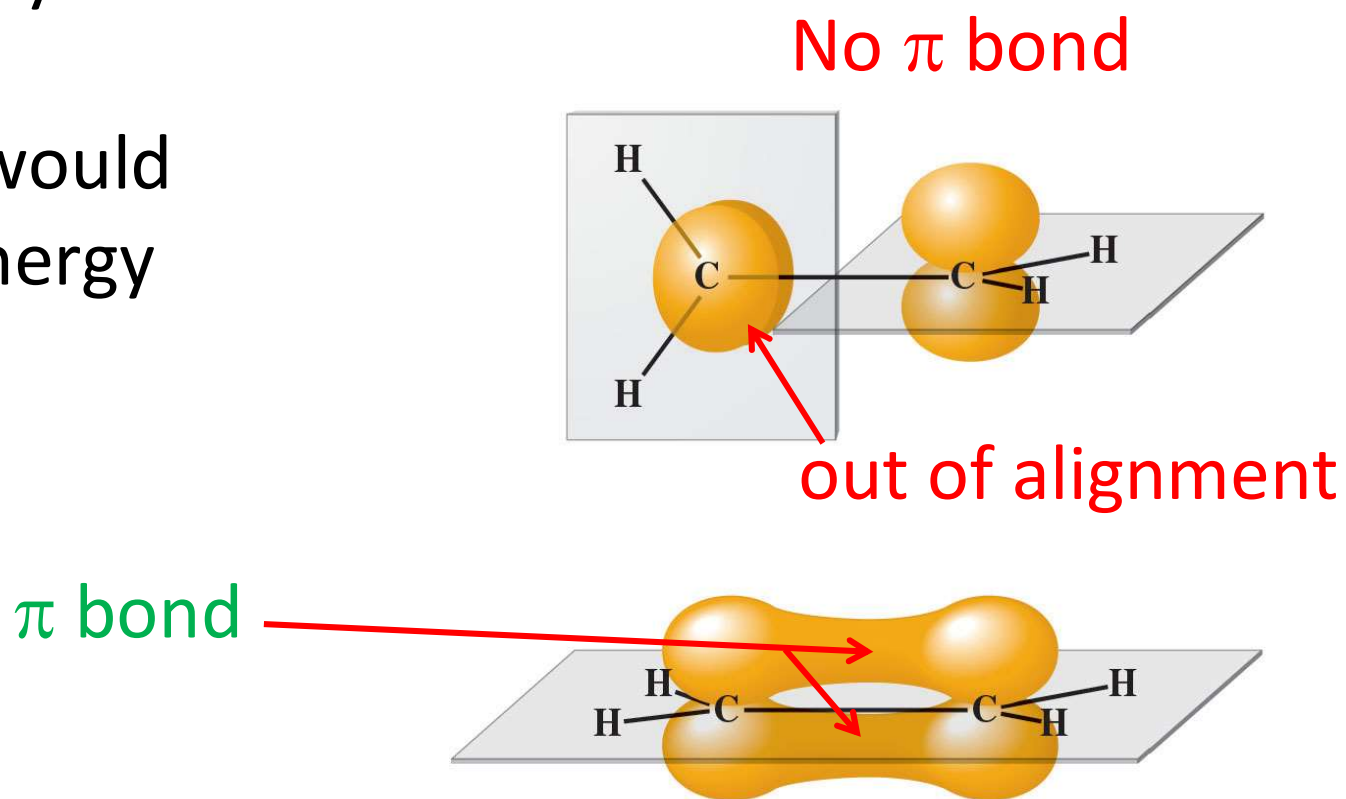
pi bond (from pure p-orbitals)
(1 pair of electrons)



- The two pi bonds are on perpendicular planes.
- If one is on the plane of this page, the “lobes” of the other are sticking into and out of the page.

Pi bonds don't allow rotation

- 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



Exercise:

Draw the Lewis structure for HCN.

Show all bonds between atoms.

Label each bond as σ or π .

Which hybrid orbitals are used?

Exercise:

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



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

The Molecular Orbital (MO) model of bonding

i.e. “the other model” of bonding

- 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!

- 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

Sigma (σ) molecular orbitals (MOs)

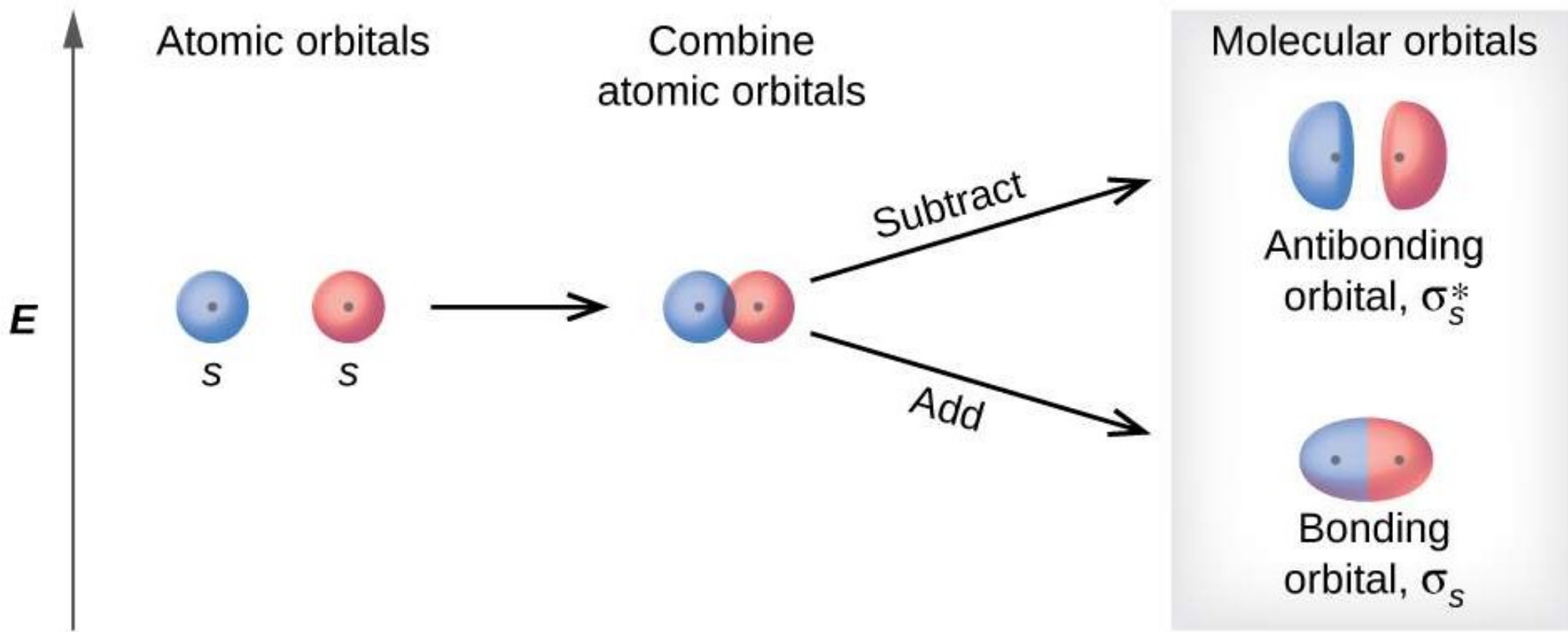
- Same shape and name as sigma (s) bonds
- The electron density of σ molecular orbitals is centered along the line passing through the two nuclei.
 - It has the same “symmetry” as a stick (or a cigar, or an egg)
 - If you spin it along its length, you won't see a change.
- Formed by “head-on” approach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

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

Example:

Combination of Hydrogen 1s Atomic Orbitals to form MOs



https://cnx.org/resources/92f991702d0b48e34361c055884b247df2391425/CNX_Chem_08_04_ssigma.jpg

Two atomic orbitals create two molecular orbitals

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

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.

