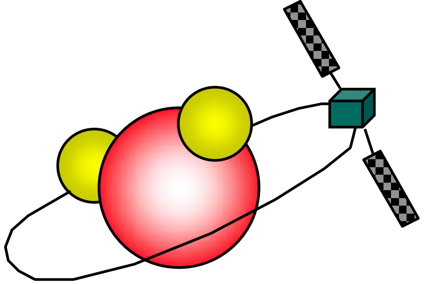
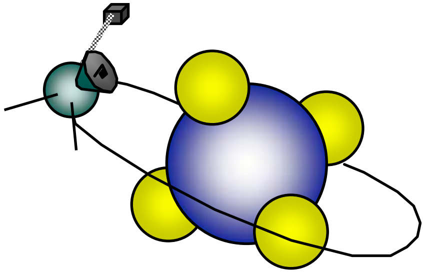


Molecular Orbital Theory

Reading: Gray: (2-5), (2-6), (3-1) to (3-6)
OGN: (16.1) and (16.3)



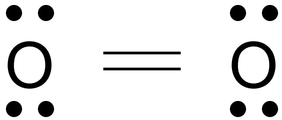
Molecular Orbital Theory

MO–LCAO: **M**olecular **O**rbital–**L**inear
Combination of **A**tomic **O**rbitals

Lewis Dot Structures don’t work for excited states; sometimes they don’t even predict the ground state accurately:

Example: O_2

expected Lewis Dot Structrure:



$O=O$

Actually O_2 has two unpaired electrons; this cannot be predicted with Lewis Dot Structures, but it can be predicted with MO-LCAO

MO-LCAO

Lewis Dot Structures tell us:

$$H_2 \longrightarrow \mathrm{H} : \mathrm{H}$$

$$H_2^{+} \longrightarrow \mathrm{H} \cdot \mathrm{H}$$

$$H_2^{-} \longrightarrow \mathrm{H} : \mathrm{H}\, \cdot$$

MO-LCAO will tell us:

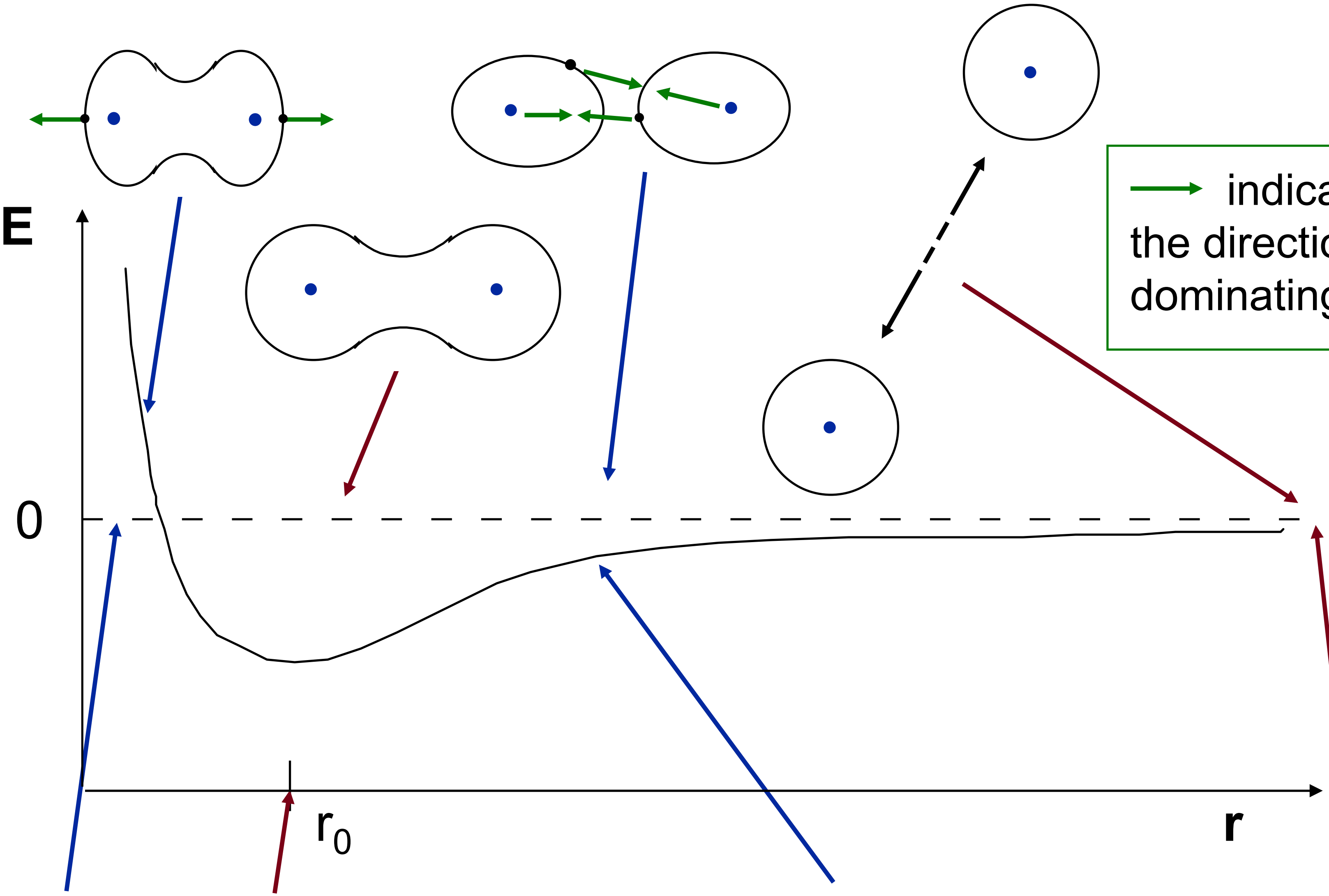
a. their local stabilities
b. their bond orders and their trend in bond lengths
c. their magnetic properties

Nobel Prize, Chemistry, 1966

Robert S. Mullikan

”For his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"

Energy dependence on inter-atomic distance



indicates the direction of dominating forces

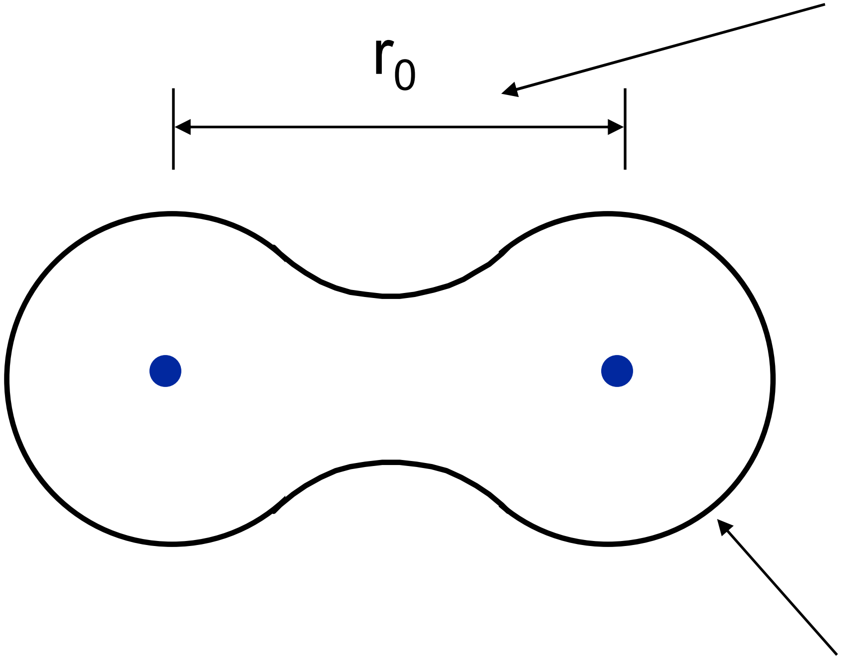
region where nuclei repel

most likely distance for a bond (lowest energy point)

