Arts, Science And Commerce College, Kolhar Department of Chemistry

Name of Faculty- Miss Jadhav P.P
Topic Name –Molecular orbital theory

Covalent Bond Theories

1. VSEPR (valence shell electron pair repulsion model).
   A set of *empirical* rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

2. Valence Bond theory.
   A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals.
   Works especially well for organic molecules.

3. Molecular Orbital theory.
   The most modern and powerful theory of bonding. Based upon QM.

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G. N. Lewis developed Dot Diagrams and realized that that covalent bonds involved sharing pairs of electrons.

Linus Pauling furthered this concept with Valence Bond theory. Using hybrid orbitals, we get an explanation for VSEPR, geometries and we discover pi bonds and the concept of geometric isomers.

But both of these electronic structure theories incorrectly focus on electron pairs. Why can't molecules share one electron? Or three?

Molecular Orbital theory explains how this is possible.

Molecular Orbital Theory - LCAO-MO

Robert S. Mulliken realized that a Linear Combination of Atomic Orbitals (LCAO) could be used to make a set of new Molecular Orbitals (MO). The energies of these new molecular orbitals could be calculated and then filled with valence electrons.

Robert S. Mulliken
1896-1986

Mulliken received the 1966 Nobel Prize for his work.

In MO theory, molecular orbitals are derived by taking linear combinations of atomic orbitals. Linear combinations implies addition AND subtraction.

Example 1:

Consider the LCAO orbitals of an H_2 molecule, which is comprised of two Hydrogen atoms, A and B:
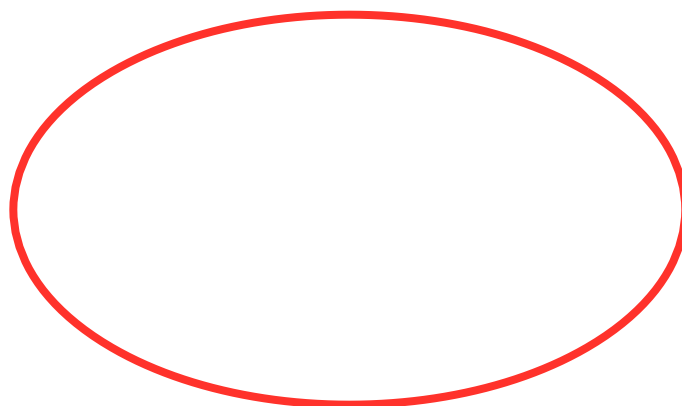
$$\sigma_s = \psi_{1s_A} + \psi_{1s_B}$$

$$\sigma_s^* = \psi_{1s_A} - \psi_{1s_B}$$

We then calculate the energies of these two molecular orbitals. The σ bonding MO leads to a lower energy state, and the σ* antibonding MO leads to a higher energy state with a node. The two electrons fill the σ bonding MO.


node

σ* antibonding molecular orbital

Energy

1s atomic orbital

1s atomic orbital

σ bonding molecular orbital
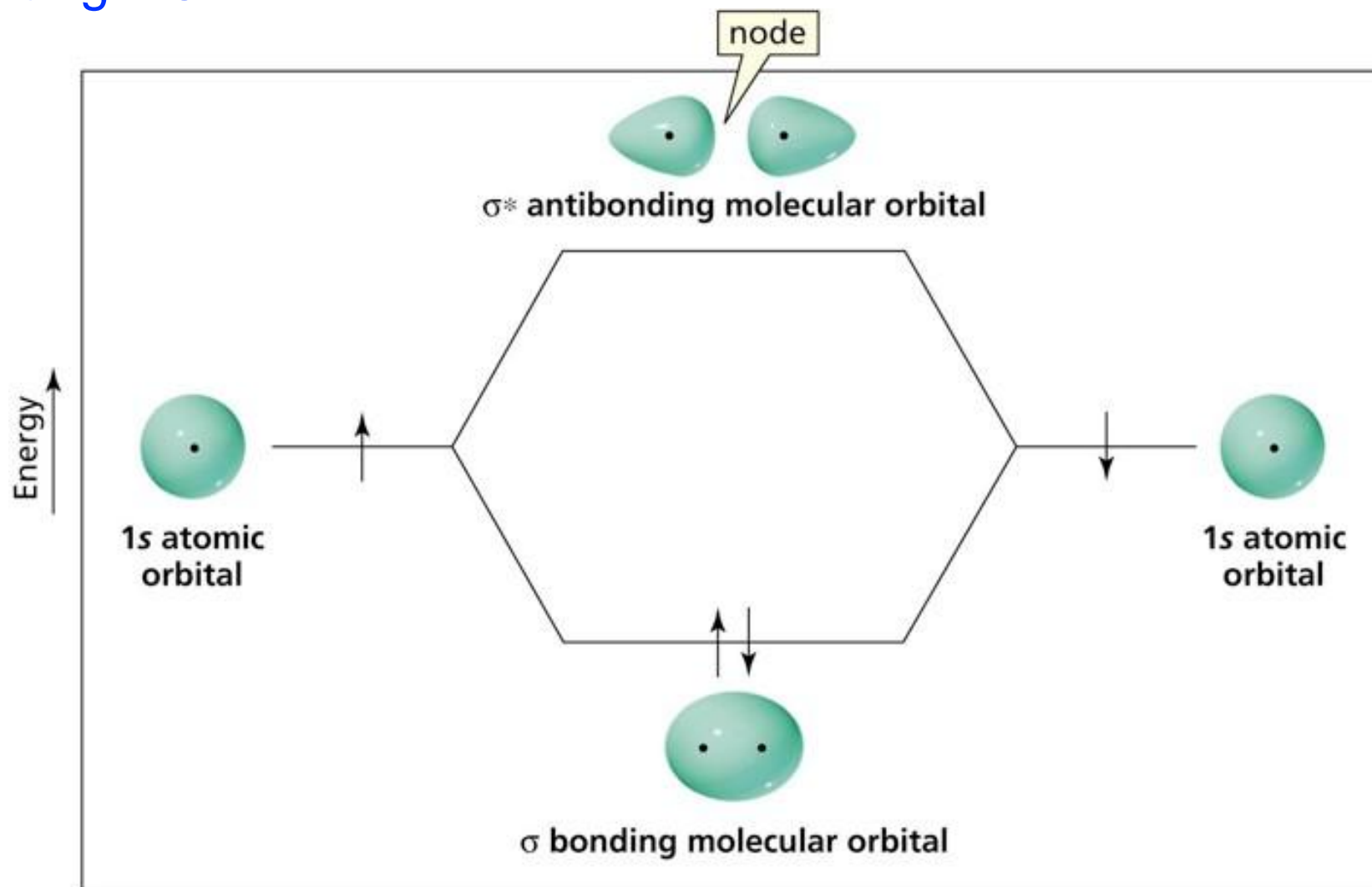
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This looks like a σ-bond, which is what we would have predicted from VB theory.