Energies of MOs:

Anti-bonding MO > parent atomic orbitals
Bonding MO < parent atomic orbitals

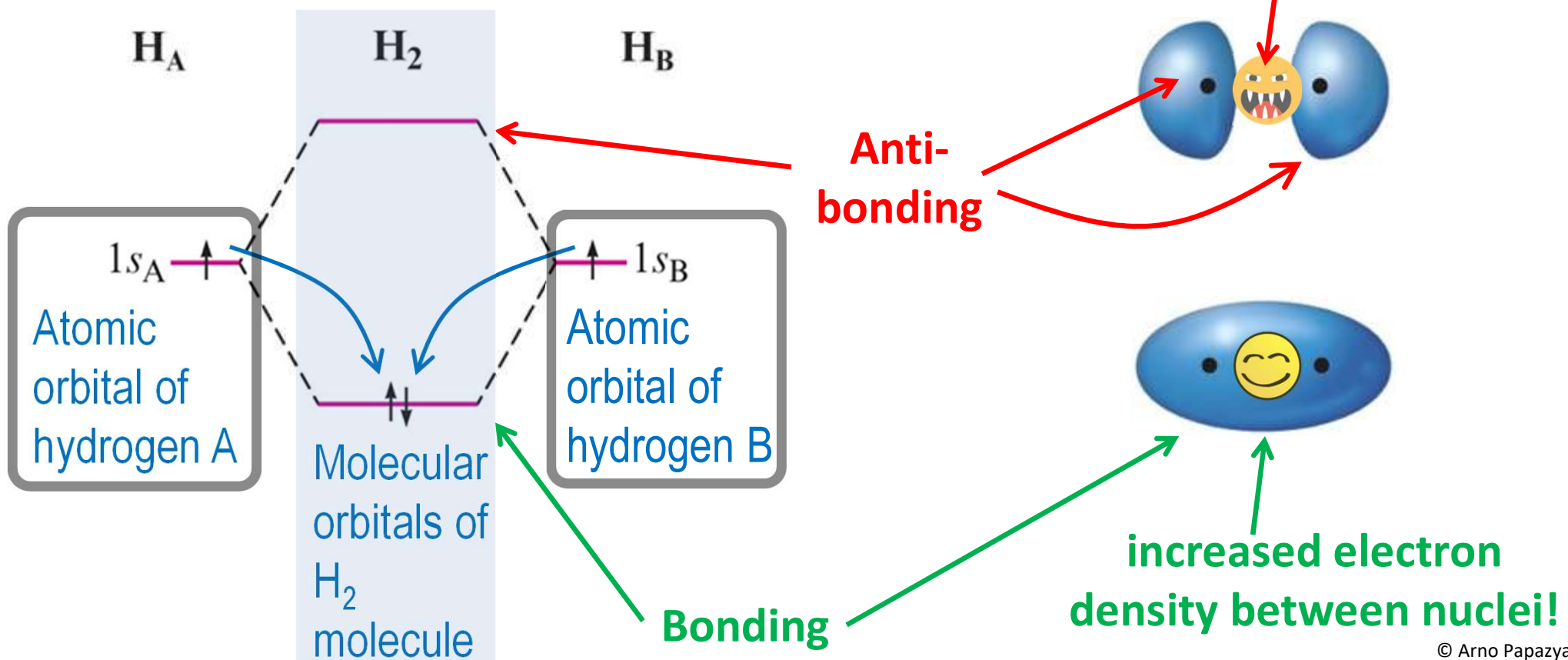
Antibonding molecular orbital: higher in energy **bad!** 

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

MO Energy-Level Diagram for the H₂ Molecule

1s orbital of hydrogen A and 1s orbital of hydrogen B disappear, and form two molecular orbitals:

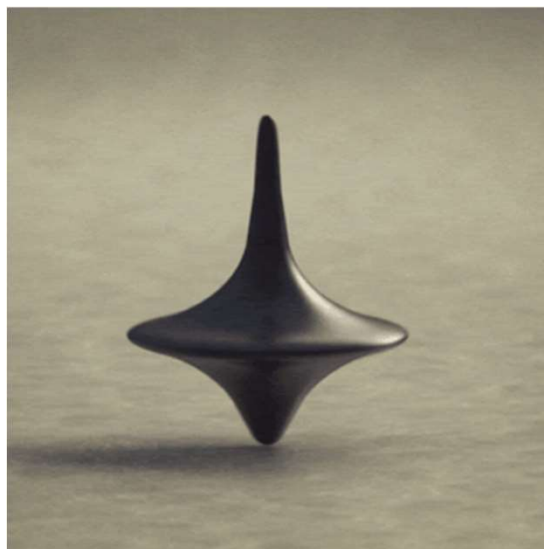
- One with lower energy (bonding)
- One with higher energy (anti-bonding)



The molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding.

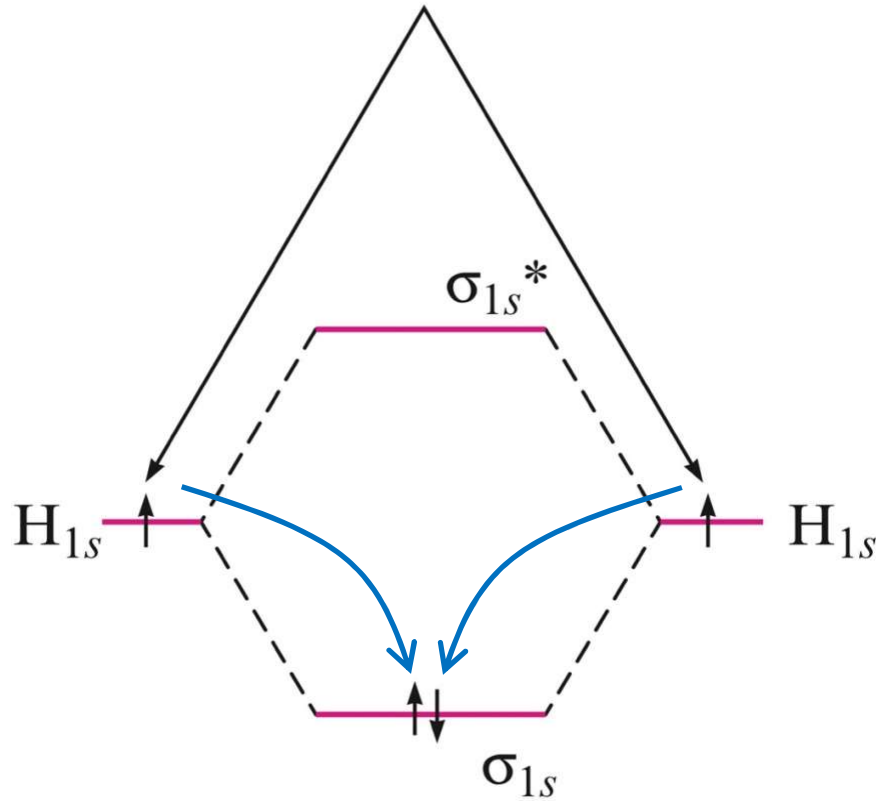
The labels on molecular orbitals indicate their symmetry (shape) and whether they are bonding or antibonding.

- “Sigma” (σ) refers to the cylindrical/egg-shaped symmetry
- This corresponds to the sigma bonds we discussed earlier.
- We can't see a change if we spin the object along its length





Atomic orbitals in
a free H atom



σ_{1s}^* and σ_{1s} are
molecular orbitals
in the H_2 molecule



If there is an
asterix, it is
“antibonding”

σ_{1s}^*

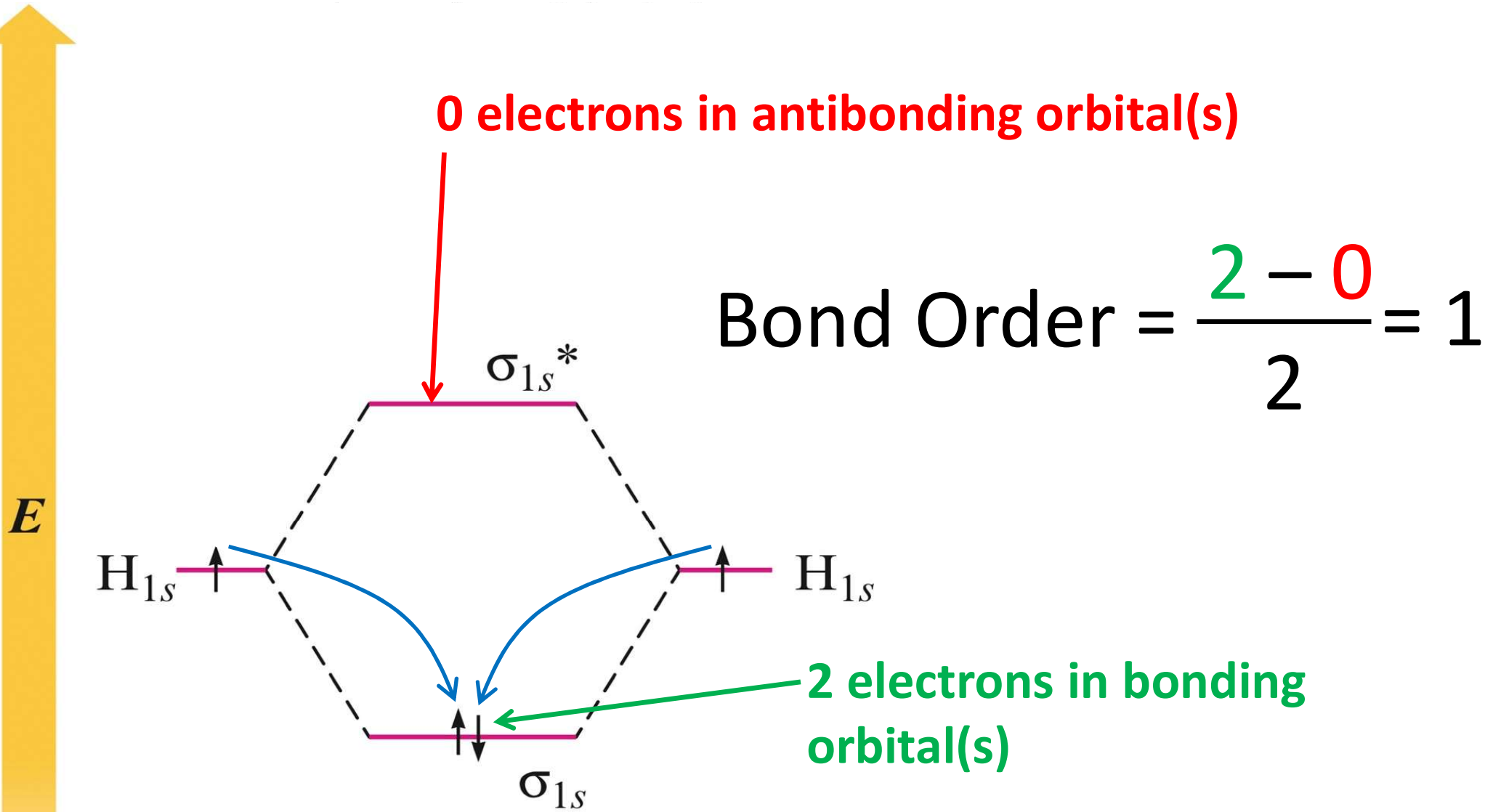
Egg-shaped,
formed by
“head-on”
approach of ...