electrons start being pulled to the other atom’s nucleus

at r = ∞, E = 0; the atoms don’t interact

H_2 Molecule

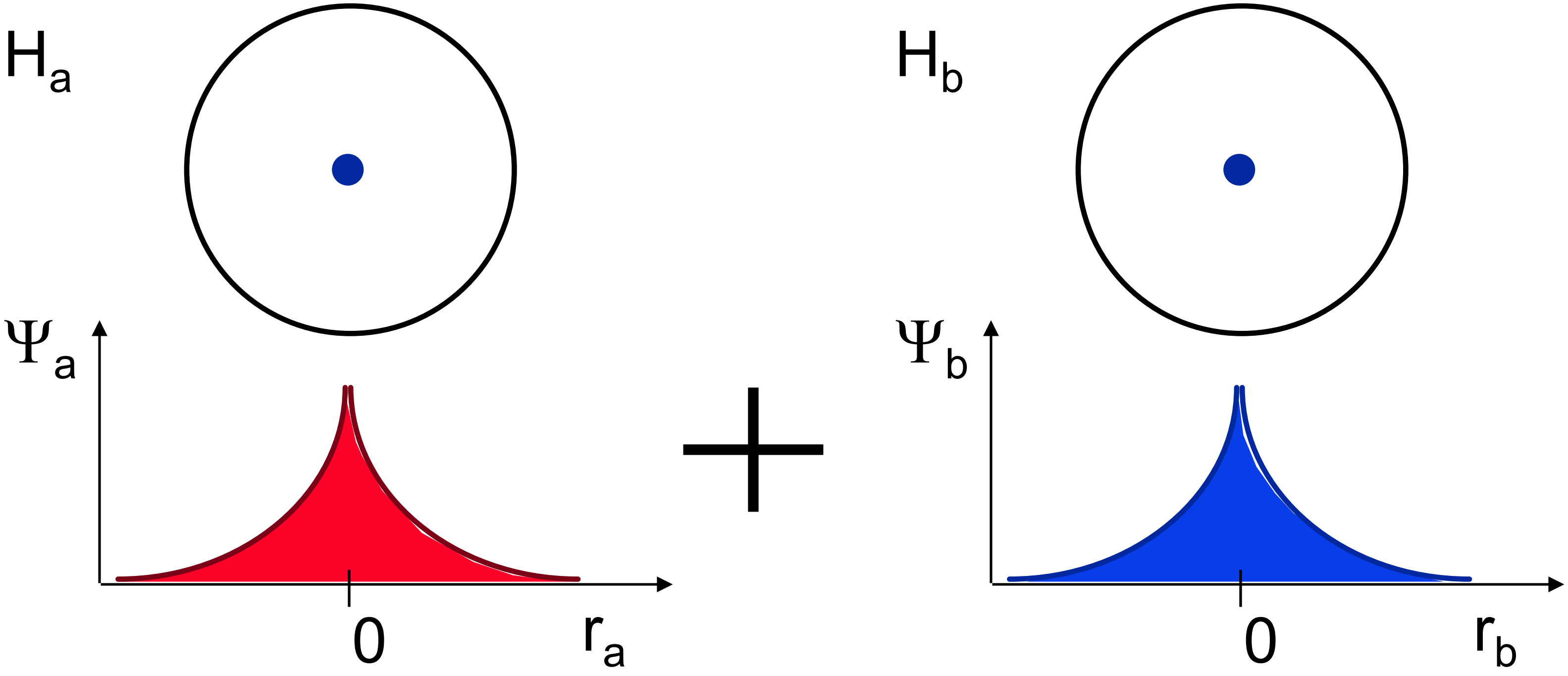


equilibrium bond distance

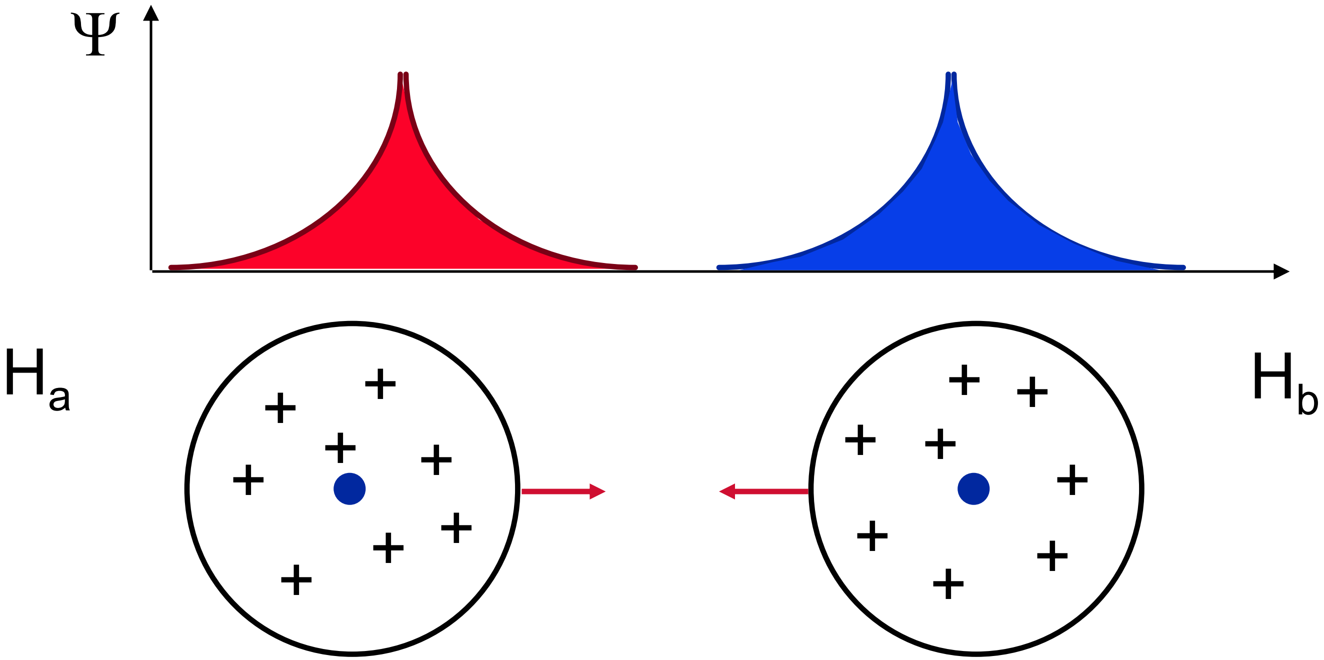
electron density in a
molecular orbital

Linear Combinations of Atomic Orbitals

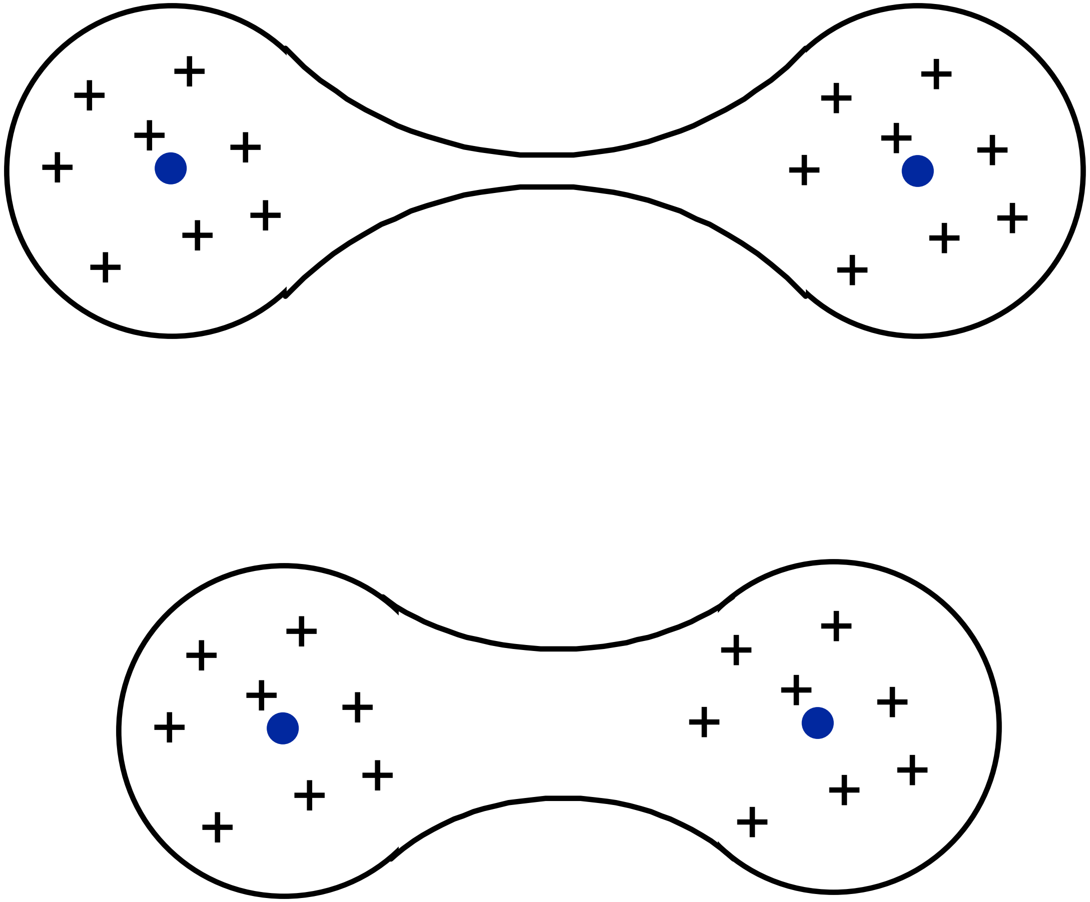
Molecular orbitals are built up from linear combinations of atomic orbitals:



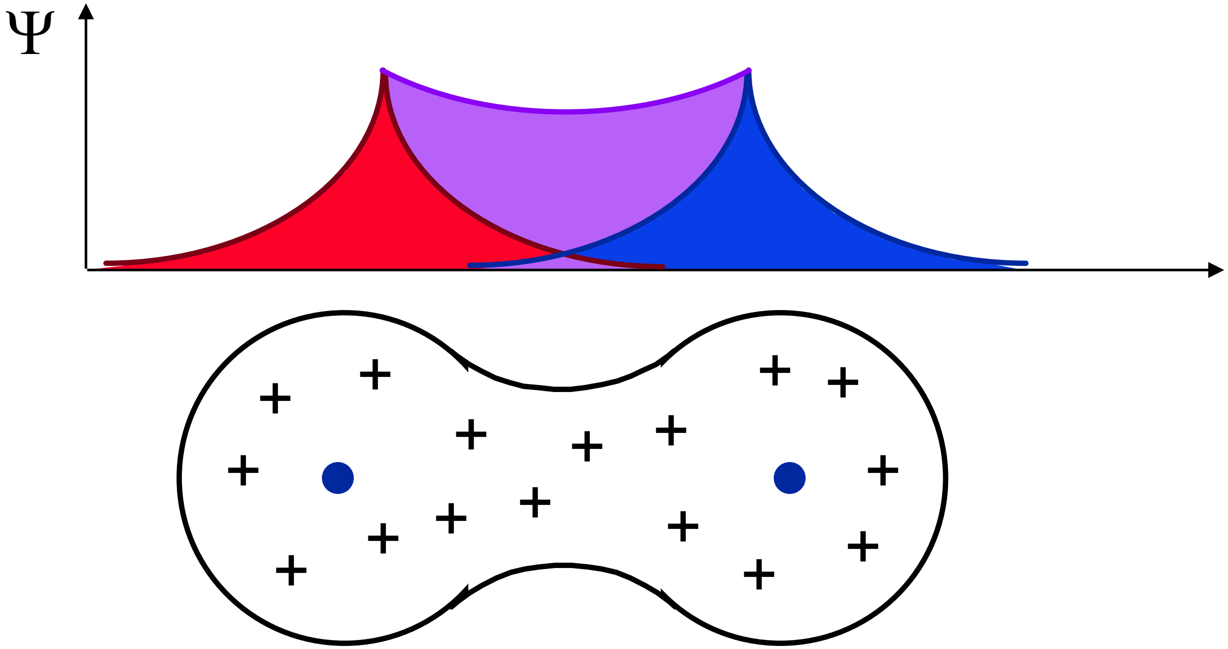
The Wavefunctions of two Separate Hydrogen Atoms