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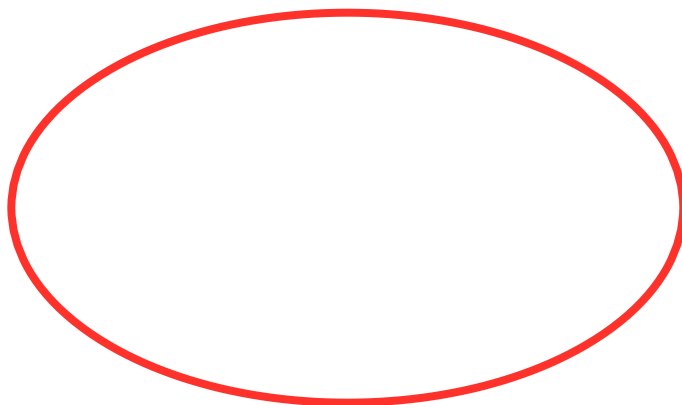
But the σ* antibonding MO is new and does not come out of VB theory

Here is the "energy level correlation diagram" for H_2...
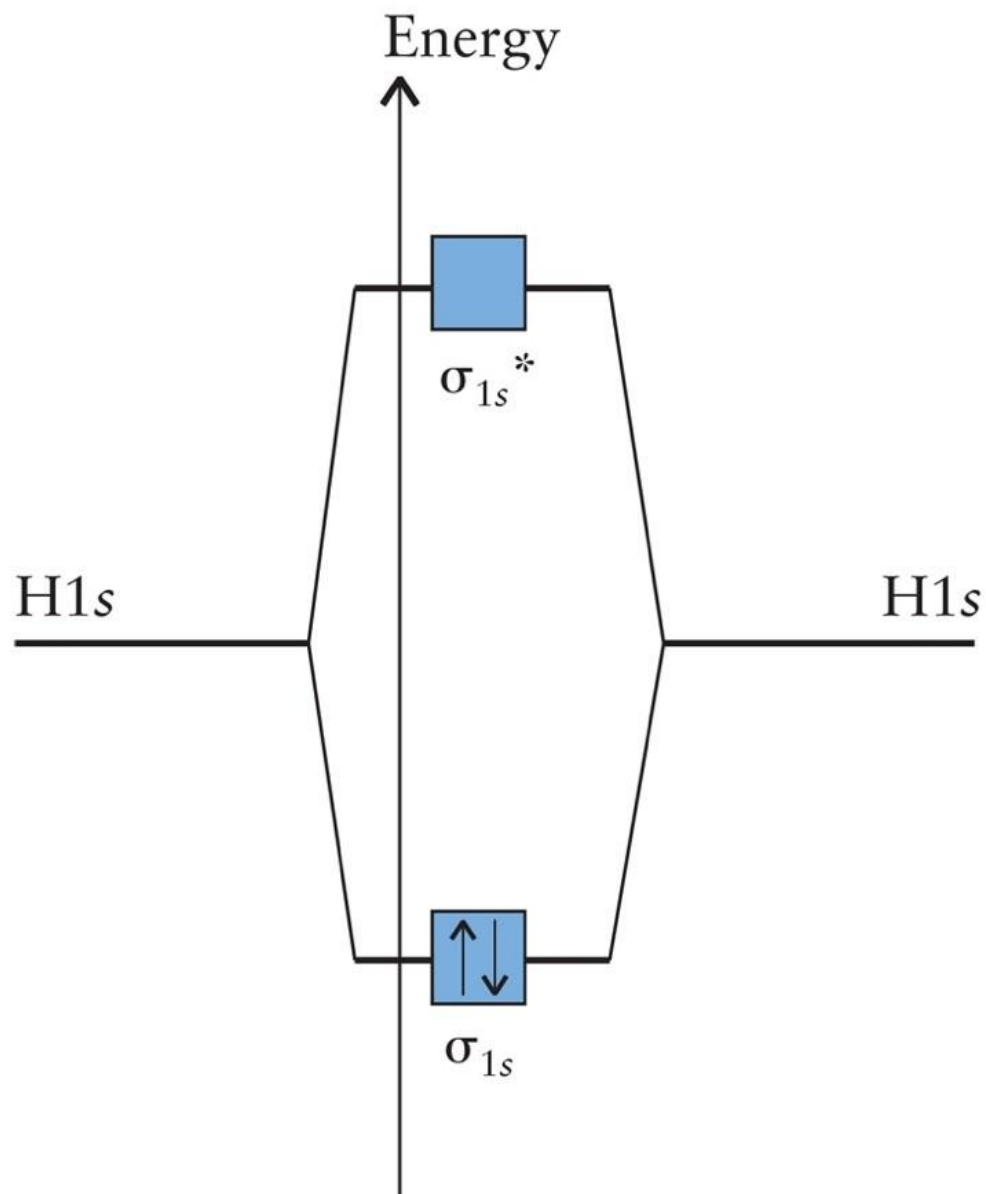
Where do these energies come from?

The energies come from Quantum Mechanics, of course!

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

WHEN we solve the Schrödinger equation, we always obtain two things:

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1. a set of eigenstates.
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WHEN we solve the Schrödinger equation, we always obtain two things:

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The eigenstates are the MOs formed from LCAOs.

The energies are obtained by solving the Schrödinger equation.

You won't have to do that in this class. However...

The energies come from Quantum Mechanics, of course!

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

WHEN we solve the Schrödinger equation, we always obtain two things:

1. aset of eigenstates.
2. aset of eigenstate energies.

If you are interested, please look up the "Hartree-Fock Method" and "Slater Determinants."