1s atomic orbitals

Bond Order

- Higher bond order means greater bond strength.
- **Bonding** electrons make a bond **stronger**
- **Antibonding** electrons make a bond **weaker**
- It's the excess (net) bonding electrons that gives the bond its strength
- Two net bonding electrons correspond to a “bonding pair” in one bond in the Lewis structures
- We can have fractional bond order (0.5, or 1.5, or 2.5) in the MO model

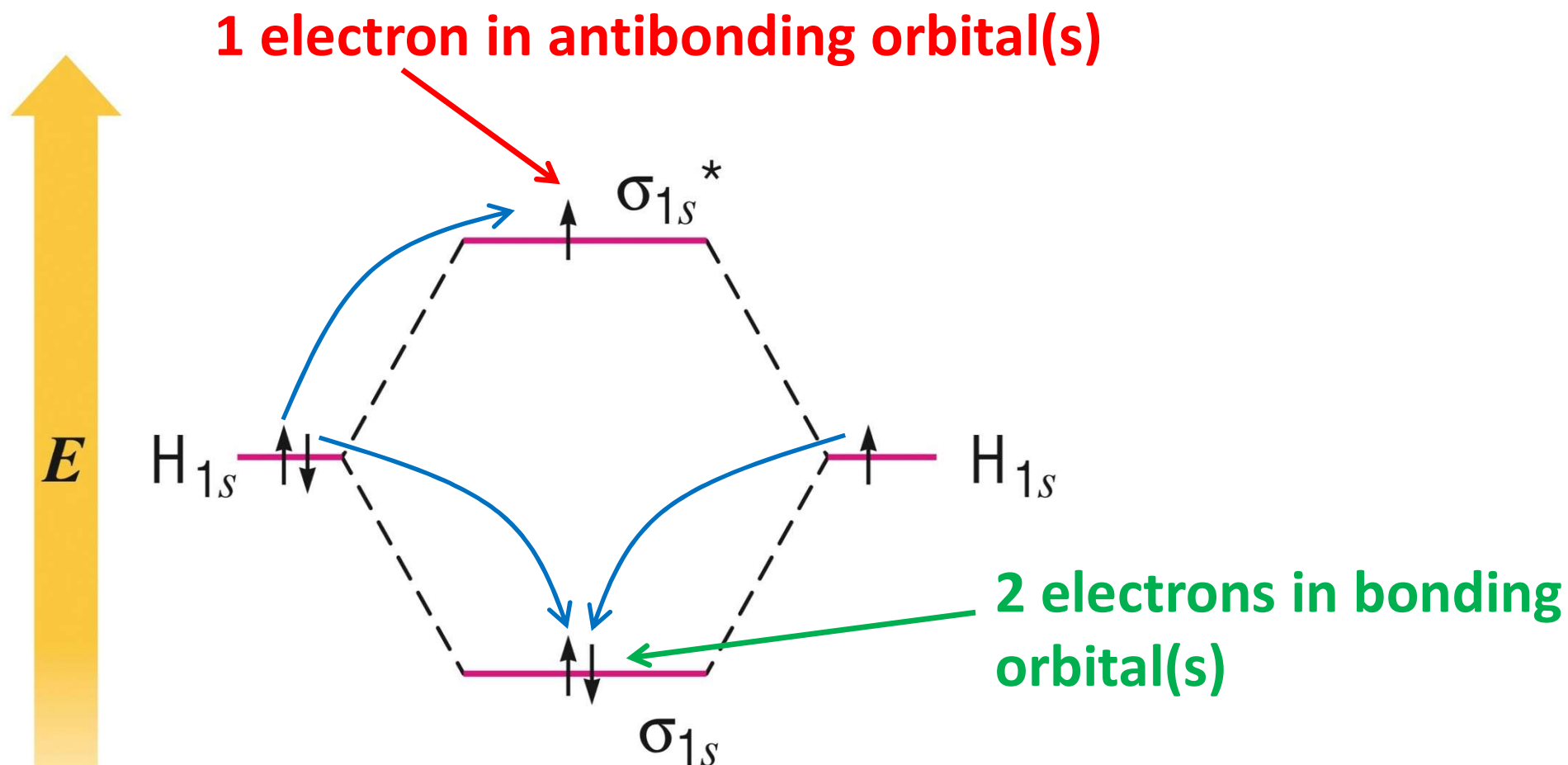
$$\text{Bond order} = \frac{\# \text{ of bonding } e^{-} - \# \text{ of antibonding } e^{-}}{2}$$

Example: H₂

Example: H_2^-

$$\text{Bond Order} = \frac{2 - 1}{2} = \frac{1}{2}$$

Putting an extra electron on H_2 makes the bond weaker!



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.

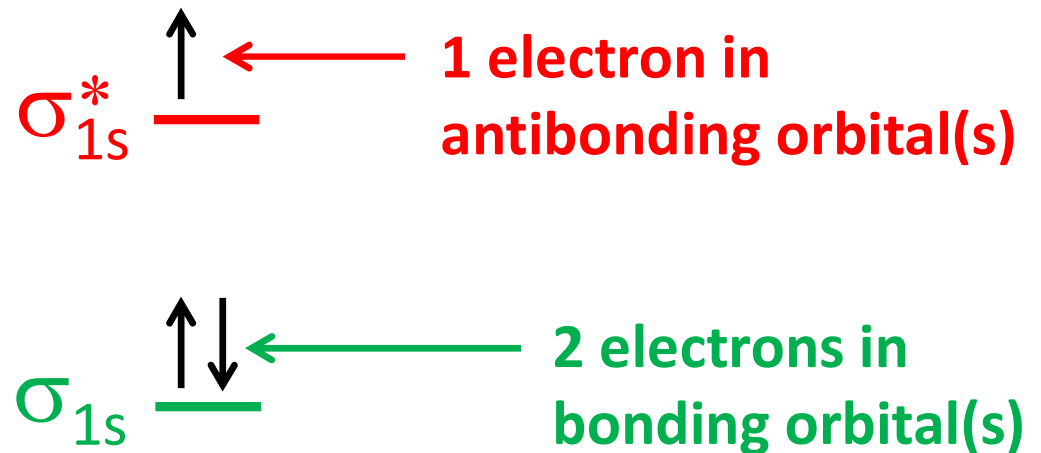
The number of electrons in those MOs is the total number of valence electrons brought by the individual atoms, minus the charge on the species.