Orbitals Start to Overlap as Atoms Approach

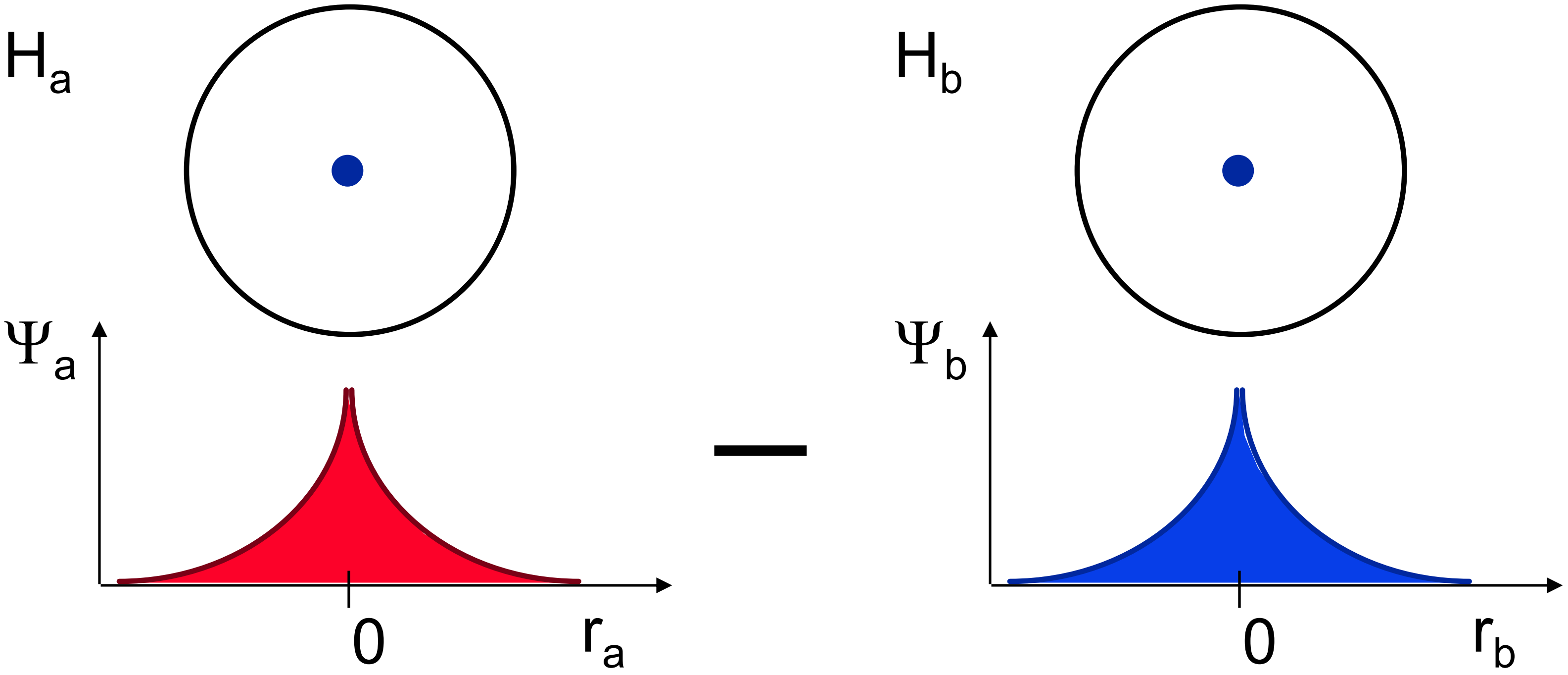


Wavefunction of H_2 Molecule in Ground State

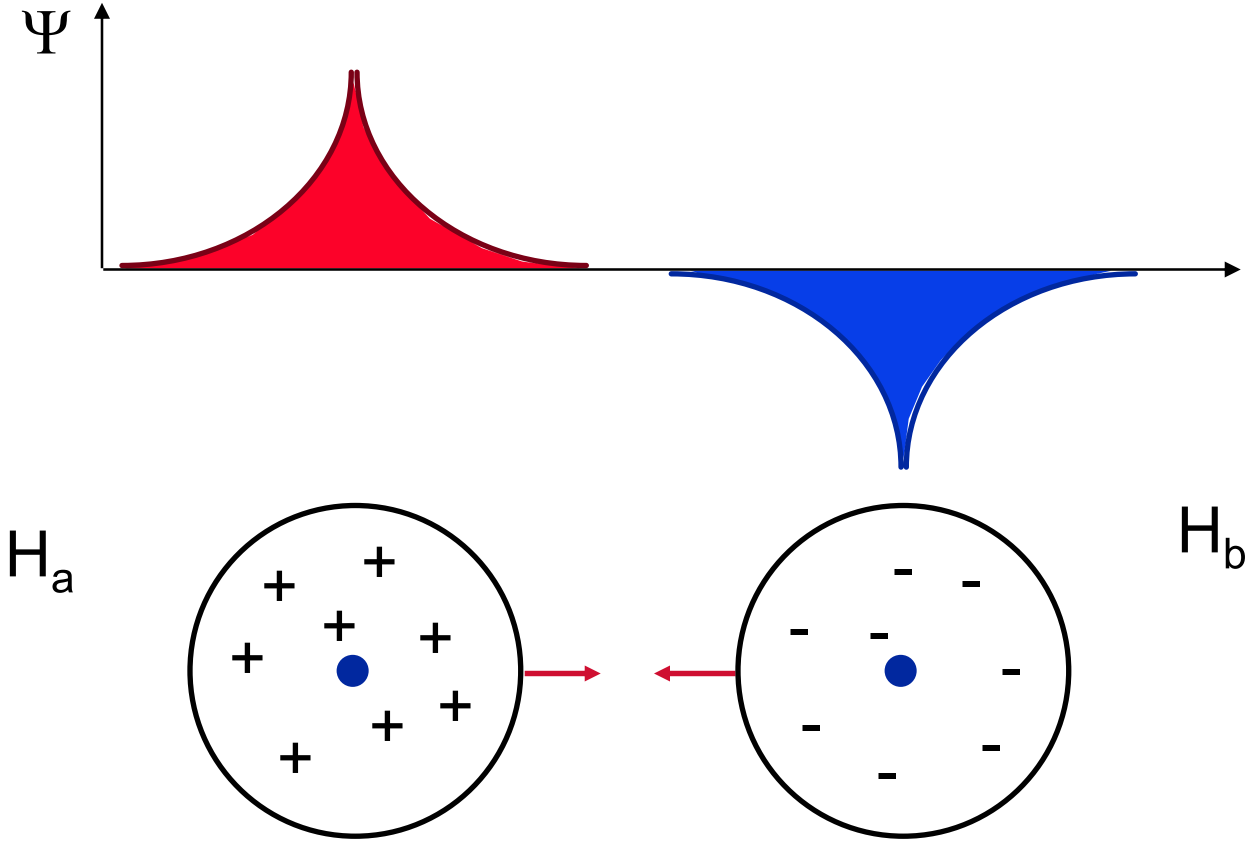


Bonding Orbital: $\Psi(1s_a + 1s_b) = 1\sigma_b$

Another Linear Combination

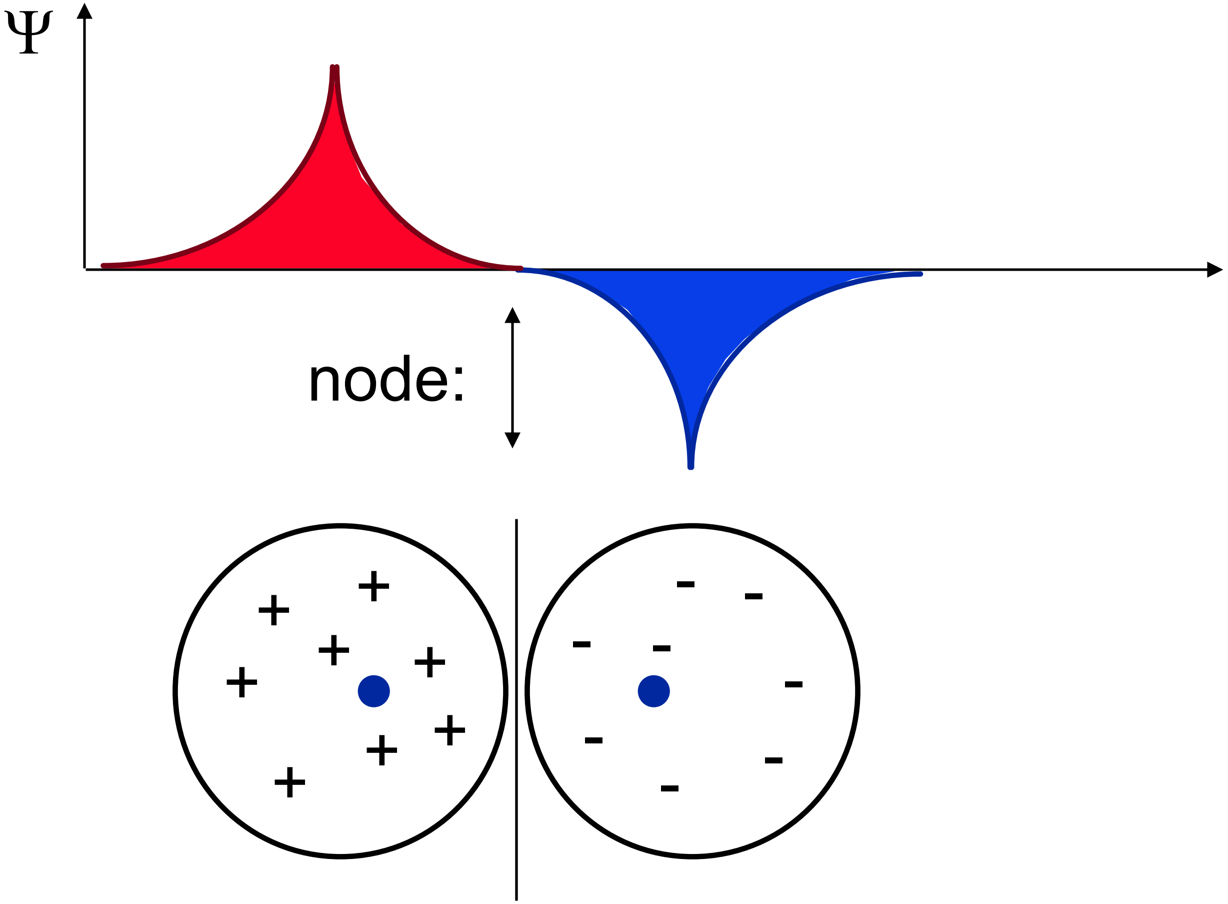


Combined Wavefunction with the Two Atoms a Distance Apart



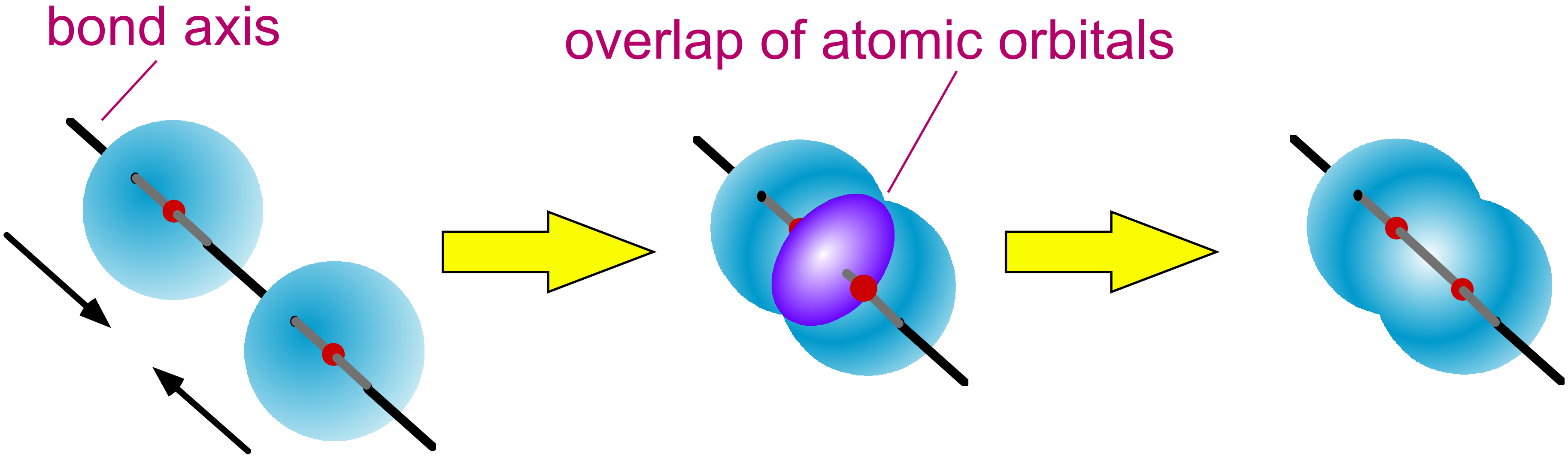
Note: Subtracting wavefunctions is the same as adding the negative of the second

Wavefunction of H_2 in Excited State



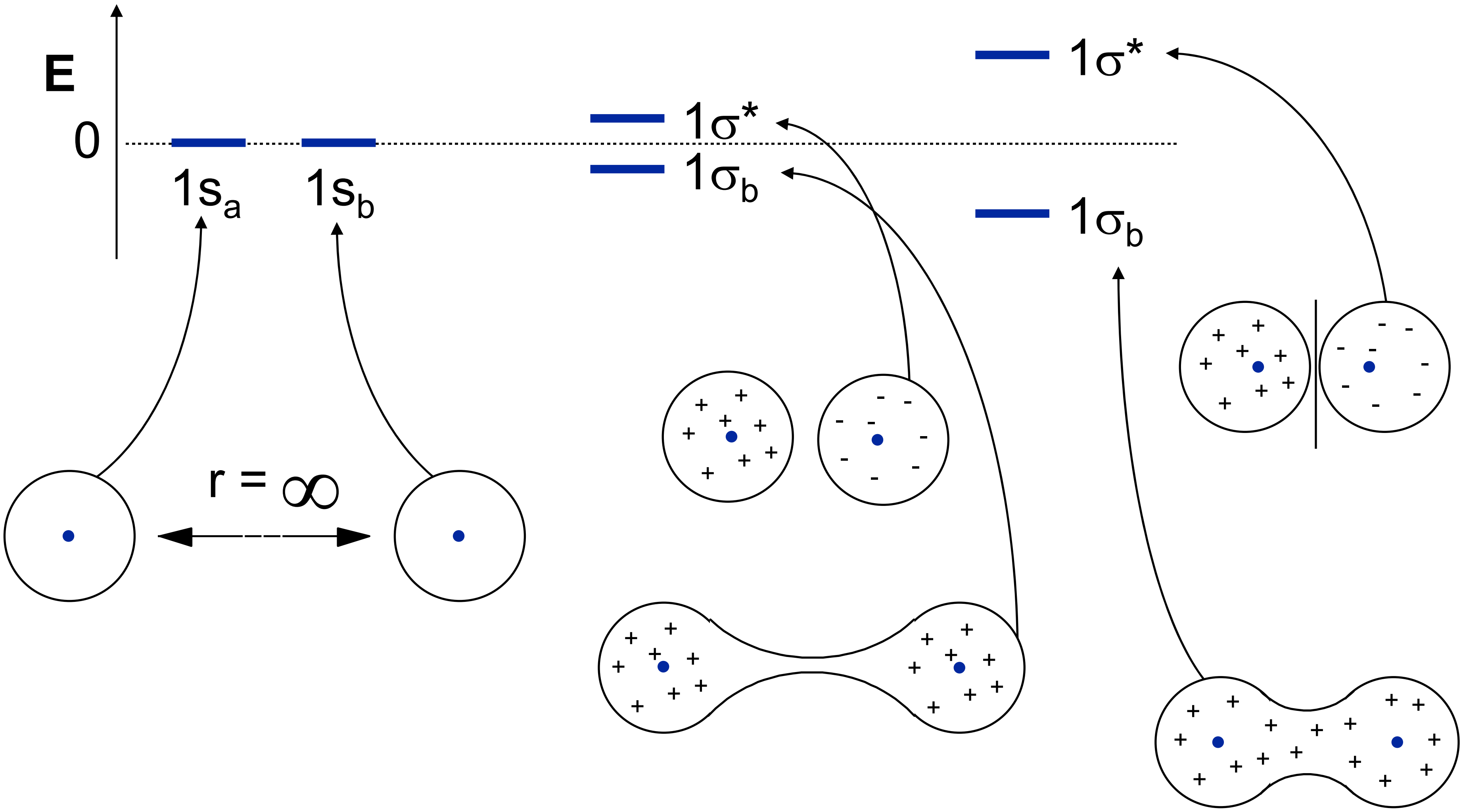
Anti-Bonding Orbital: $\Psi(1s_a - 1s_b) = 1\sigma^*$