D. R. Hartree
1897-1958

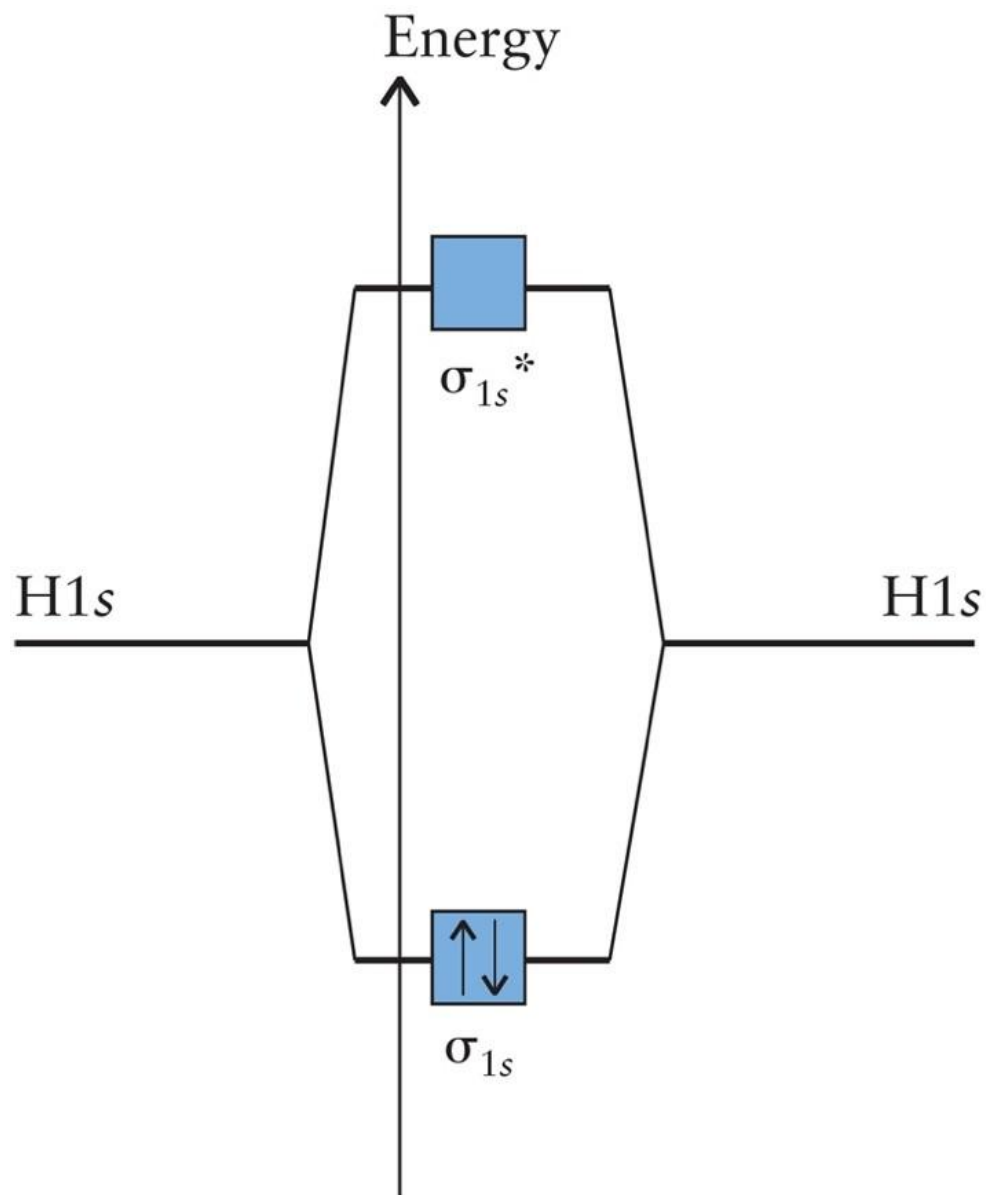V.A. Fock
1898-1974
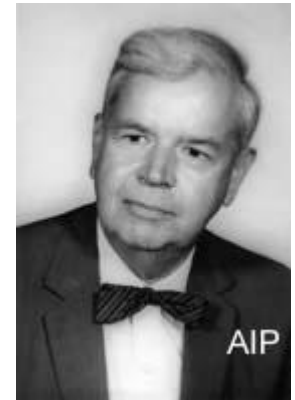
J.C. Slater
1900-1976

Molecular Orbital theory introduces the concept of Bond Order.

The bond order is given by:

$$B.O. = \frac{1}{2} \text{[# bonding electrons – antibonding electrons]}$$

The bond order does not need to be an integer number.

The bond order of H_2 is 1.0. We say that H_2 has a single bond.

Energy

σ_{1s}^*

H1s   H1s

σ_{1s}

We are also able to predict the *paramagnetic properties* of a molecule from MO theory, based on whether it possesses unpaired electrons:

For a molecule, there are two possibilities:

Diamagnetic: All electrons are paired.

Paramagnetic: Unpaired electrons are present.

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$$\mu = xB$$

x < 0: Diamagnetic

x > 0: Paramagnetic

B is the applied magnetic field. μ is the induced magnetic dipole. x is the magnetic susceptibility. Paramagnetic molecules are attracted by a magnetic field.

We are also able to predict the *paramagnetic properties* of a molecule from MO theory, based on whether it possesses unpaired electrons:
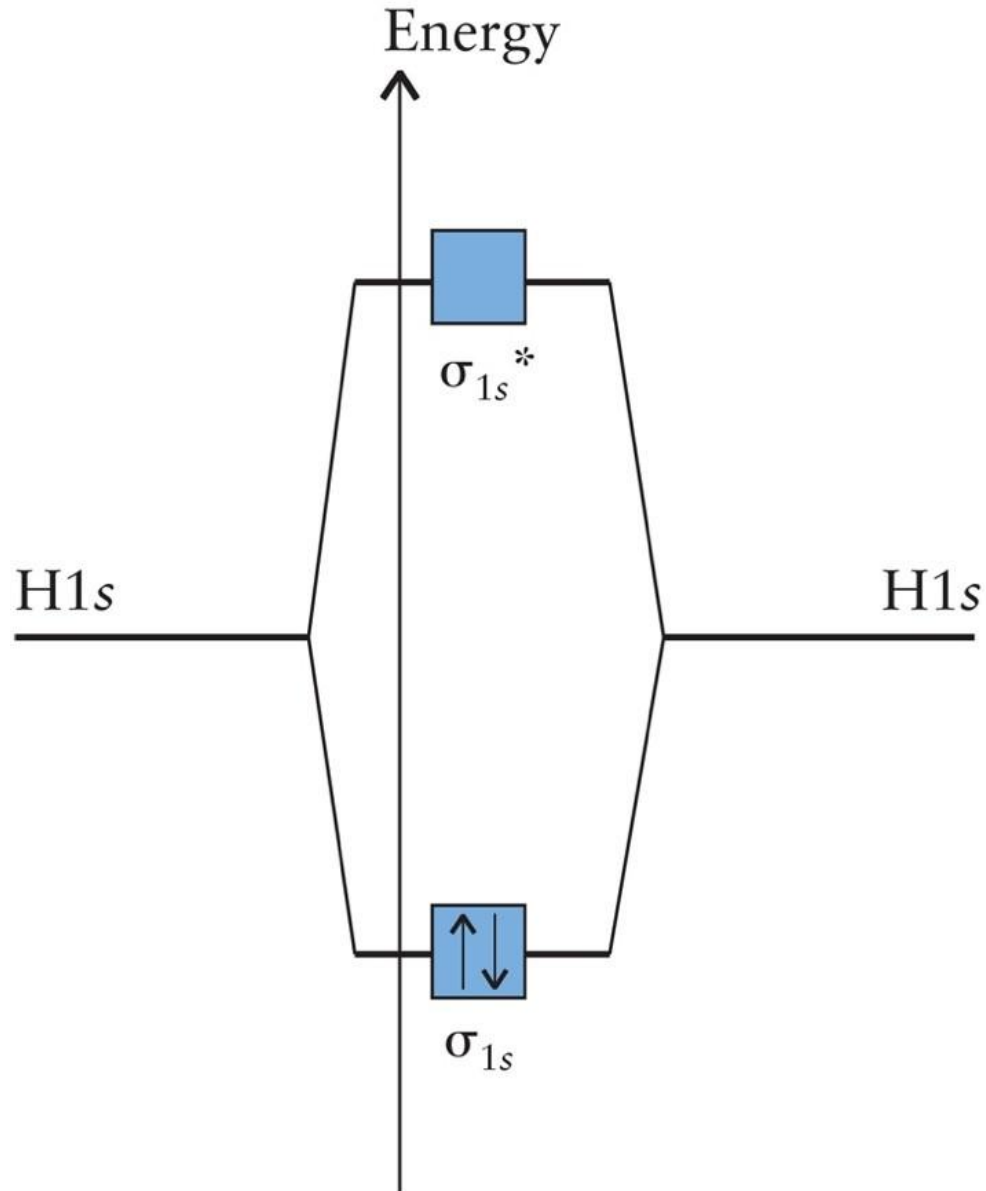
For a molecule, there are two possibilities:

Diamagnetic: All electrons are paired.