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



Sigma and Pi orbitals

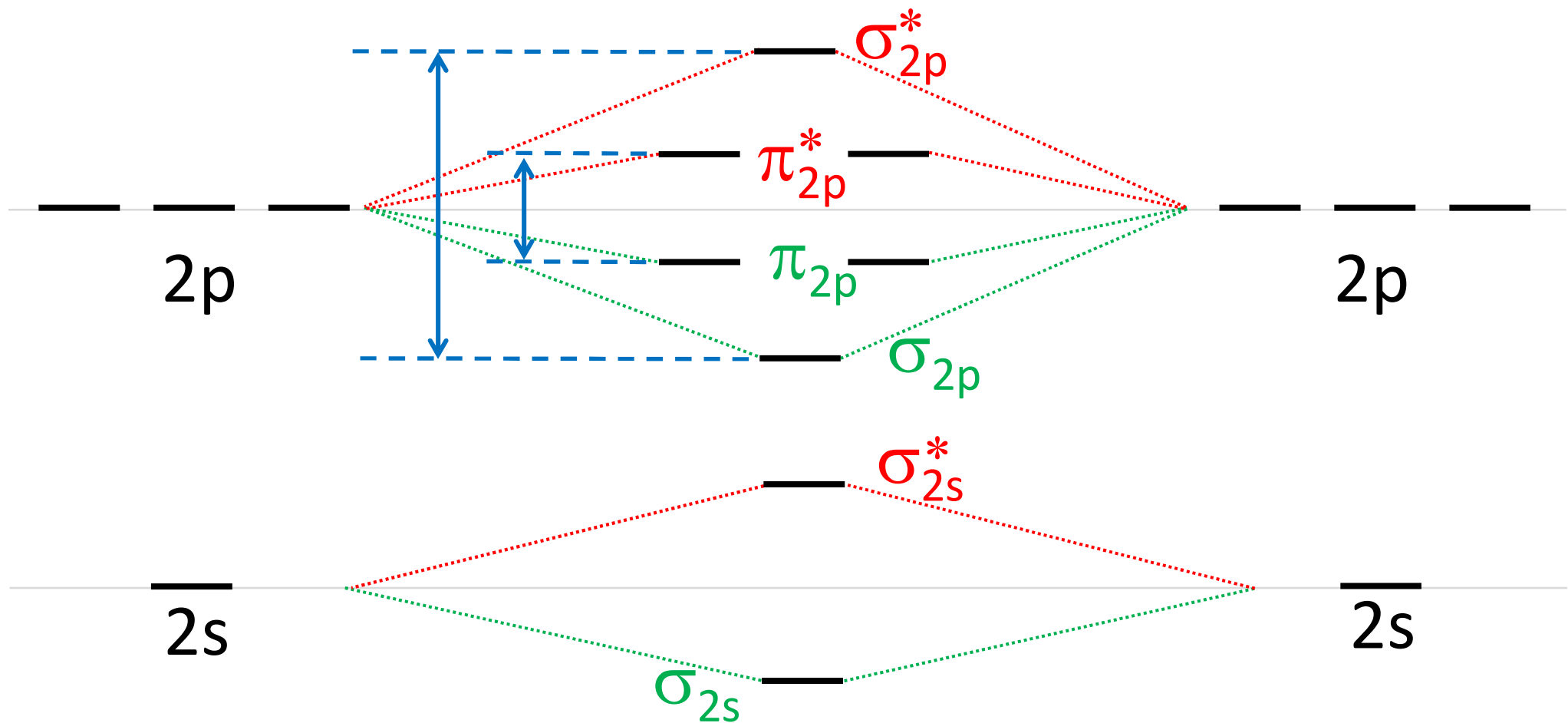
Sigma (σ) MO (when it is the “bonding” kind) corresponds to the σ bond we created using **head-on** overlap of hybrid atomic orbitals.

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

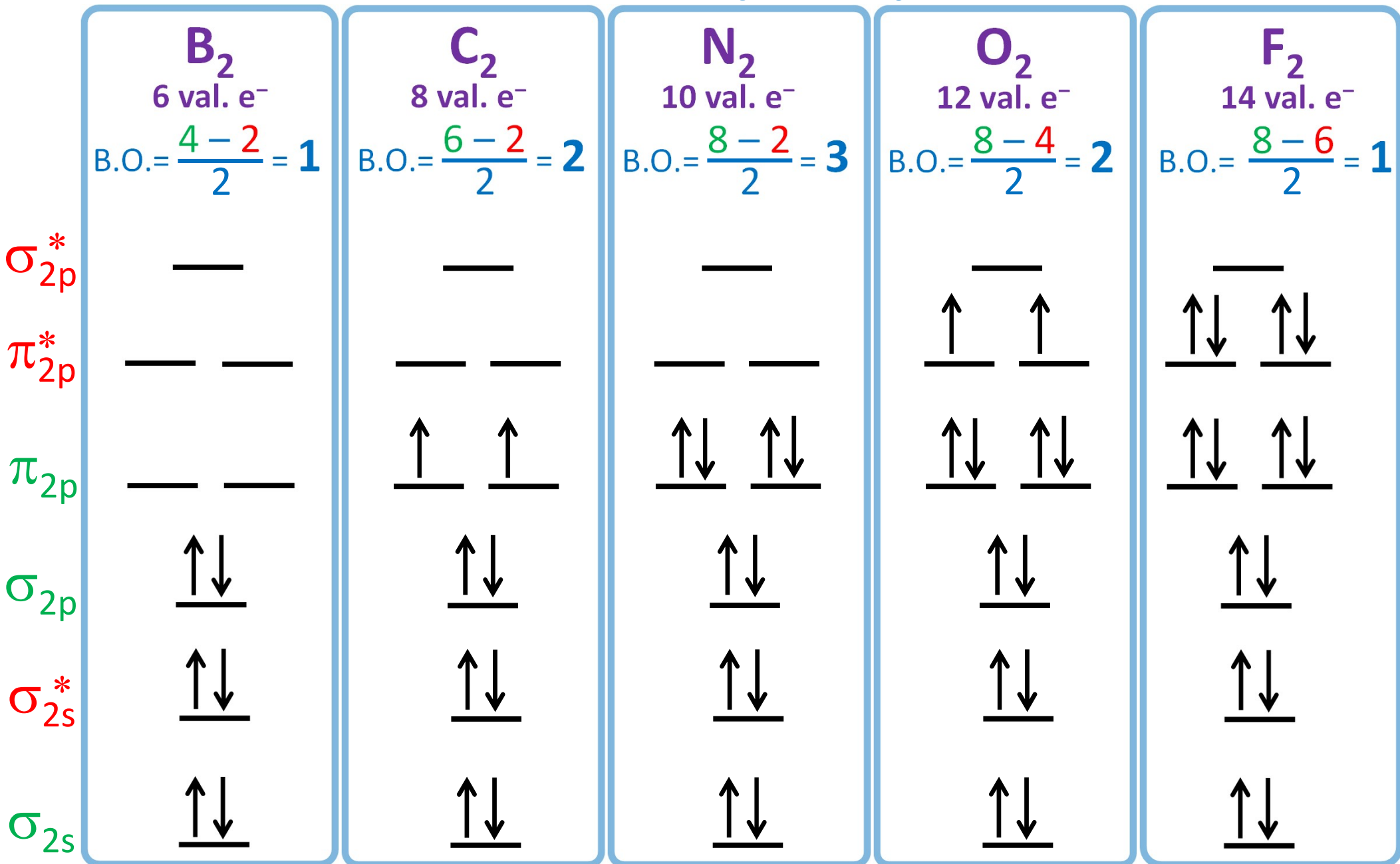
Pi (π) MO (when it is the “bonding” kind) corresponds to the π bond we created using sideways overlap of the **atomic pure p-orbitals.**

Expected energy diagram for Molecular Orbitals

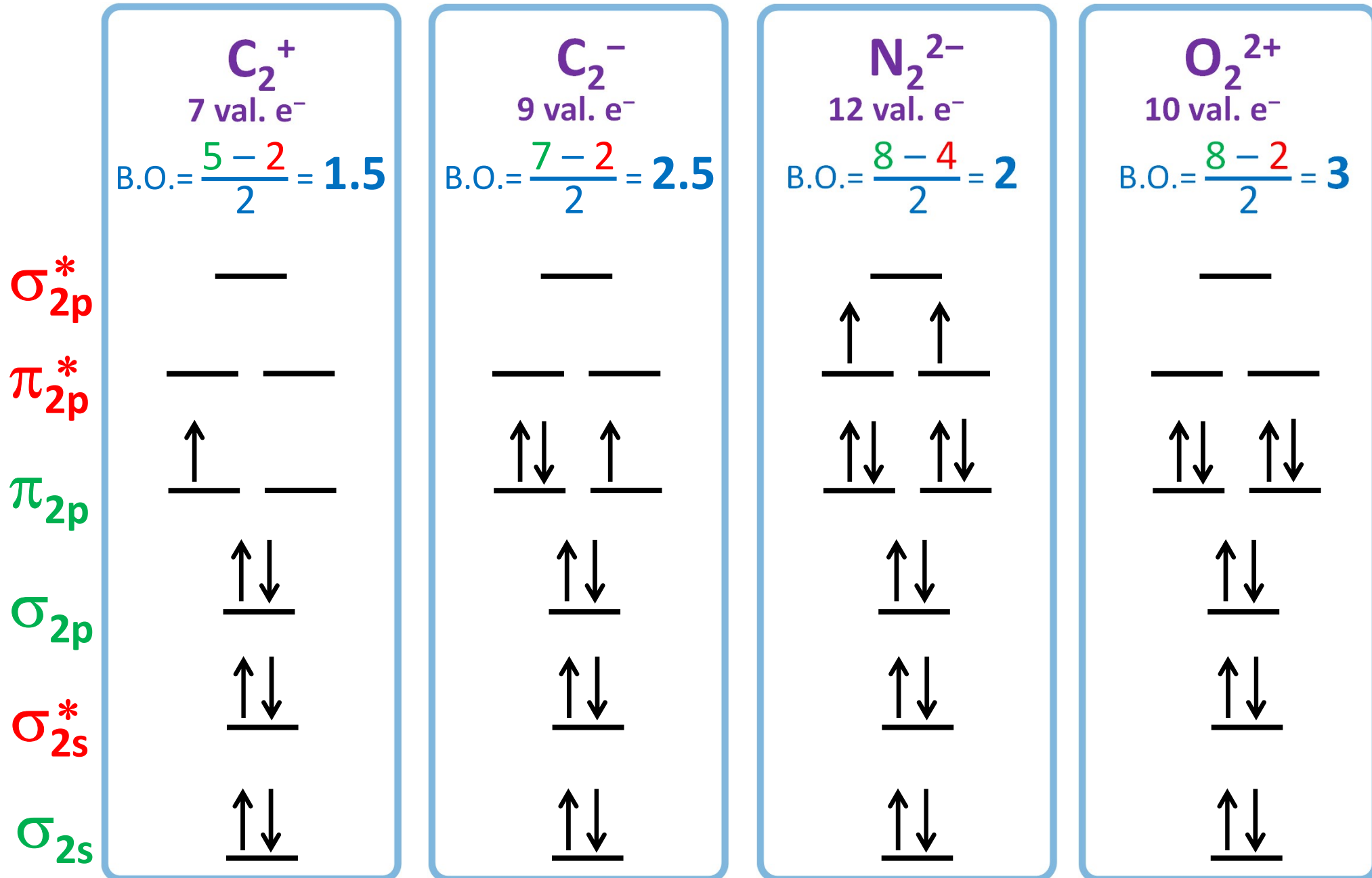
π orbitals from the sideways-overlap of p-orbitals are expected to have smaller “reward” (lowering of energy) and “penalty” (raising of energy) for being bonding and “anti-bonding” than the corresponding σ orbitals