Another Perspective on the σ_s MO

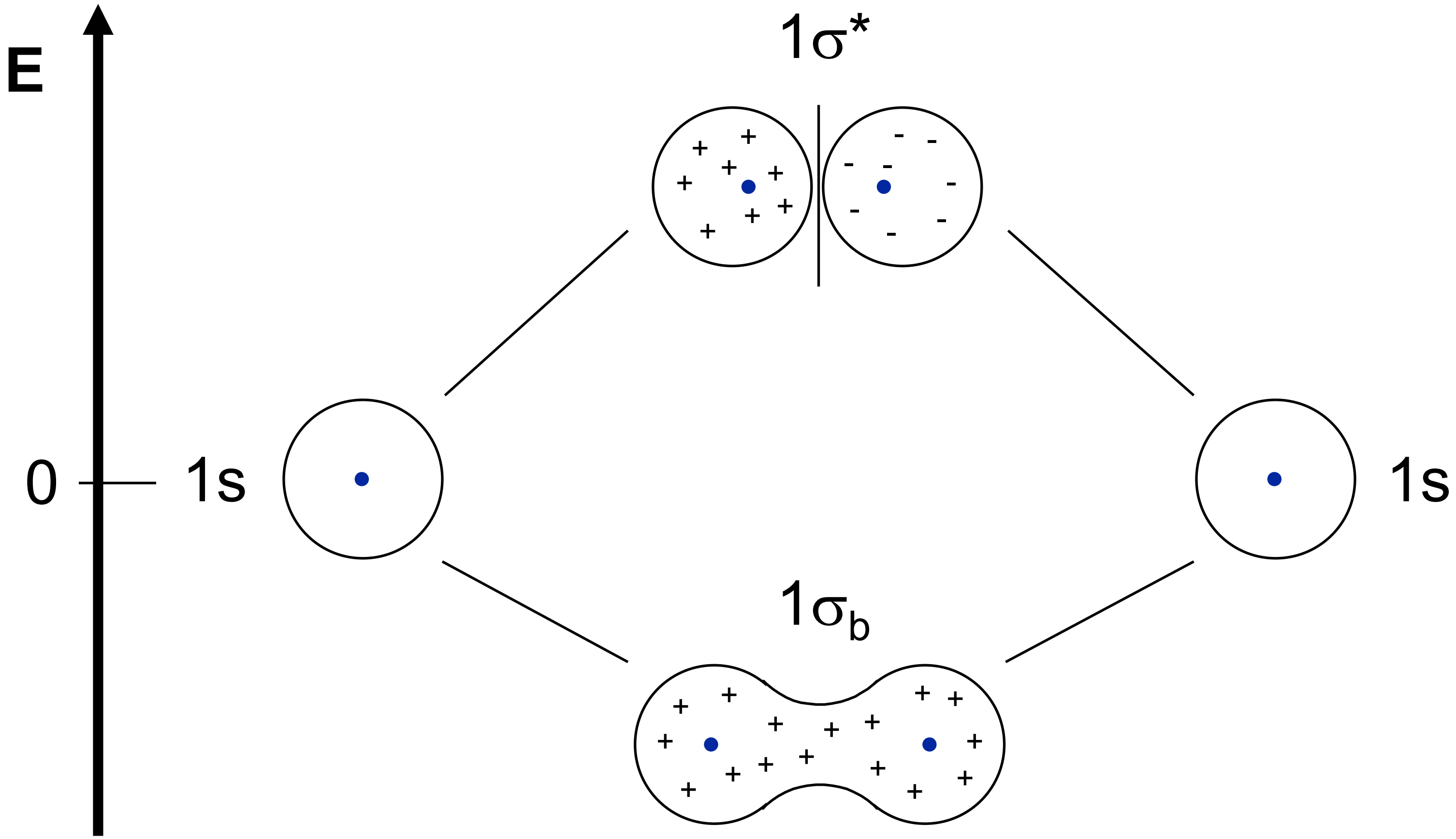


- The 1s atomic orbitals are symmetric about the bond axis.
- The overlap of the atomic orbitals is also symmetric about the bond axis.
- Therefore, the complete molecular orbital is symmetric around the bond axis.

Molecular Orbital Energy Dependence on Distance



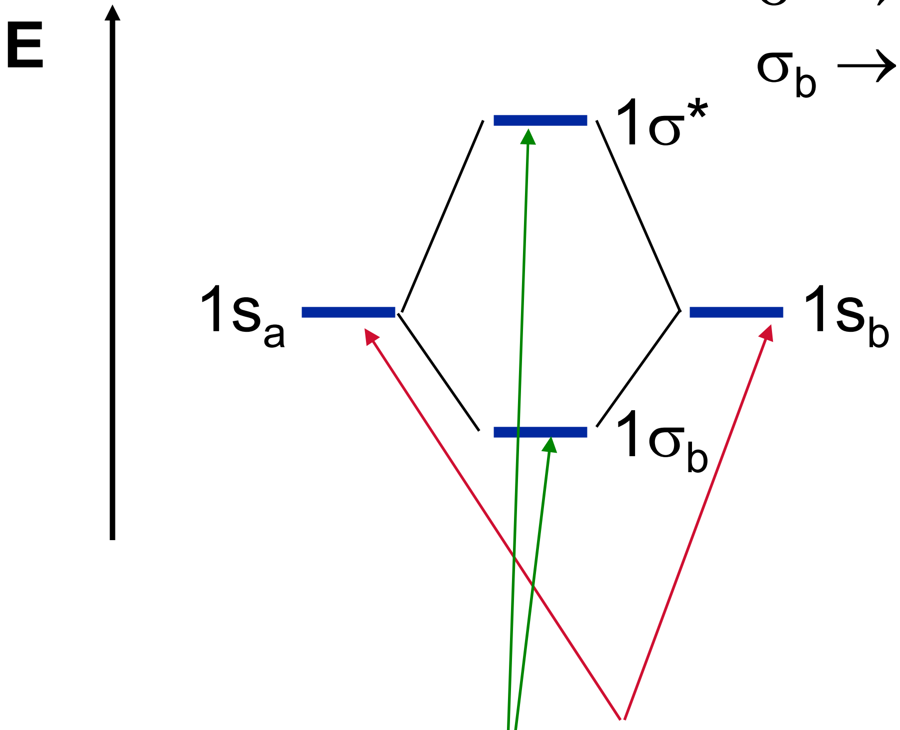
Separation of Energies



Molecular Orbital Energies

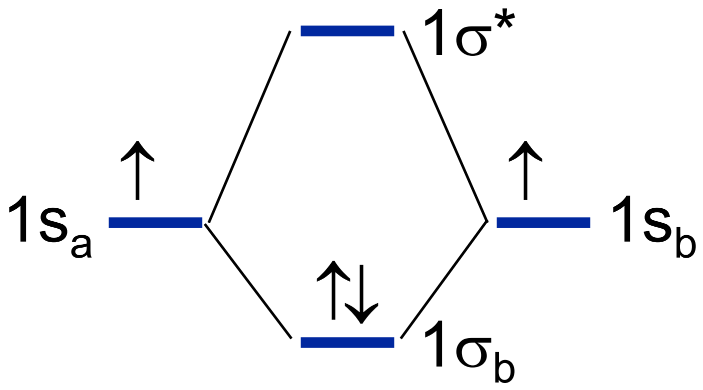
σ^* → one node (higher energy)

σ_b → no nodes (lower energy)



Note: For every atomic orbital used, you must have a molecular orbital

H_2 Energy Diagram



Since H atoms have one electron apiece, both electrons go into the $1\sigma_b$ MO – to lower the net energy

Definitions:

Bond Order $\equiv \dfrac{(\#\text{ of } e^- \text{ in } \sigma_\mathbf{b}) - (\#\text{ of } e^- \text{ in } \sigma^*)}{2}$

e.g. Bond Order for H_2 = $\dfrac{2 - 0}{2}$ = 1 => single bond

Note: Bond lengths are related to bond order:
larger bond order => shorter bond length

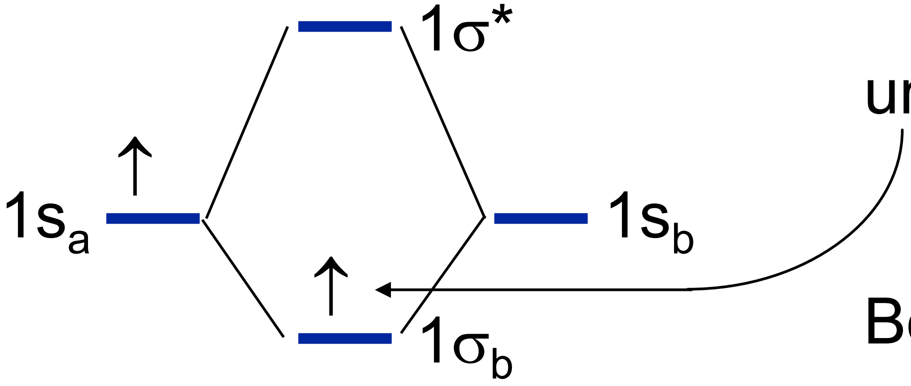
Magnetic Properties:

Paramagnetic - there are unpaired electrons

Diamagnetic - no unpaired electrons

e.g. H_2 is diamagnetic

H_2^+



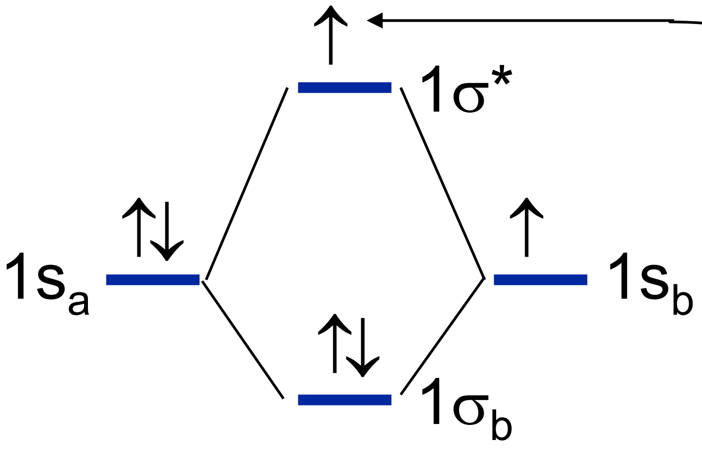
unpaired electron

=> H_2^+ is paramagnetic

$$\text{Bond order} = \frac{1 - 0}{2} = \frac{1}{2} < 1$$

=> longer bond than H_2

H_2^-



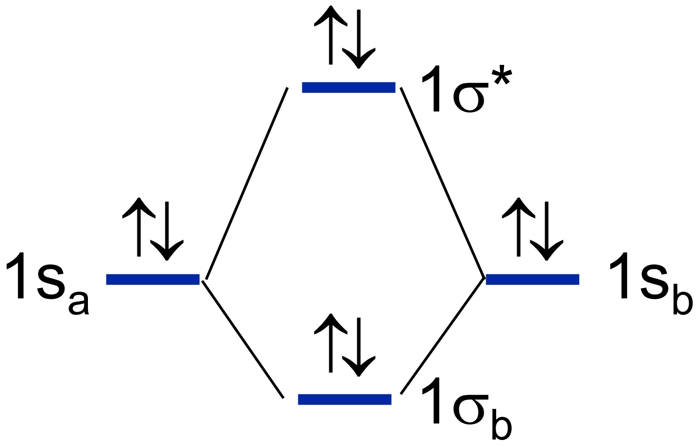
unpaired electron

=> H_2^- is paramagnetic

$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2} < 1$$

=> longer bond than H_2;
same bond length
as H_2^+

H_2^{2-} // He_2



no unpaired electrons

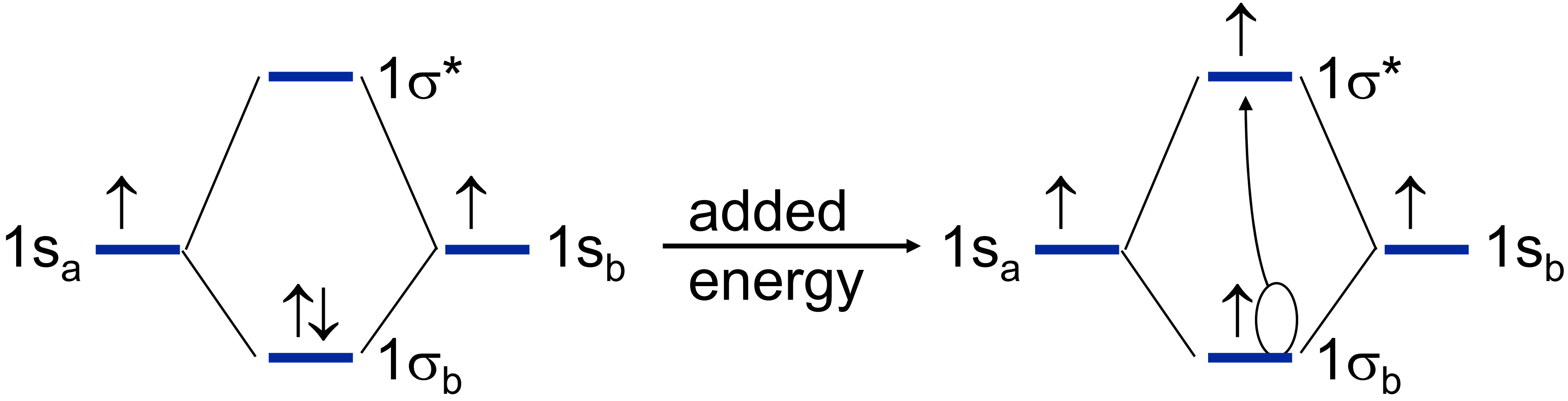
=> H_2^{2-} is diamagnetic

$$\text{Bond order} = \frac{2 - 2}{2} = 0$$

=> no bond - H_2^{2-} unstable; molecule doesn’t exist

He_2 has a MO diagram similar to H_2^{2-}; He_2 doesn’t exist either.
He_2^{2+} has a MO diagram similar to H_2; He_2^{2+} exists.