Paramagnetic: Unpaired electrons are present.

FYI: there is also ferromagnetic and ferrimagnetic. They are more complicated and involve the interaction of many spins.
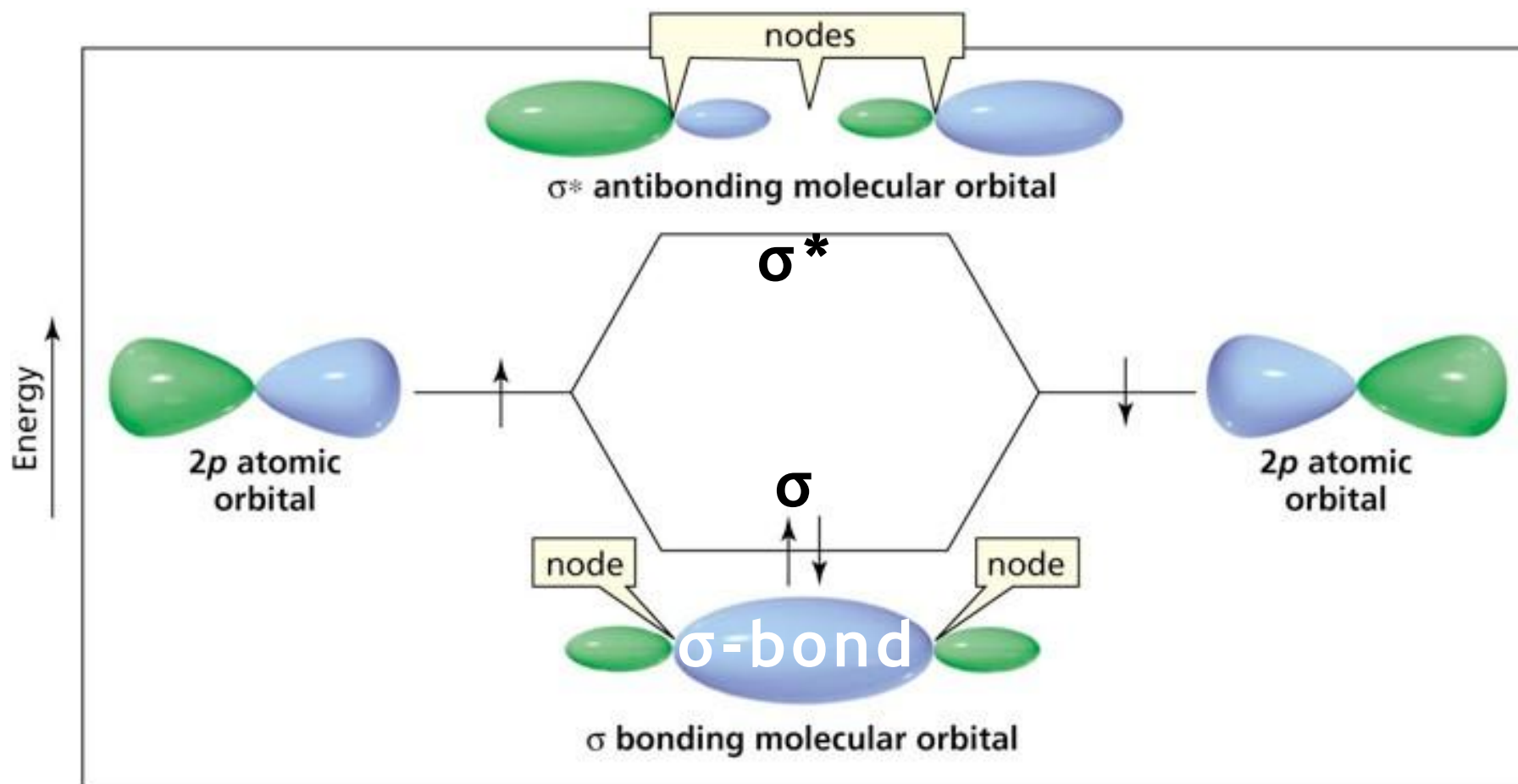
H_2 has no unpaired spins and therefore is diamagnetic.

Energy

σ_{1s}^*

H1s

H1s

σ_{1s}

MO theory correctly predicts the electronic structure of the diatomic molecules of hydrogen and helium:

	H_2^+	H_2	He_2^+	He_2
σ_{1s}^*			↑	↑↓
σ_{1s}	↑	↑↓	↑↓	↑↓
magnetism	para	dia	para	-
bond order	1/2	1	1/2	0
bond energy, eV	2.79	4.52	2.60	-
bond length, pm	106	74	108	-

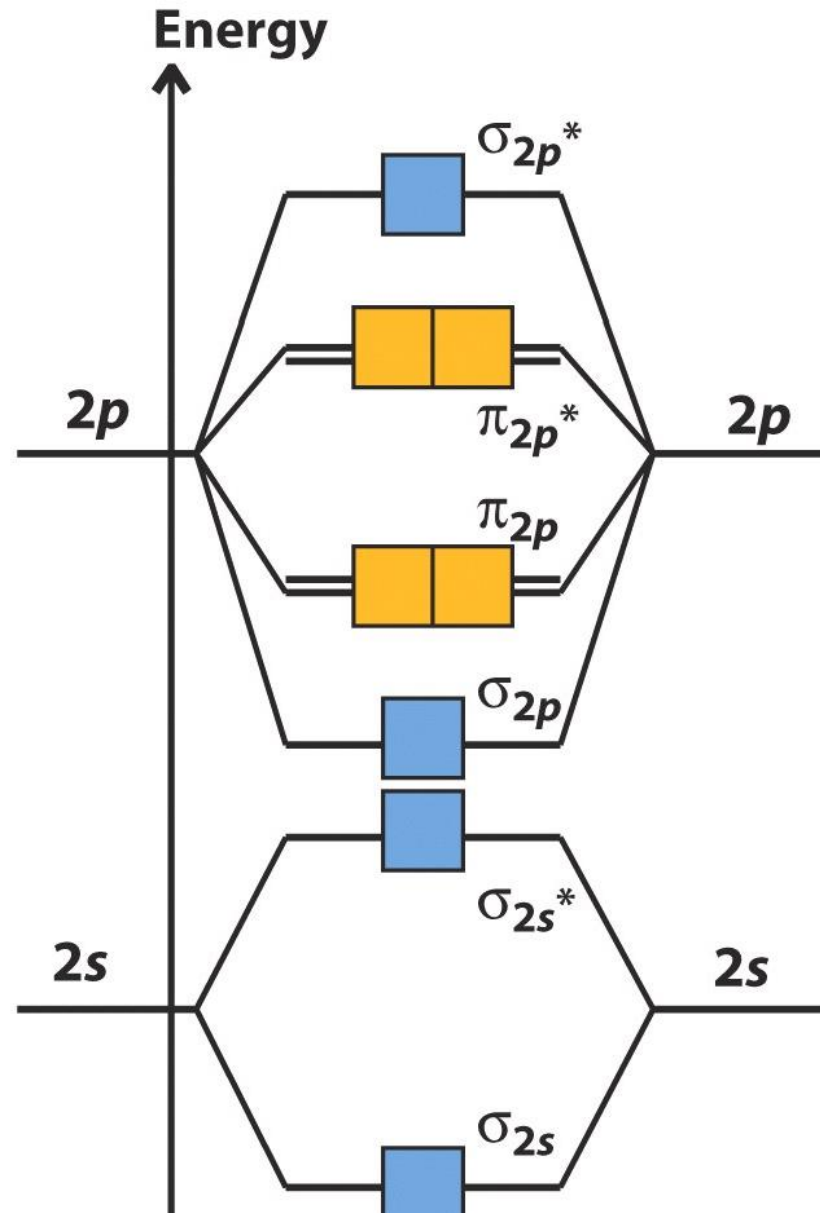*Let's move on to LCAO-MOs from p orbitals...*