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



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



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!**

Quick reminder

Paramagnetism:

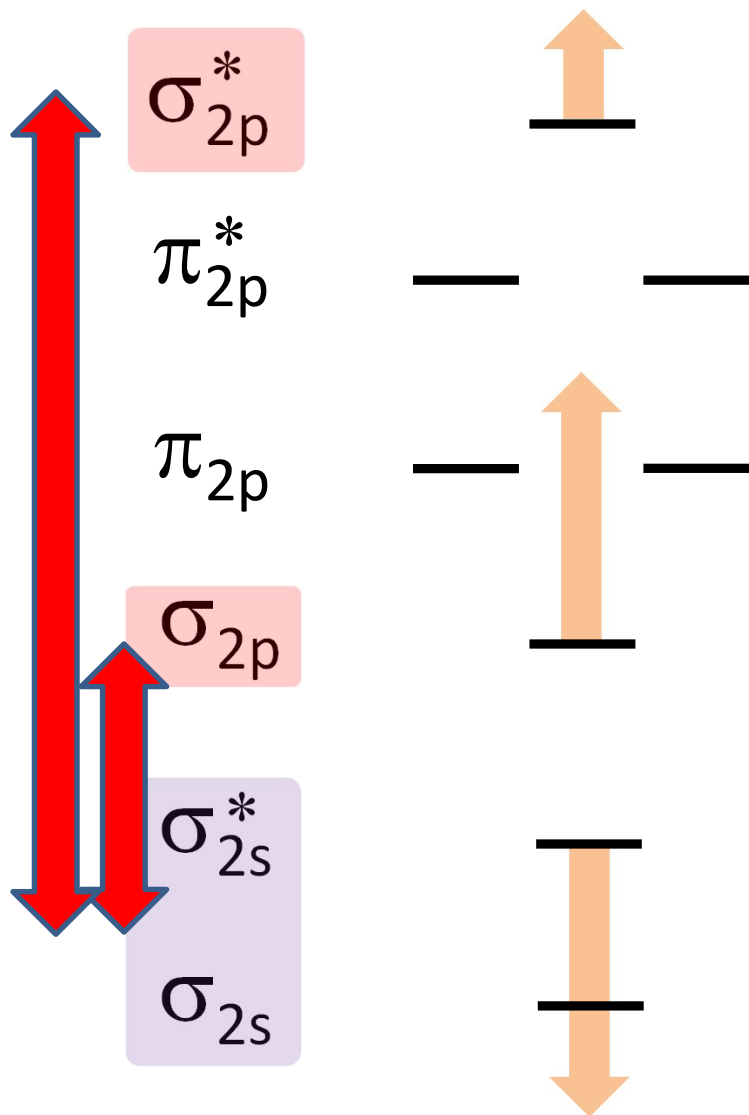
- Substance is **attracted** to a magnetic field
- One or more unpaired electrons

Diamagnetism:

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

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

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.

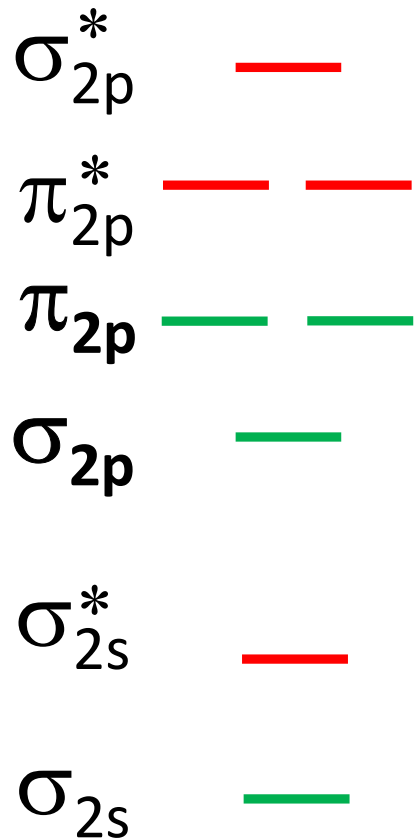
When the energy levels of the σ_{2s} and σ_{2p} MOs are less similar, their interaction is less relevant.

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

The energy order of the MOs is as expected.

“Expected” Diagram

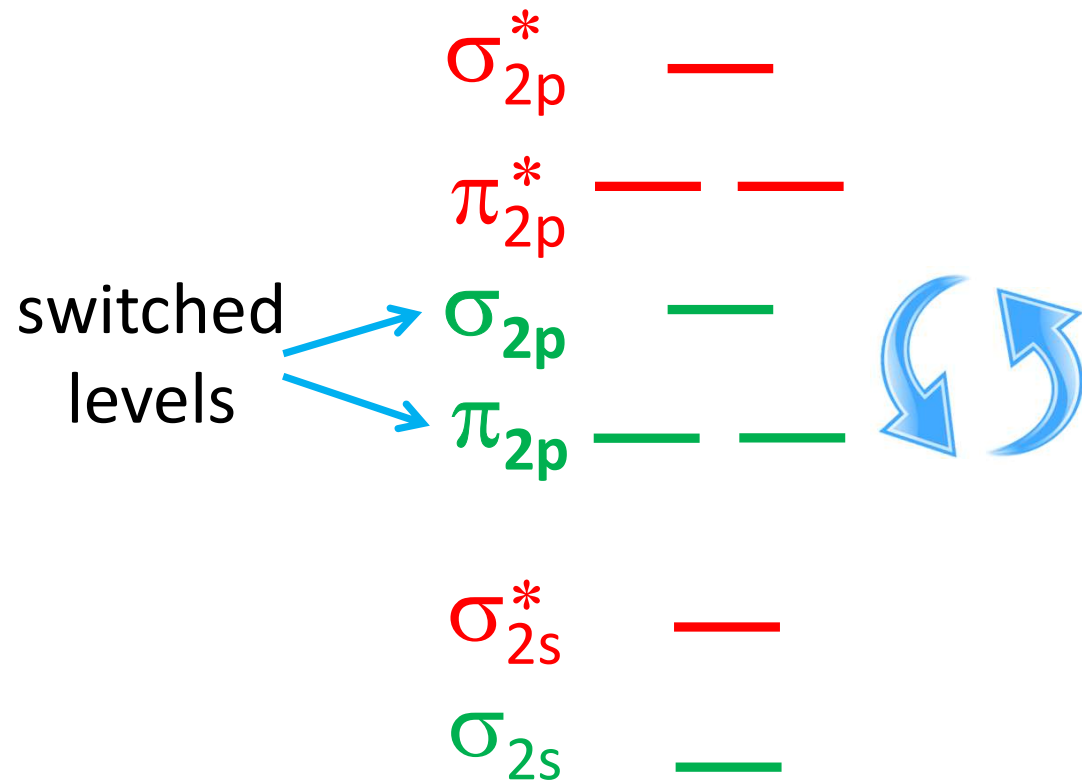
Applies only to O, F



“Switched” Diagram

π_{2p} is lower than σ_{2p}

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



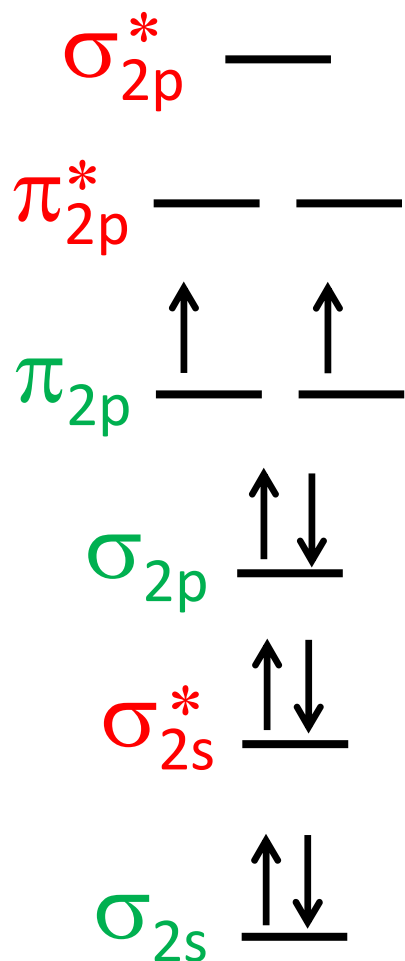
“Expected” energy diagram predicts the bond order just fine because the switch is between bonding MOs

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.