H_2 Excited State



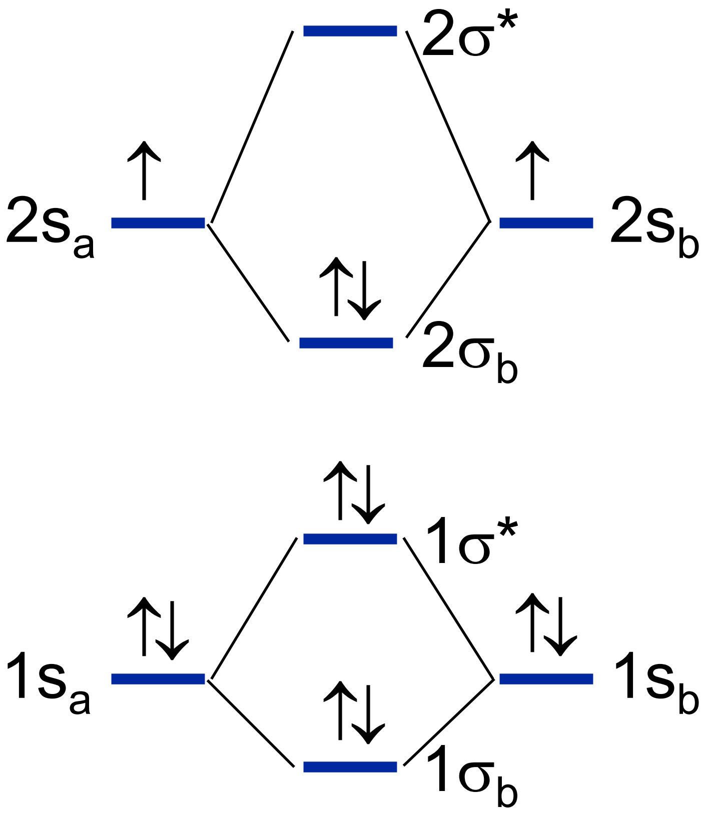
ground, B.O. = 1

excited, B.O. = 0

the bond breaks when the H_2 molecule becomes excited

Li_2

Li: $(1s)^2(2s)^1$; we must combine 2s's and 1s's



$$\text{Bond order} = \frac{4 - 2}{2} = 1$$

=> single bond

No unpaired electrons
=> diamagnetic

Notice that although $2\sigma_b$ is bonding, it is still higher in energy than $1\sigma^*$, an anti-bonding orbital.
So we fill up $1\sigma^*$ with electrons before starting on $2\sigma_b$.

Overlap Rule

The closer the atoms are, the more the orbitals overlap, the bigger the splitting between the bonding and the anti-bonding orbitals, and the shorter the bond length.

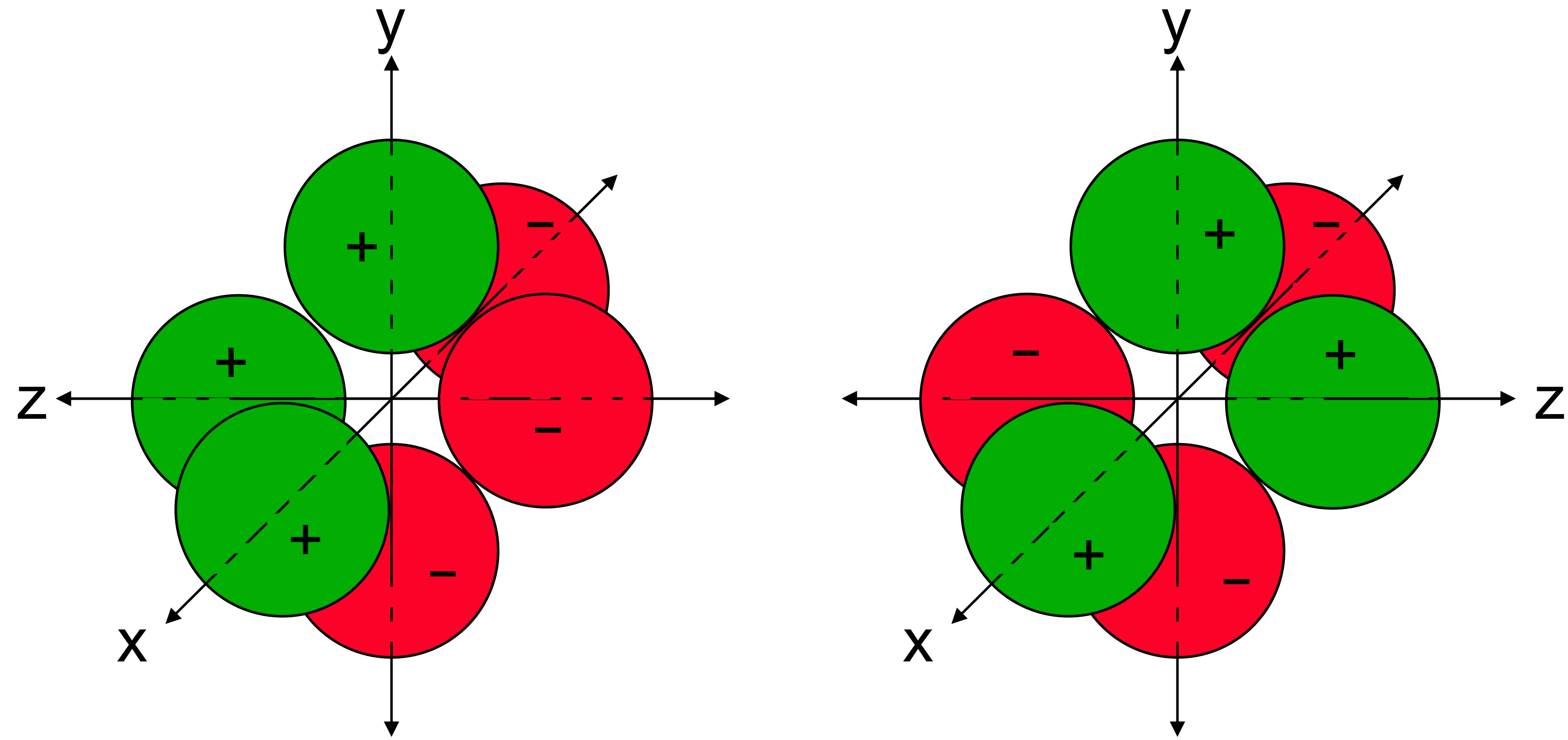
e.g. for H_2 vs Li_2: 2s doesn’t overlap as well as 1s and since Li’s are bonded with 2s orbitals, H_2 has the shorter bond.

Energy Condition:

Different orbitals of **similar** energies will also split into bonding and anti-bonding orbitals.

e.g. HF: 1s of H is very close in energy to the 2p orbital in F. They bond well.

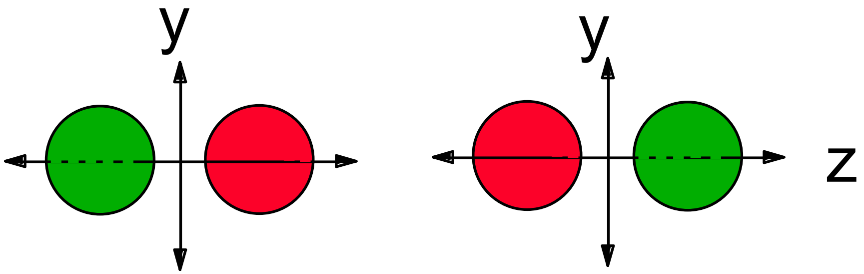
P orbitals

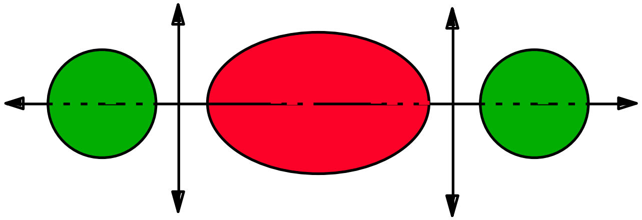


How are P orbitals added?

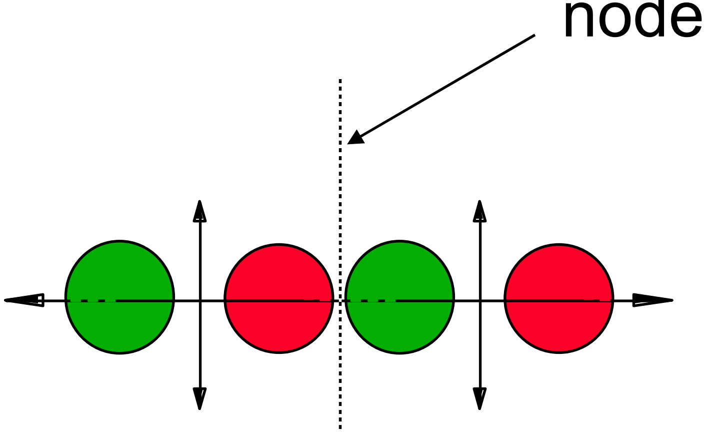
The Z Axis

The z-axis is defined as the **internuclear axis**; p_z’s are combined differently from p_x’s and p_y’s.





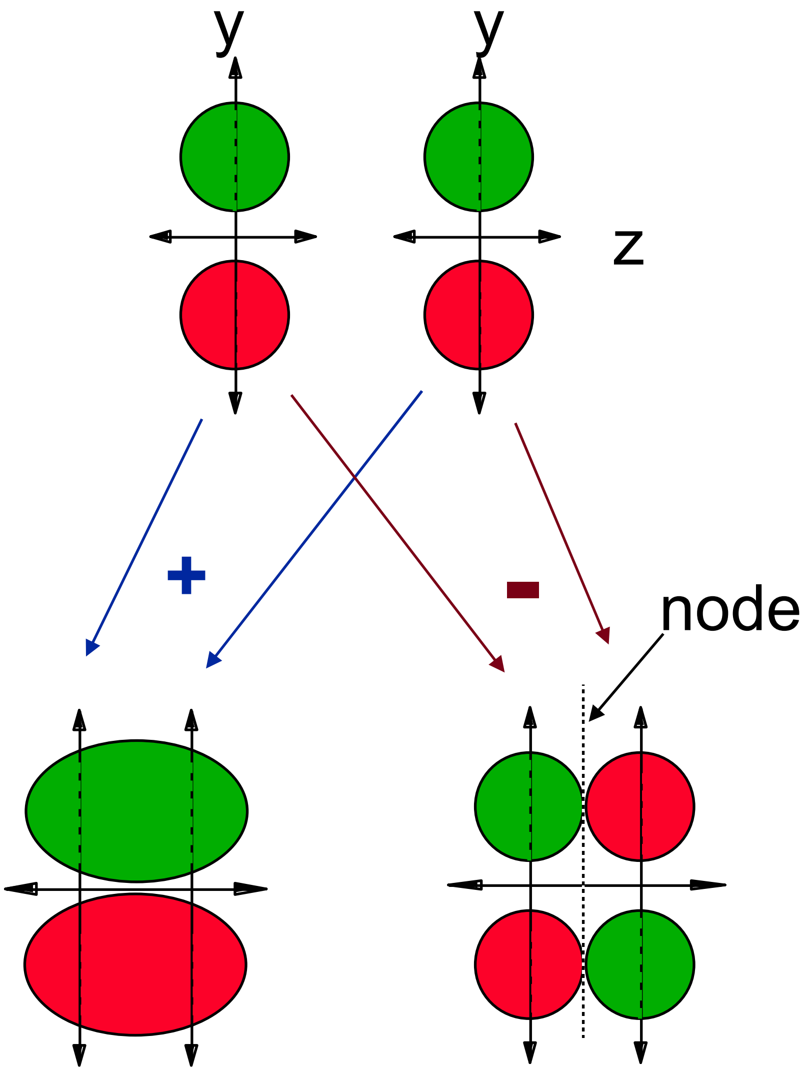
bonding (2p σ_b)



anti-bonding (2p σ^*)

These MO’s are called σ **orbitals**: the sign doesn’t change as you rotate the orbitals about the internuclear axis.