There are two ways to combine p-orbitals: for p_x (where both orbitals are aligned with the internuclear axis), we get a bonding and an antibonding MO:

nodes

σ* antibonding molecular orbital

σ*

Energy

2p atomic orbital

σ

2p atomic orbital

node

node

σ-bond

σ bonding molecular orbital

For p_y and p_z orbitals (both of which are oriented perpendicular to the internuclear axis), we get π and π* orbitals:
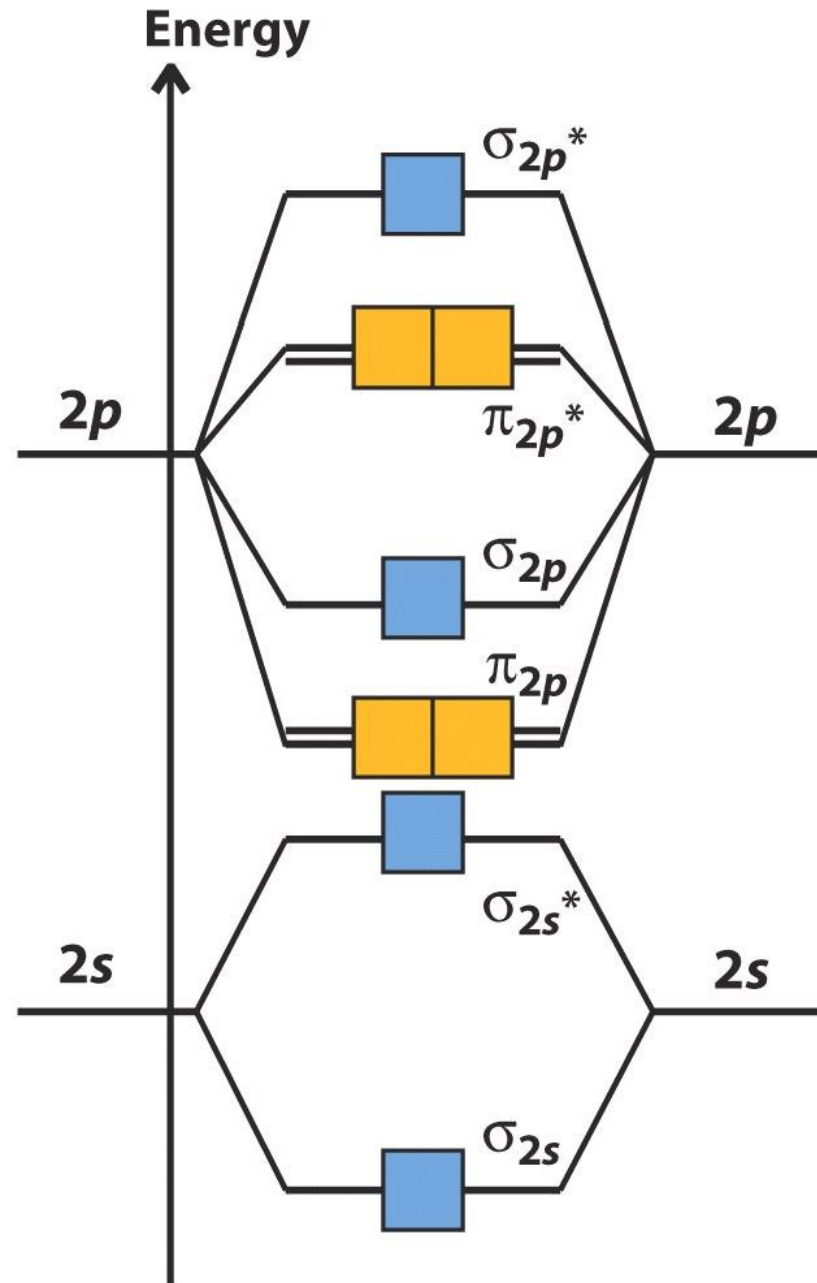