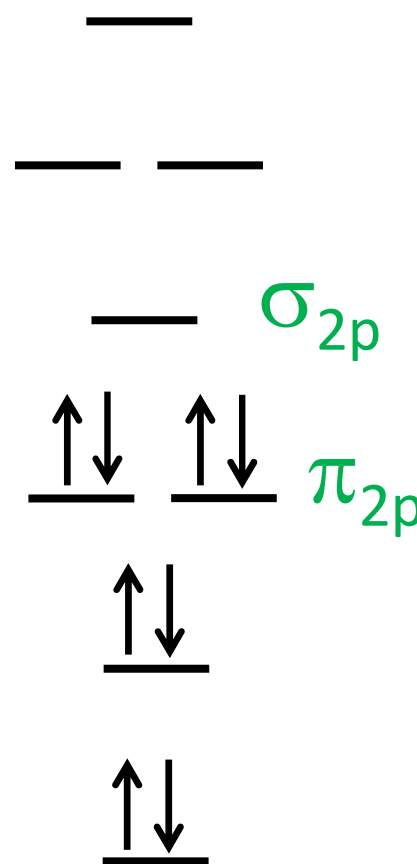
Number of electrons in bonding orbitals is still correct.

Example:**Predict whether C_2 is paramagnetic or diamagnetic**

“Expected diagram”
predicts **paramagnetic**

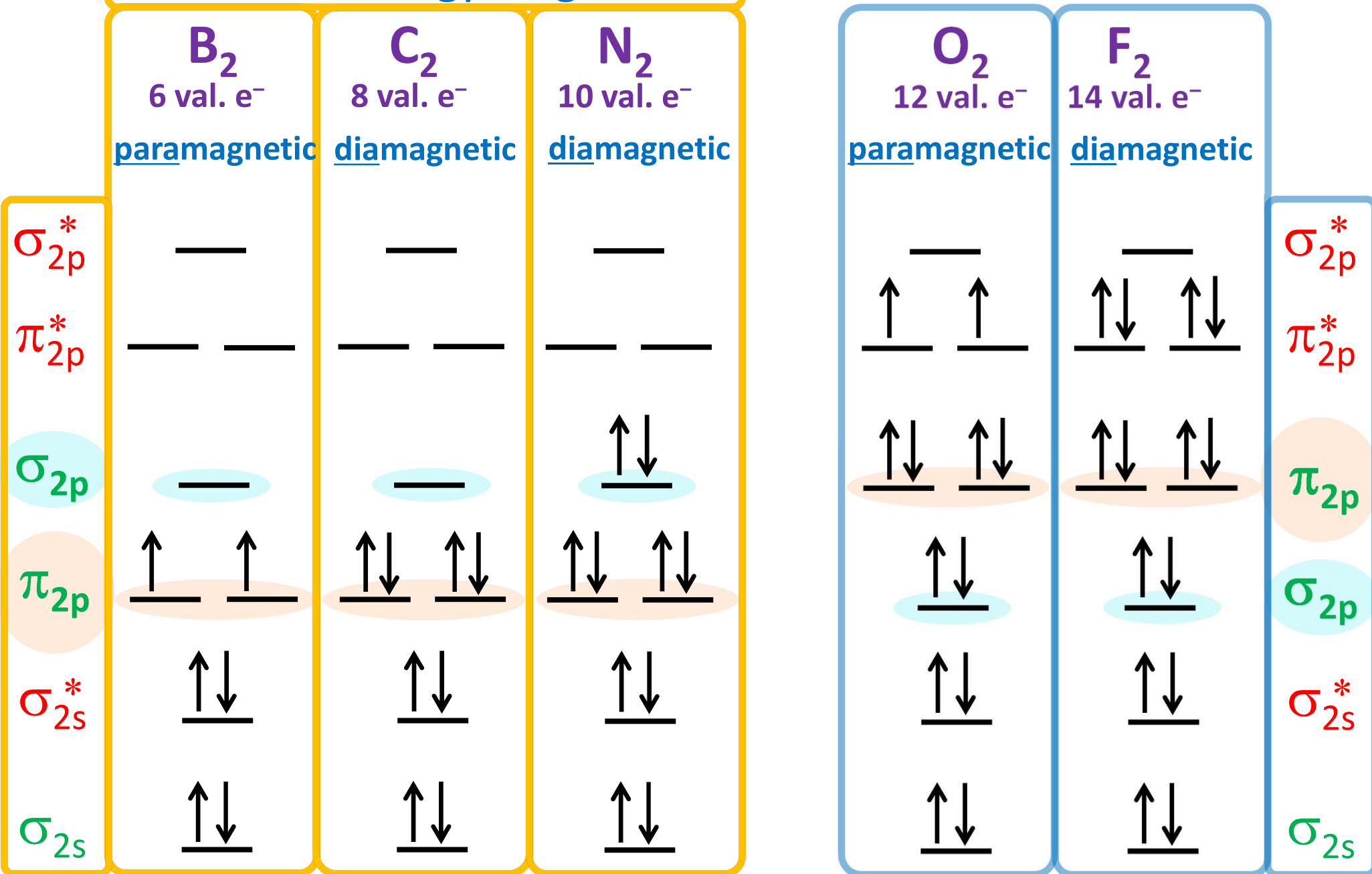


“Switched diagram”
predicts **diamagnetic** ✓

 **C_2 is actually diamagnetic**

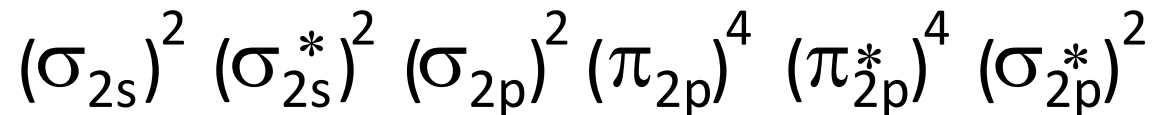
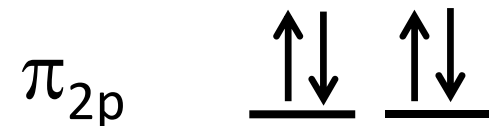
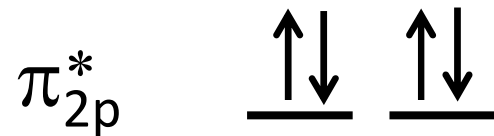
The correct energy diagrams can predict magnetism correctly

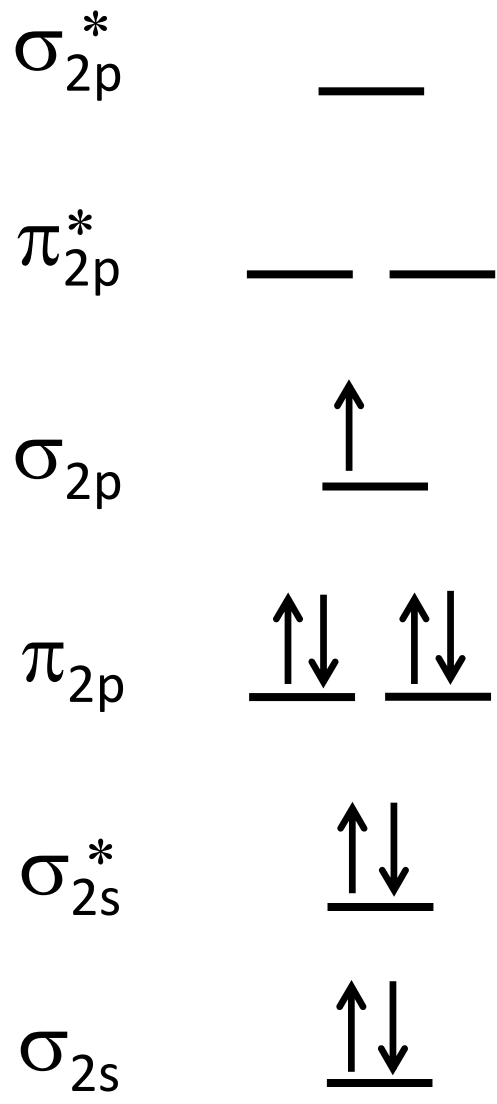
Switched energy diagrams



Molecular orbital populations can be described similar to the electron configurations of atoms