The X and Y Axes



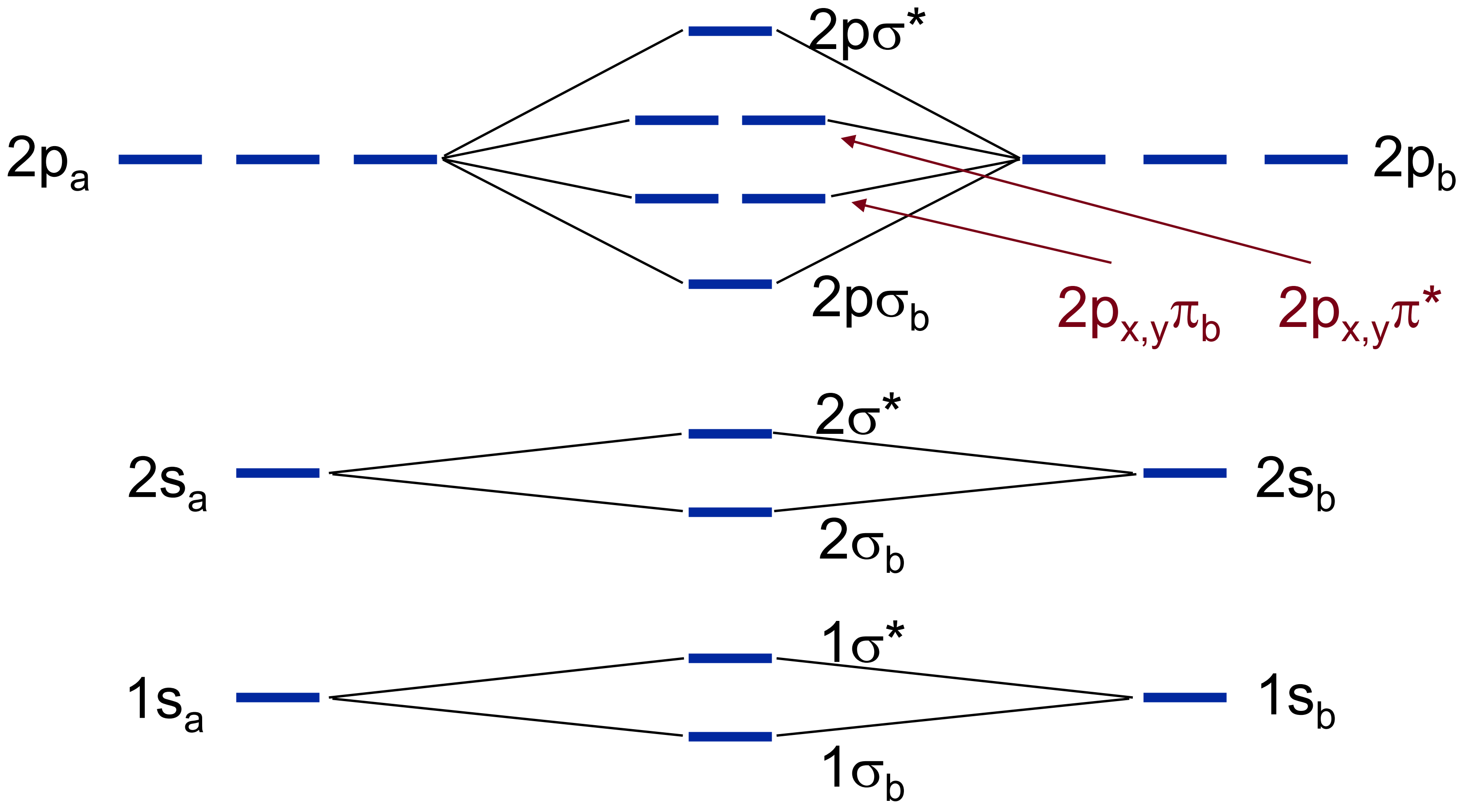
bonding
($2p_y\pi_b$)

anti-bonding
($2p_y\pi^*$)

These m.o.'s are called **π orbitals**: the sign changes as you rotate the orbitals around the internuclear axis. (i.e. they are not symmetrical about the z-axis)

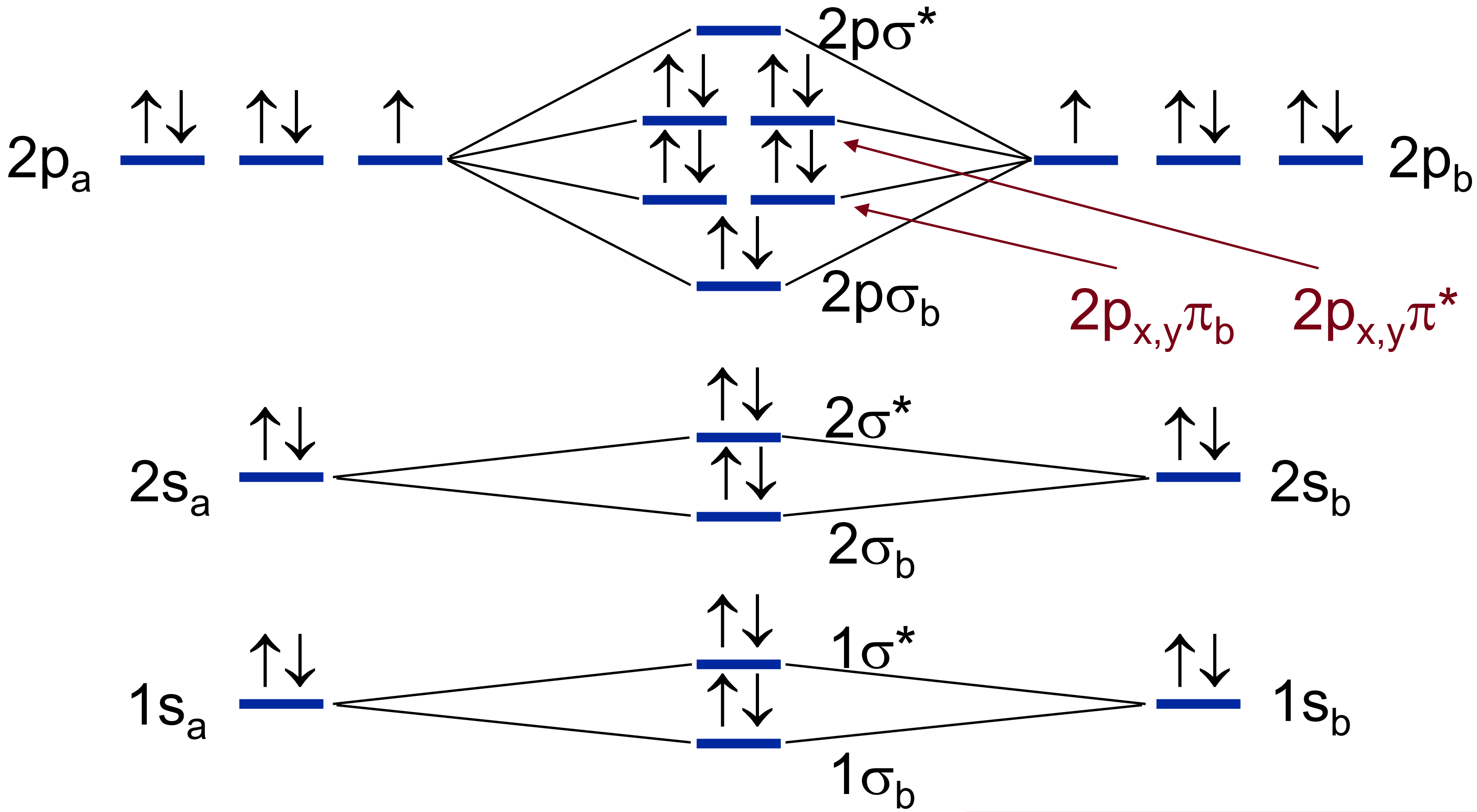
p_x behaves exactly as p_y.

Energy diagram with π MO's



F_2

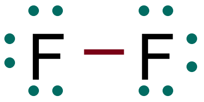
Each F has 9 electrons:



$$\text{B.O.} = \frac{10 - 8}{2} = 1$$

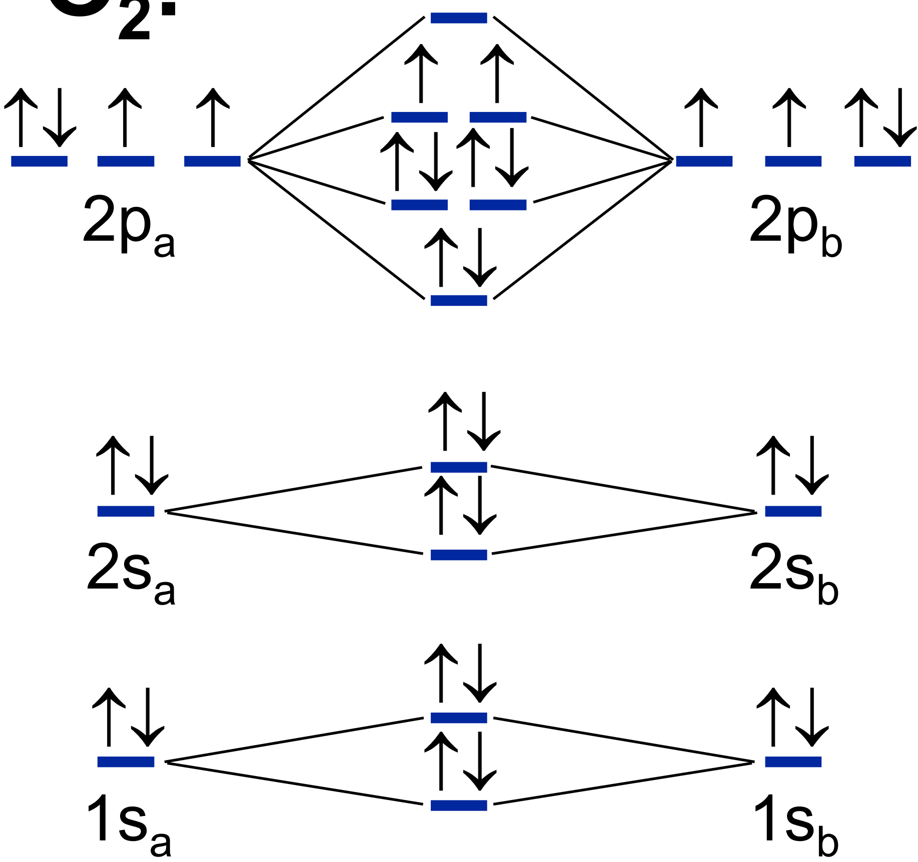
Predict single bond
and diamagnetic

Agrees with



Homonuclear problem: Compare O_2, O_2^{2+}, O_2^{+}, O_2^{-}, and O_2^{2-}

O_2:



O_2: 16 e$^-$, B.O.$= \frac{10 - 6}{2} = 2$ (double bond)

2 unpaired electrons (paramagnetic)

O_2^{2+}: 14 e$^-$, B.O.$= \frac{10 - 4}{2} = 3$ (triple bond)

0 unpaired electrons (diamagnetic)

O_2^{+}: 15 e$^-$, B.O.$= \frac{10 - 5}{2} = 2.5$

1 unpaired electron (paramagnetic)

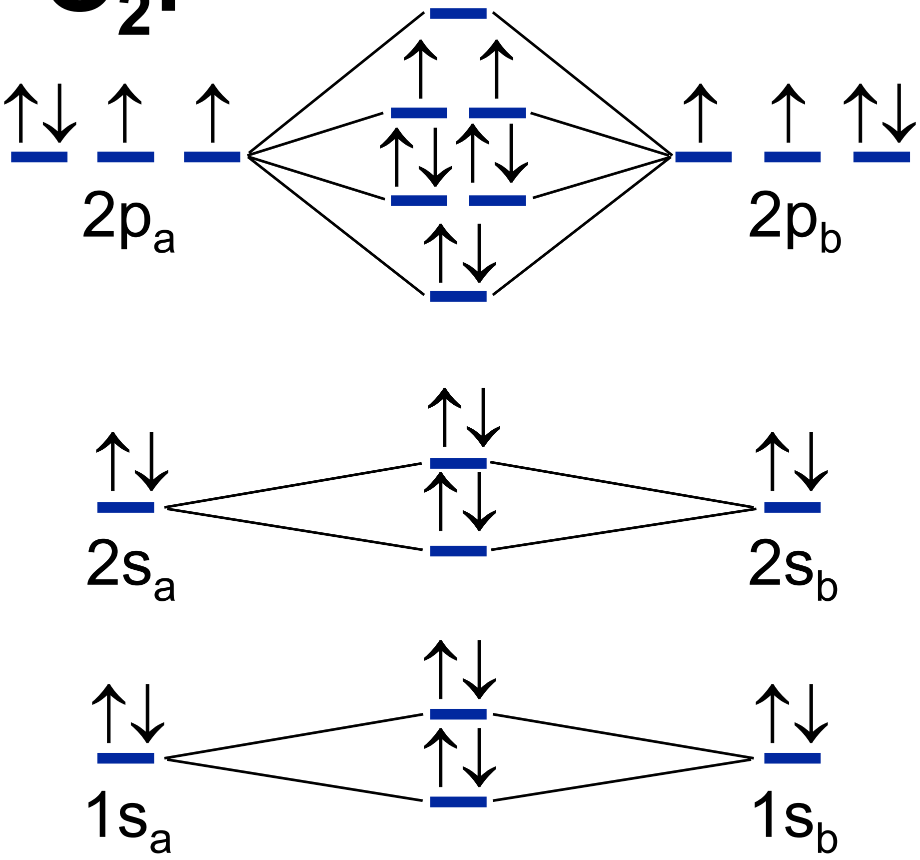
O_2^{-}: 17 e$^-$, B.O.$= \frac{10 - 7}{2} = 1.5$

1 unpaired electron (paramagnetic)

Homonuclear problem:

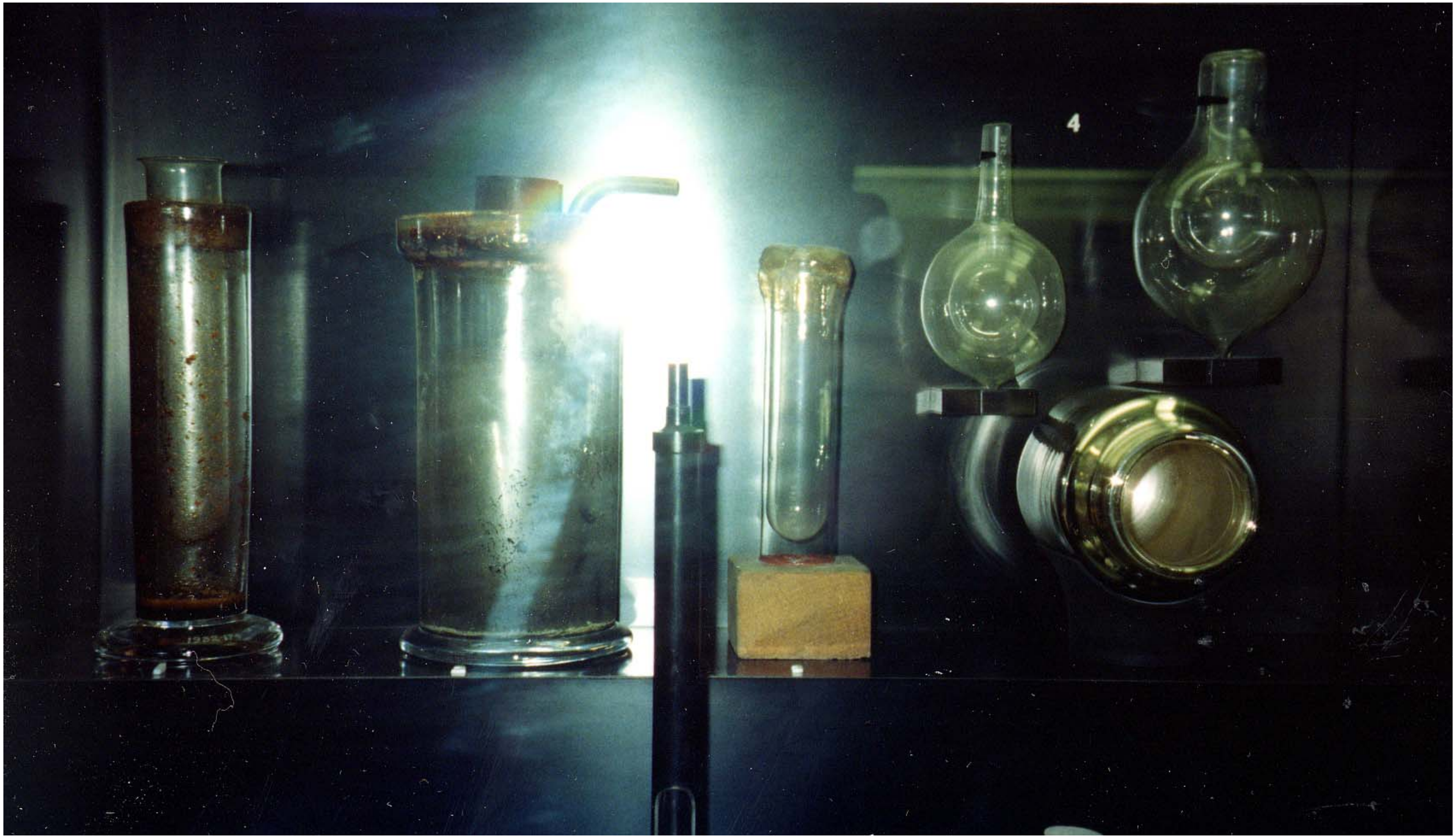
Compare O_2, O_2^{2+}, O_2^{+}, O_2^{-}, and O_2^{2-}

O_2:



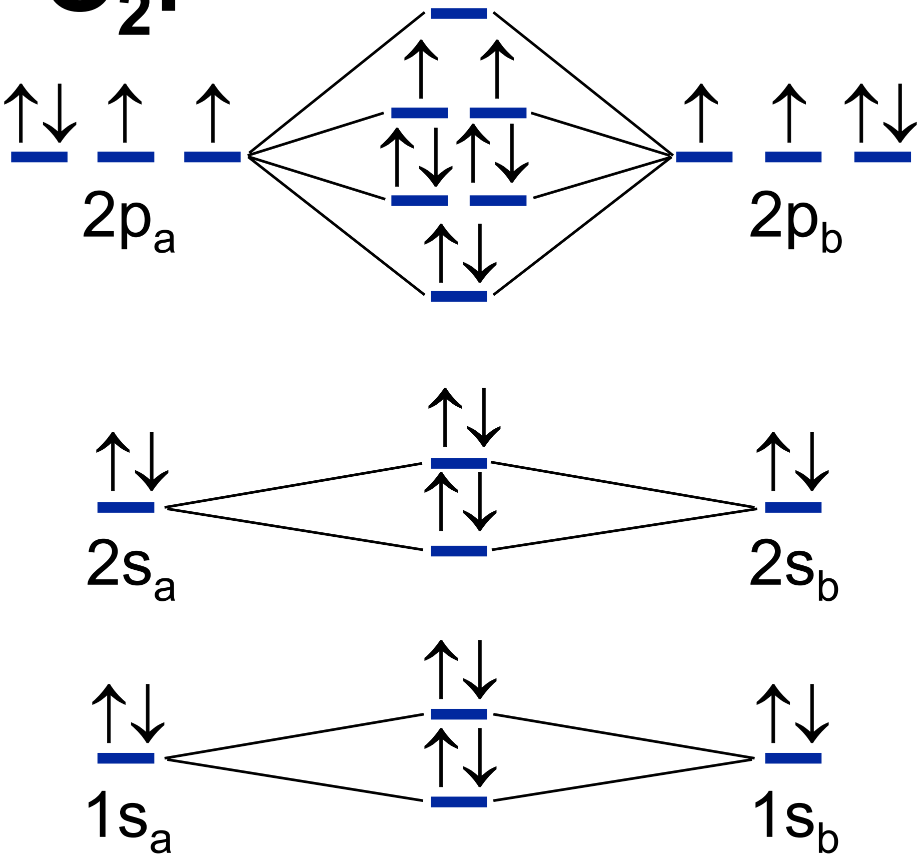
QuickTime™ and a Sorenson Video decompressor are needed to see this picture.

Sir Dewar’s Original “Dewars”



Homonuclear problem: Compare O_2, O_2^{2+}, O_2^{+}, O_2^{-}, and O_2^{2-}

O_2:



O_2: 16 e^-, B.O.= $\frac{10 - 6}{2}$ = 2 (double bond)

2 unpaired electrons (paramagnetic)

O_2^{2+}: 14 e^-, B.O.= $\frac{10 - 4}{2}$ = 3 (triple bond)

0 unpaired electrons (diamagnetic)

O_2^{+}: 15 e^-, B.O.= $\frac{10 - 5}{2}$ = 2.5

1 unpaired electron (paramagnetic)

O_2^{-}: 17 e^-, B.O.= $\frac{10 - 7}{2}$ = 1.5

1 unpaired electron (paramagnetic)

O_2^{2-}: 18 e^-, B.O.= $\frac{10 - 8}{2}$ =1 (single bond)

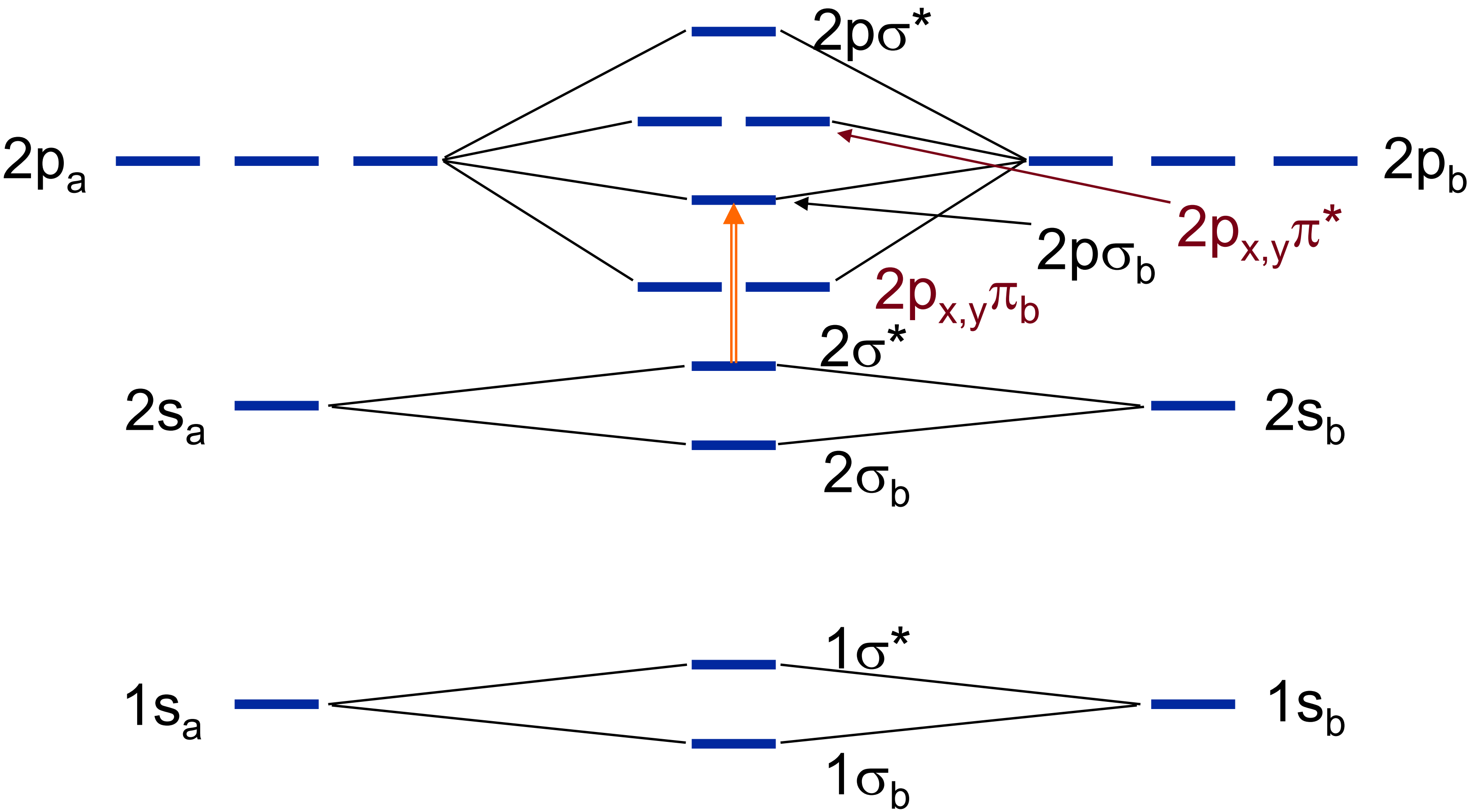
0 unpaired electrons (diamagnetic)

Bond Lengths (depend on B.O.):