nodal plane

nodal plane

π* antibonding molecular orbital

Energy

2p atomic orbital

2p atomic orbital

nodal plane

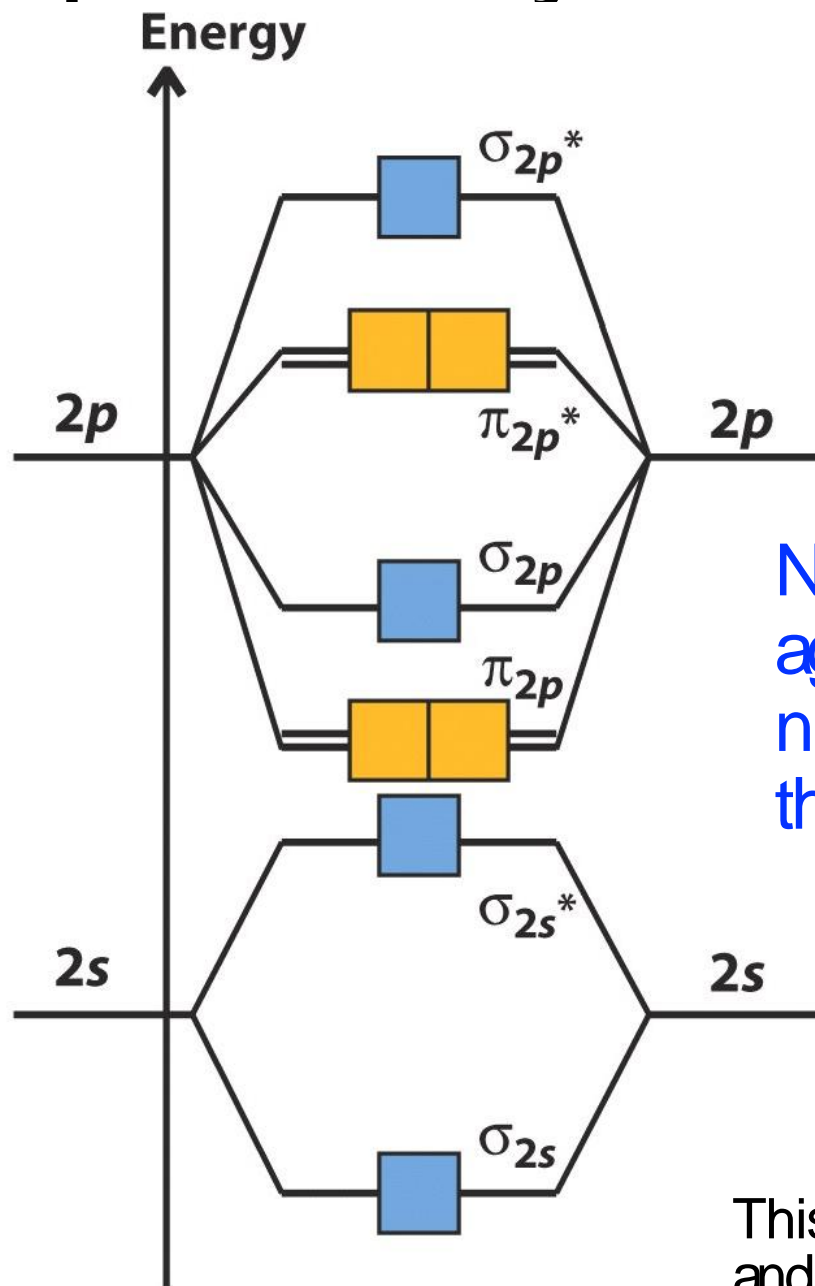π bonding molecular orbital
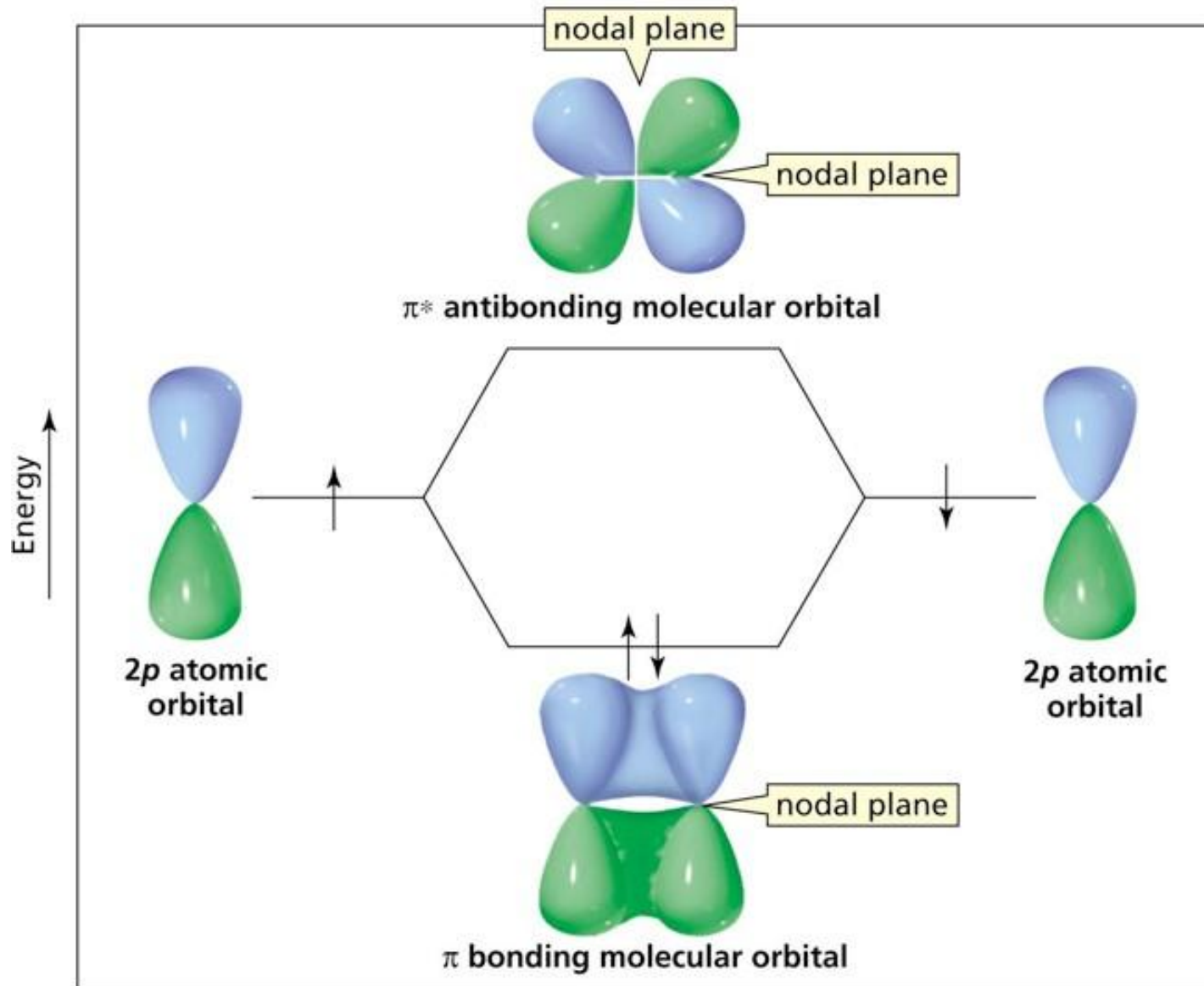
Now, when 2s and 2p atomic orbitals mix

...usually, but not always.
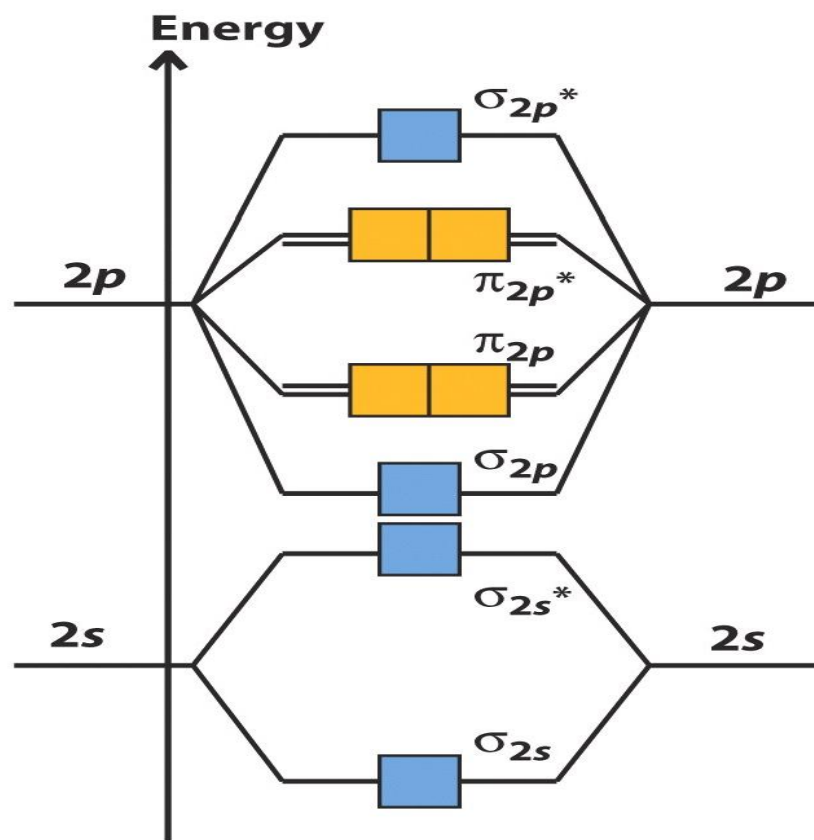The other possibility is this:

...usually, but not always.
The other possibility is this:

Note that σ^*_{2p} is again the highest, but now π_{2p} is lower than σ_{2p}.