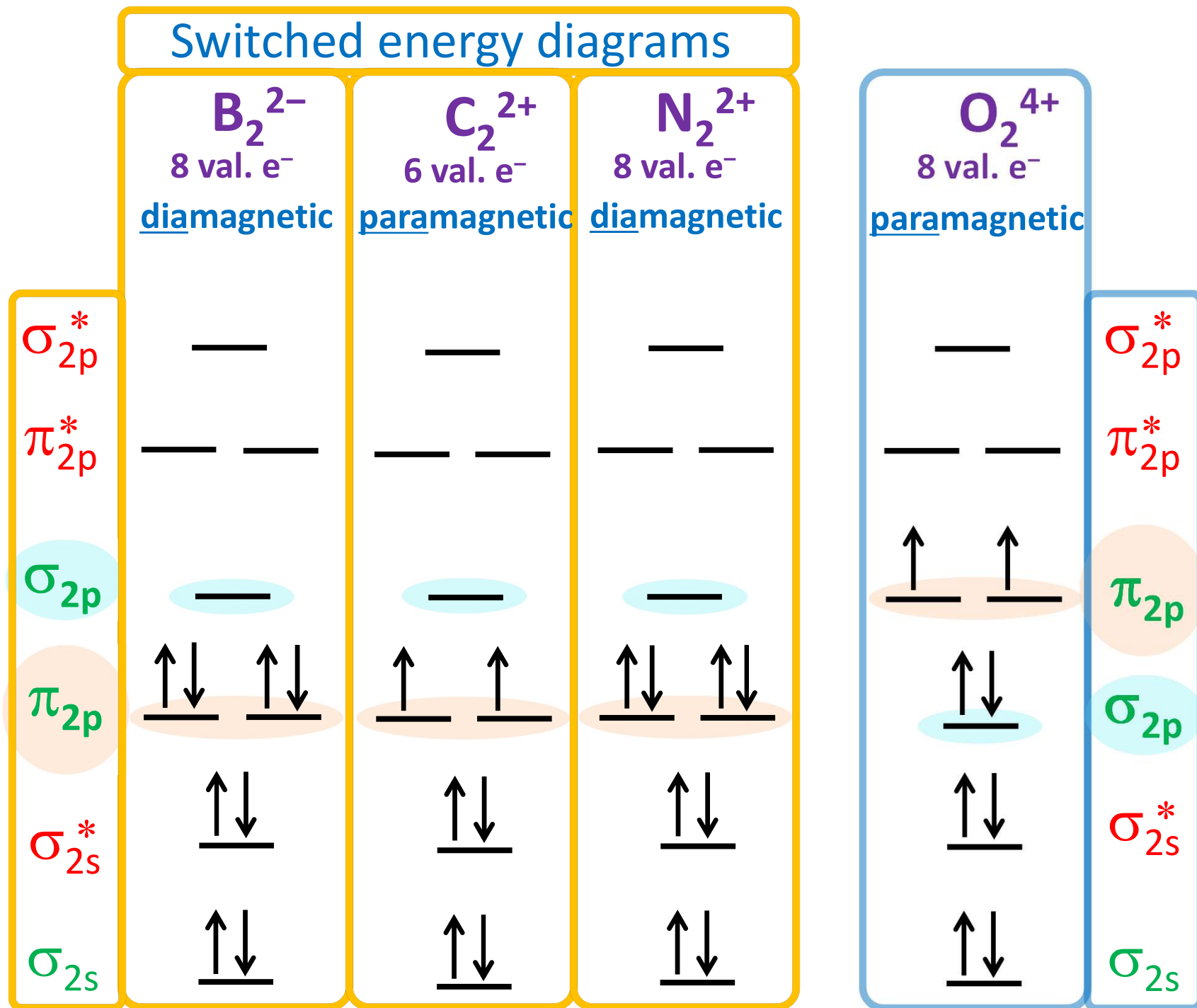
We just use the MO symbols instead





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

The correct energy diagrams can predict magnetism correctly



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

Heteronuclear diatomics with Switched energy diagrams

CO10 val. e⁻

$$\text{B.O.} = \frac{8 - 2}{2} = 3$$

diamagnetic**CN⁻**10 val. e⁻

$$\text{B.O.} = \frac{8 - 2}{2} = 3$$

diamagnetic**BN**8 val. e⁻

$$\text{B.O.} = \frac{6 - 2}{2} = 2$$

diamagnetic**BC⁺**6 val. e⁻

$$\text{B.O.} = \frac{4 - 2}{2} = 1$$

paramagnetic σ_{2p}^* π_{2p}^* σ_{2p} π_{2p} σ_{2s}^* σ_{2s}

—

— —

↑↓

↑↓ ↑↓

↑↓

↑↓

—

— —

↑↓

↑↓ ↑↓

↑↓

↑↓

—

— —

—

↑↓ ↑↓

↑↓

↑↓

—

— —

—

↑ ↑

↑↓

↑↓

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.

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.

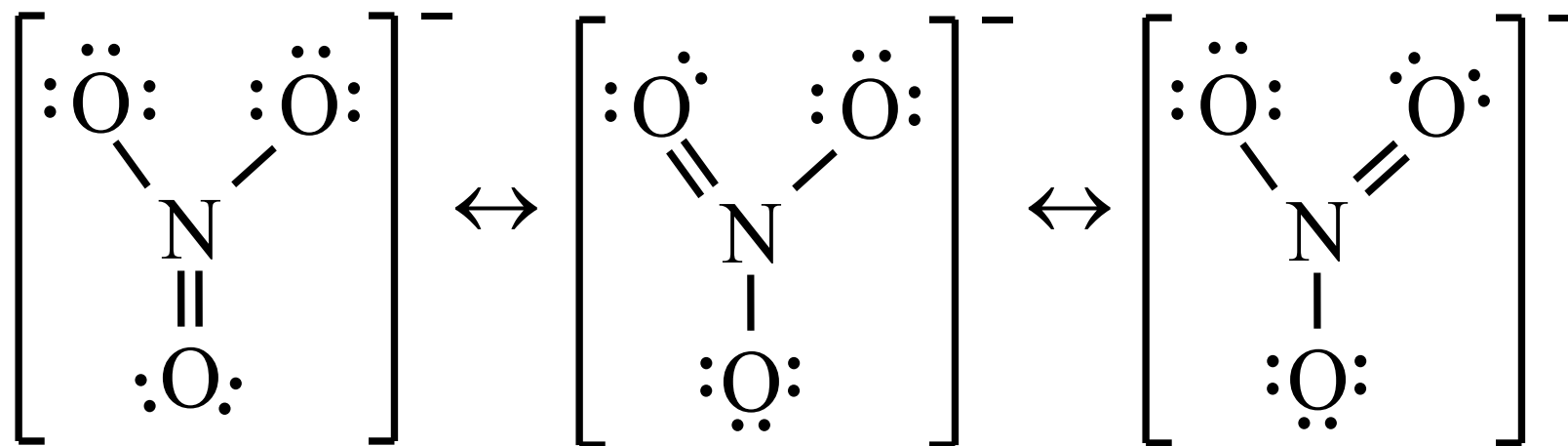
➤ Ironical, since Lewis structures use localized
bonding model.

Remember “resonance structures” when we learned Lewis structures?

About the nitrate ion, we said:

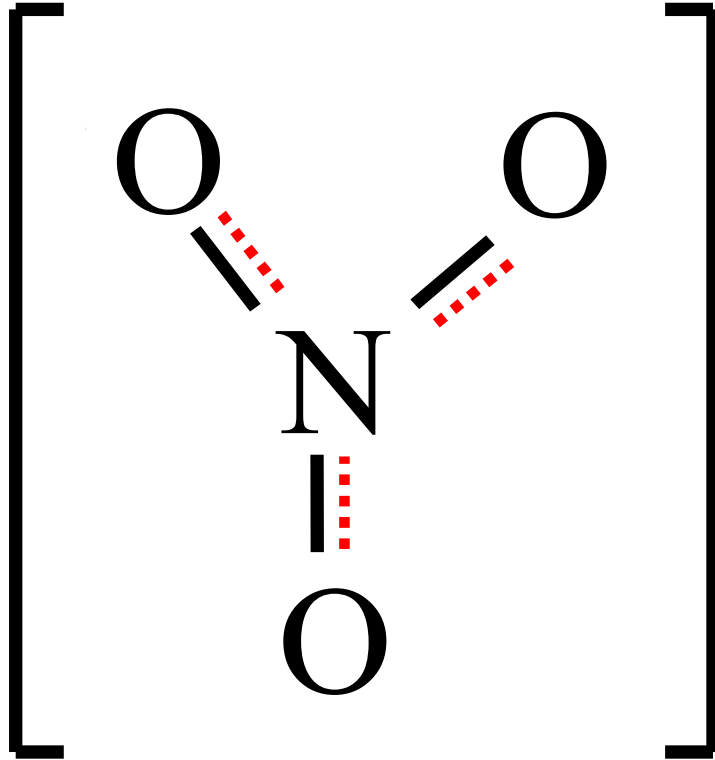
More than one valid Lewis structure can be written for a particular molecule.