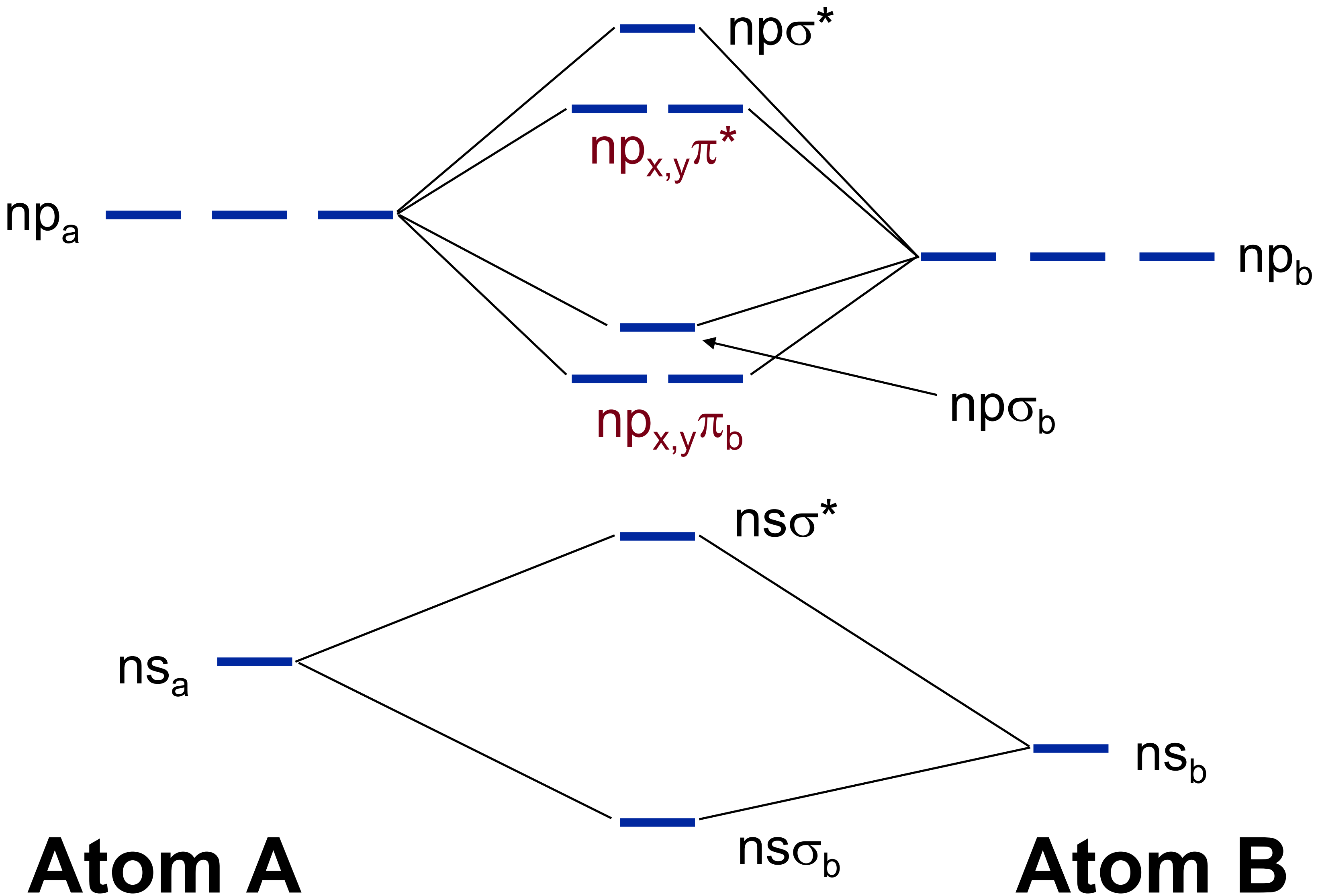
$O_2^{2+} < O_2^{+} < O_2 < O_2^{-} < O_2^{2-}$

Actually, O_2 and F_2 are exceptions.

For all molecules except those including O_2, Cl_2, S_2, and F_2, and other diatomics with atoms both in those two columns, the $2p\sigma_b$ and $2p\pi_b$ are flipped. The $2s\sigma^*$ push up on the $2p\sigma_b$ and cause them to be at a higher energy level than the $2p\pi_b$.



A Heteronuclear Diatomic MO



Atom A

(less electronegative)

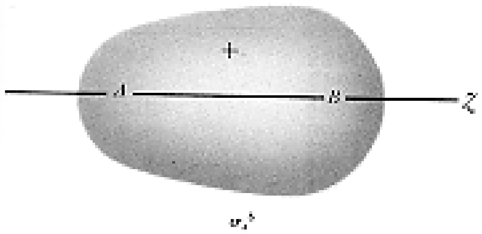
AB

Atom B

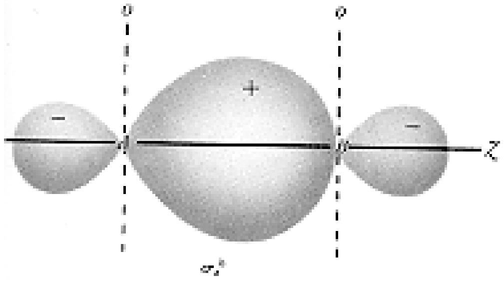
(more electronegative)

Heteronuclear A–B MO Pictures

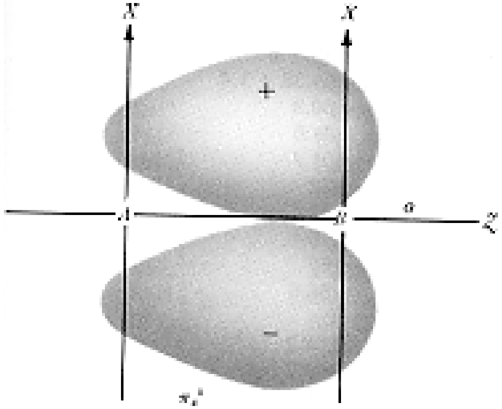
σ_{sb}



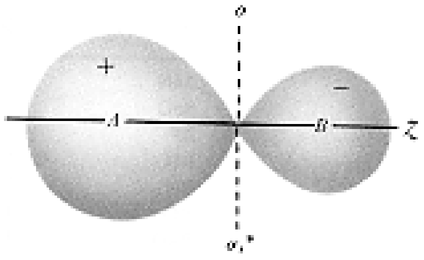
σ_{zb}



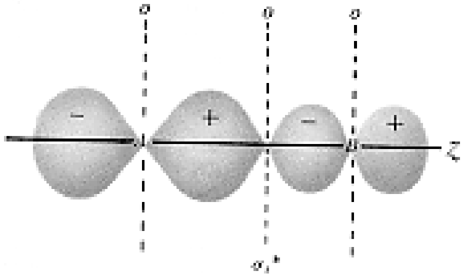
π_{xb}



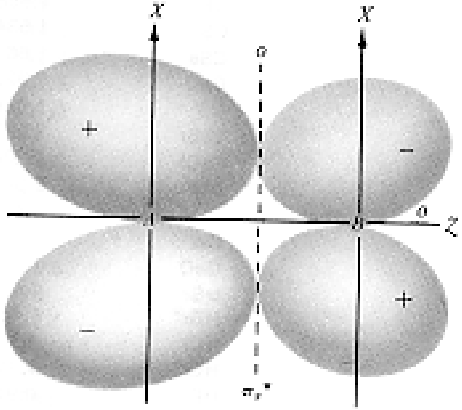
σ_s^*



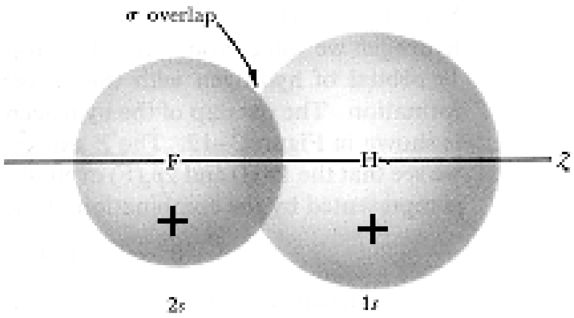
σ_z^*



π_x^*

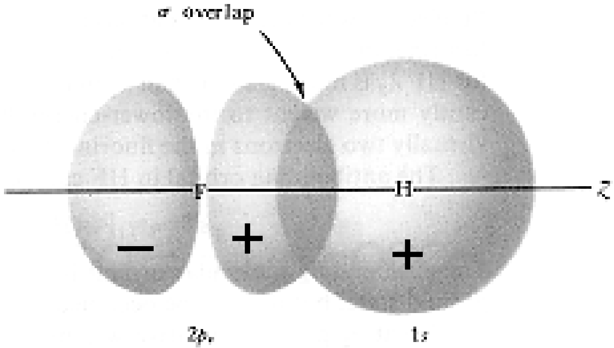


Atomic Orbital Overlap in HF

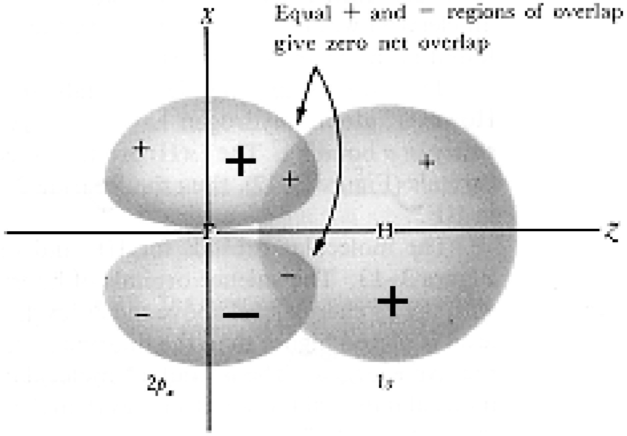


F 2s H 1s

σ overlap



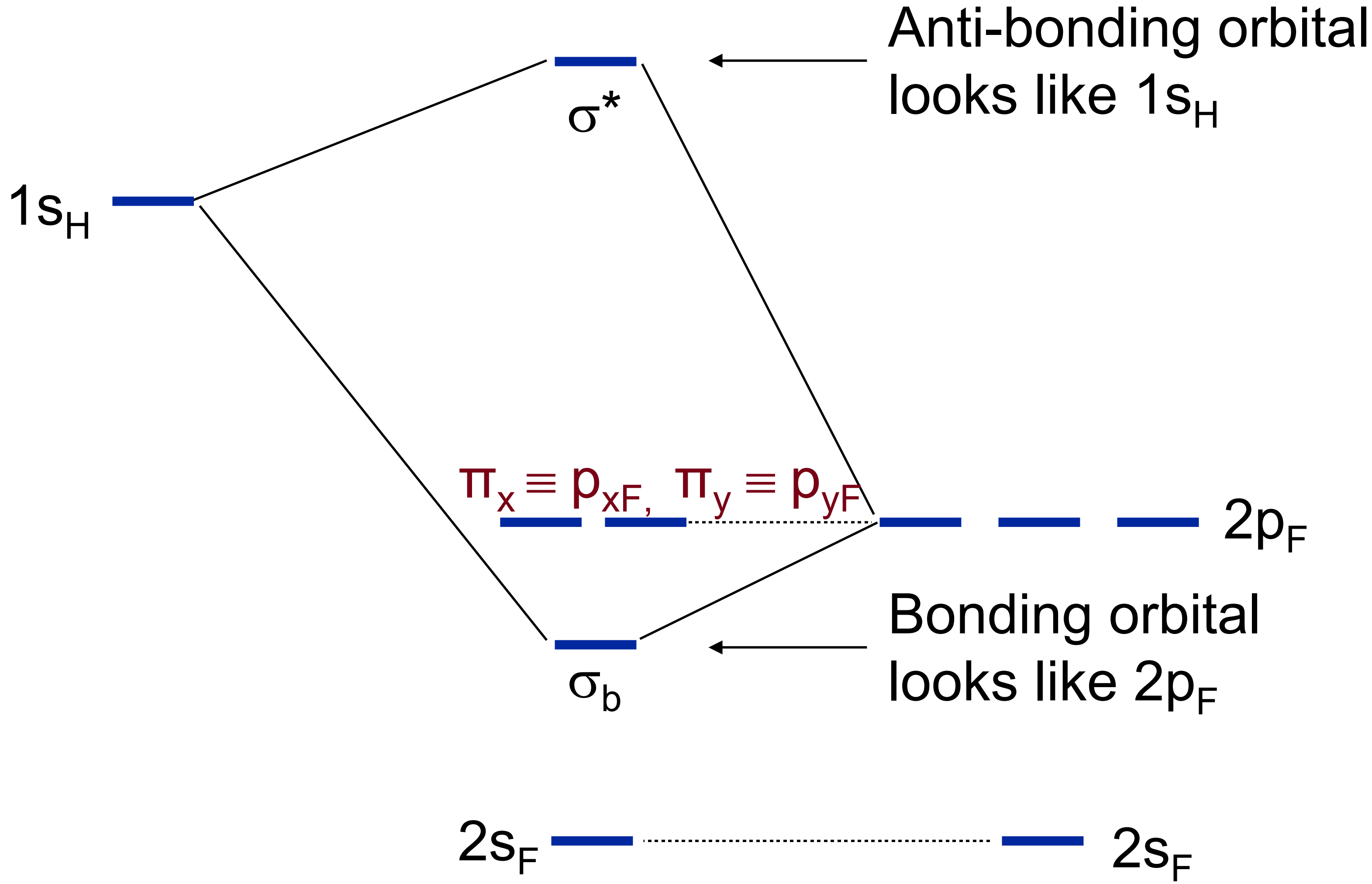
F $2p_z$ H 1s



F $2p_z$ H 1s

No net overlap: Non-Bonding!

MO Diagram for HF



σ^*

Anti-bonding orbital
looks like $1s_H$

$1s_H$

$\pi_x \equiv p_{xF},\ \pi_y \equiv p_{yF}$

$2p_F$

Bonding orbital
looks like $2p_F$

σ_b

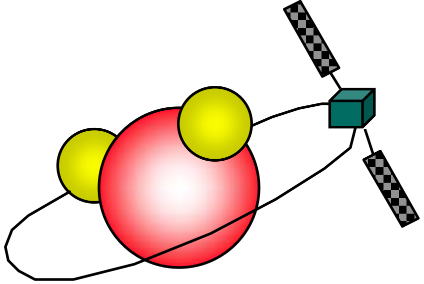
$2s_F$

$2s_F$

Hydrogen
(less electronegative)

HF

Fluorine
(more electronegative)



END

Molecular Orbital Theory

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OGN: (16.1) and (16.3)