This is due to a mixing of s and p sigma orbitals.

Okay, let's now fill in some diatomic MO energy level diagrams. A favorite is oxygen (O_2):

Energy

$\sigma_{2p}*$

$\pi_{2p}*$

2p
2p

π_{2p}

σ_{2p}

$\sigma_{2s}*$

2s
2s

σ_{2s}

How many valence electrons?

Okay, let's now fill in some diatomic MO energy level diagrams. A favorite is oxygen (O_2):

Energy

σ_{2p}^*

$2p$

π_{2p}^*

$2p$

π_{2p}

12 valence electrons!

σ_{2p}

σ_{2s}^*

$2s$

$2s$

σ_{2s}
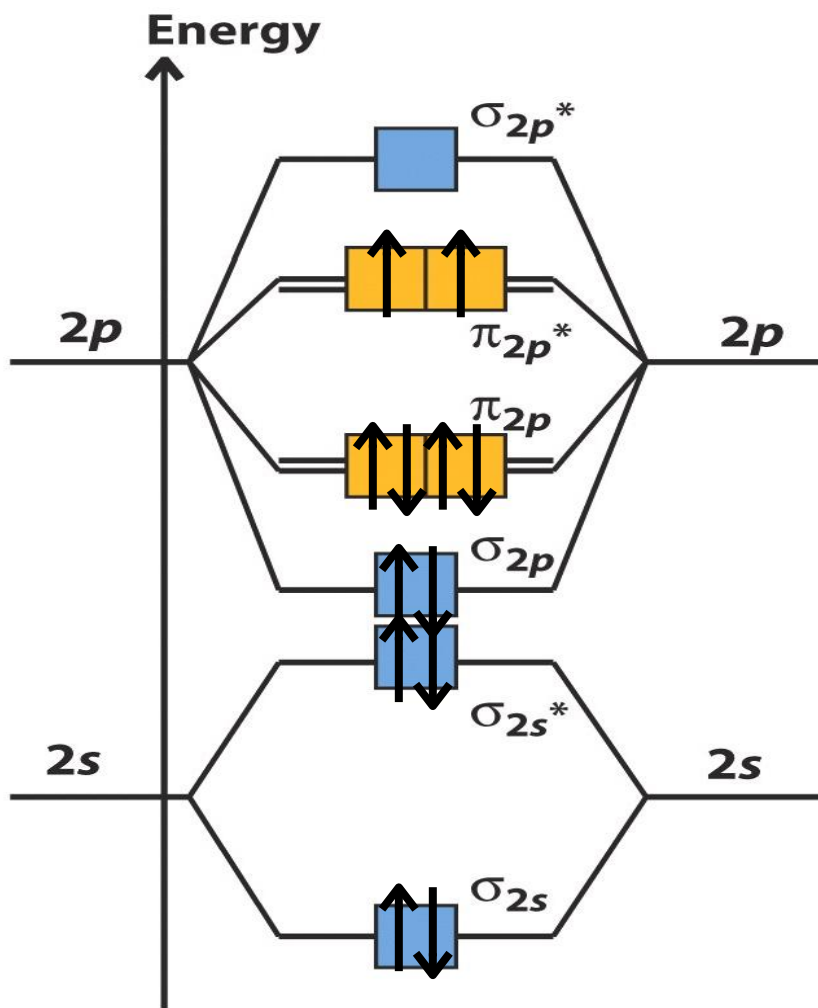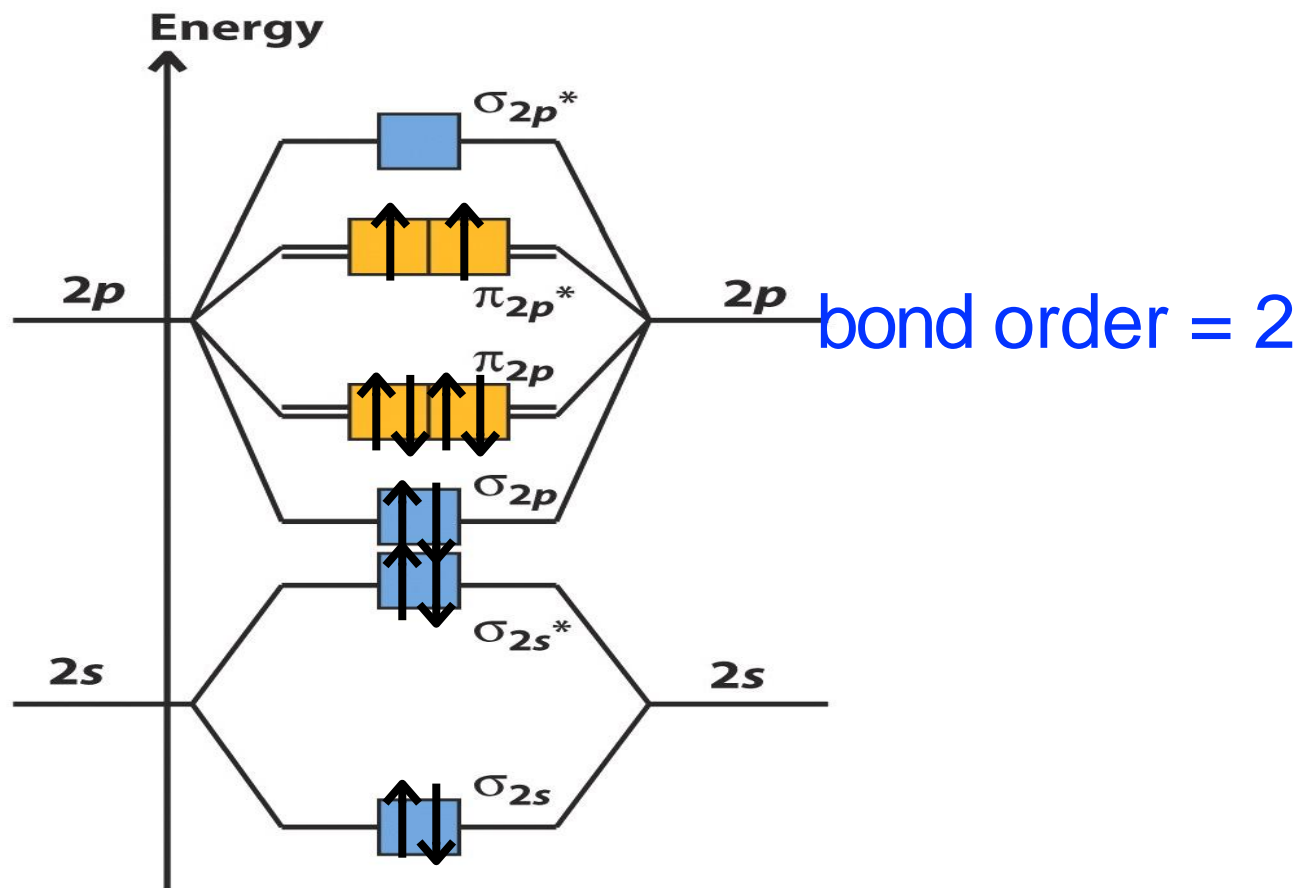
bond order = ?