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.

Delocalized electrons in the nitrate ion



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

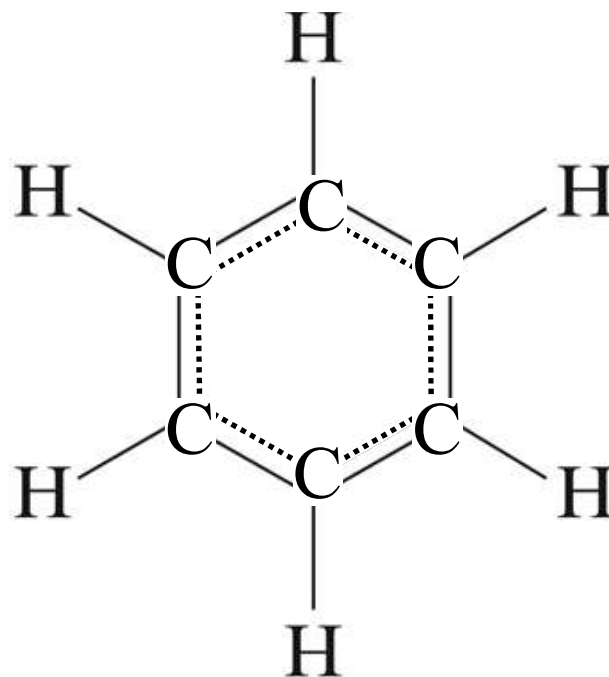
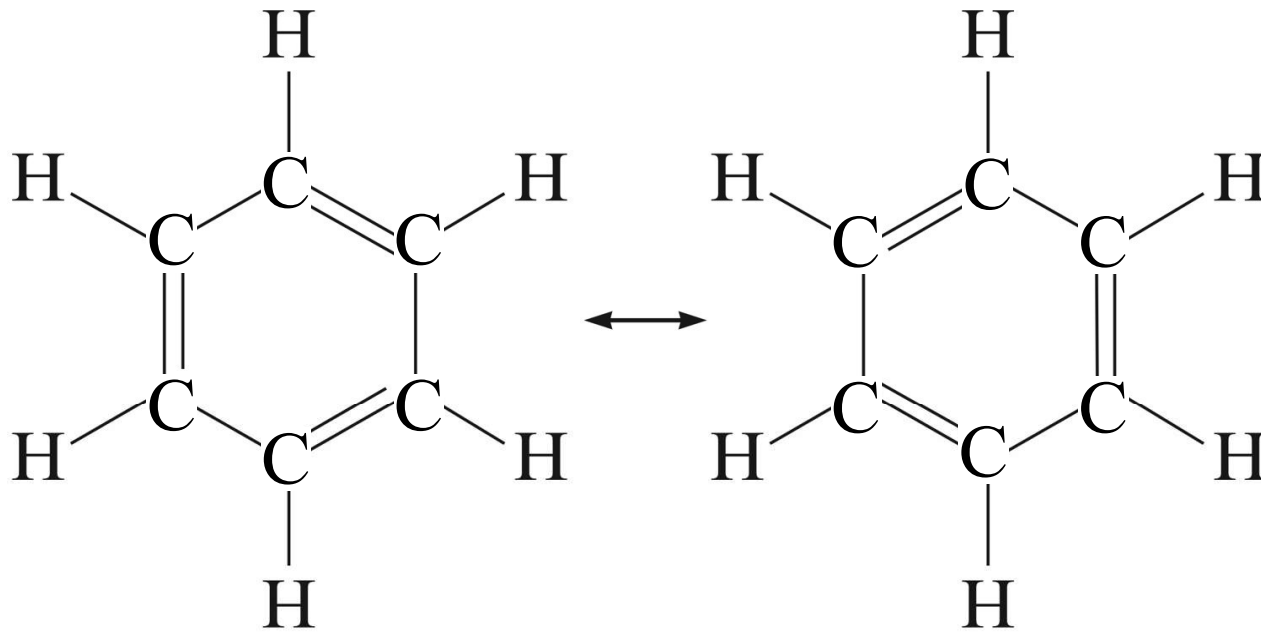
Each N-O bond is $1 + 1/3 = 1.33$ bond

Slightly stronger and shorter than a single bond

But not quite a double bond

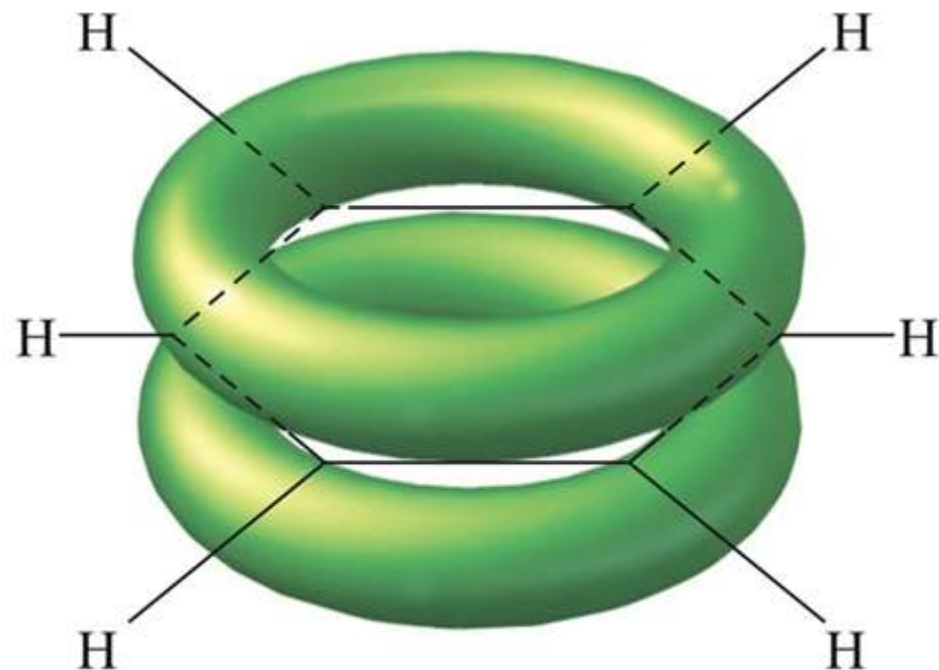
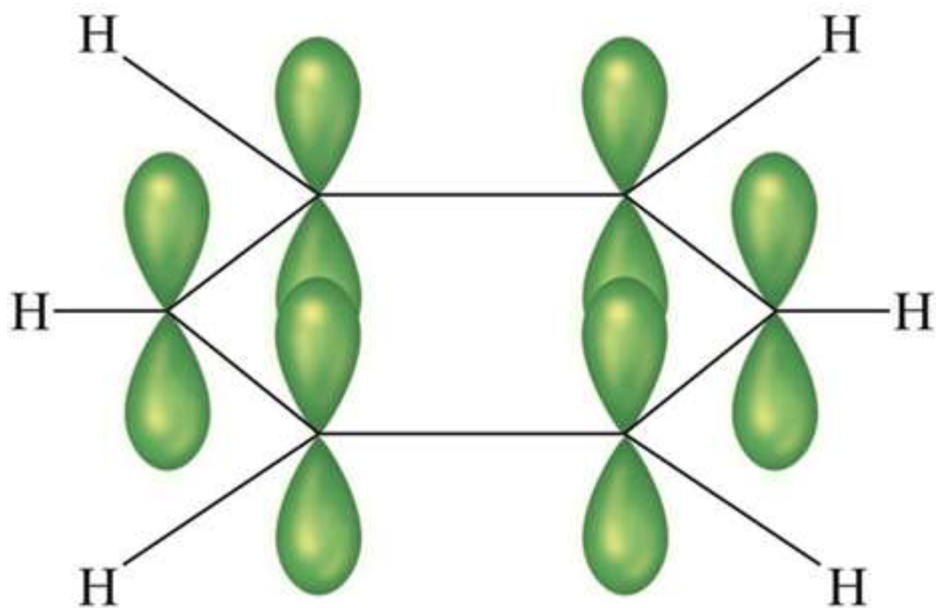
- Actual structure is an average of the resonance structures.
- Electrons are really **delocalized** – they can move around the entire molecule.

Resonance in Benzene



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

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.