Okay, let's now fill in some diatomic MO energy level diagrams.
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12 valence electrons!

bond order = 2

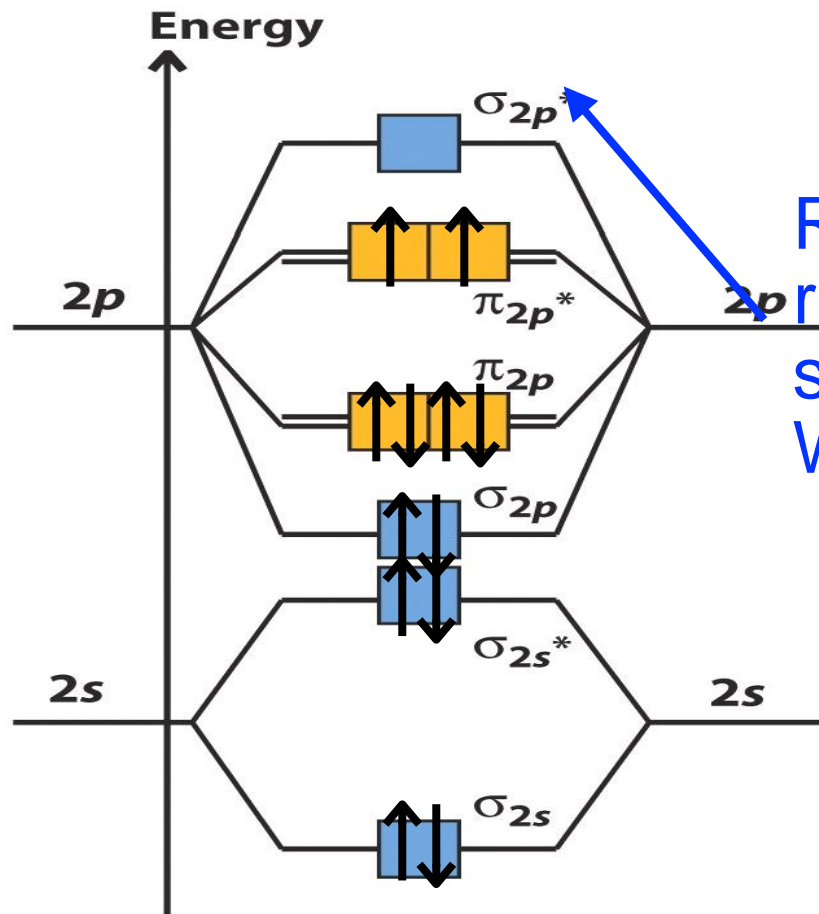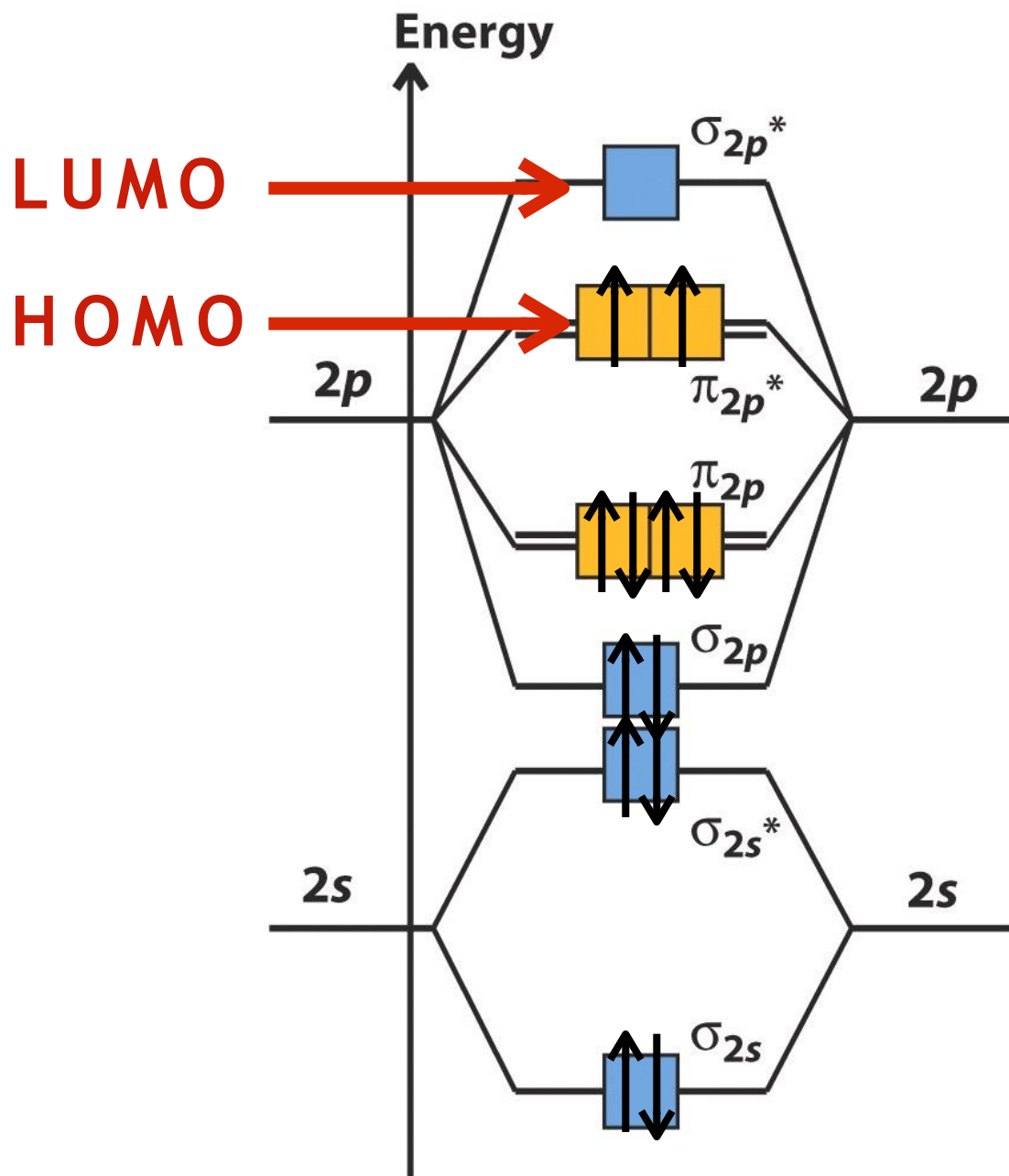Okay, let's now fill in some diatomic MO energy level diagrams.
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12 valence electrons!

Remember Hund's rule of maximum spin multiplicity? We use it here too.

Some new terminology: the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO):
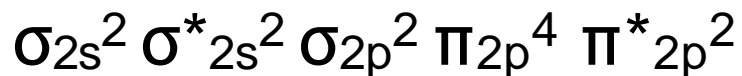
Okay, let's now fill in some diatomic MO energy level diagrams. A favorite is oxygen (O_2):

We therefore predict:

Bond Order = $1/2(8-4)$ = **2.0**

O_2 is **paramagnetic**

Its electron configuration is:

$\sigma_{2s}^2 \, \sigma^*_{2s}^2 \, \sigma_{2p}^2 \, \pi_{2p}^4 \, \pi^*_{2p}^2$

Compare with Lewis Dot Structure or VB Theory.