Chemical Bonding

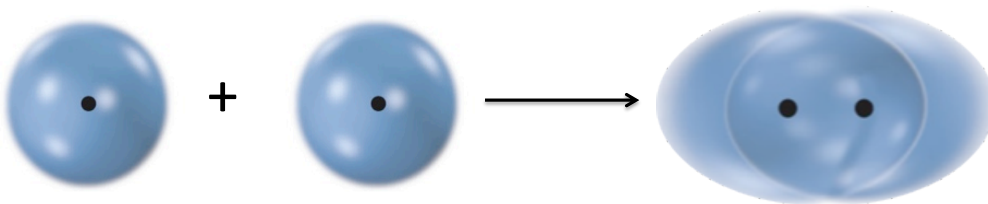
Why do atoms form molecules???

Chemical Bonding

We will examine this first using the simplest molecule: **H_2**

$H + H \rightarrow H_2$

Why is the H_2 molecule more stable than 2 separate H atoms?



Answer comes from Quantum Mechanics!

Chemical Bonding in H_2

We will examine this first using the simplest molecule: **H_2**

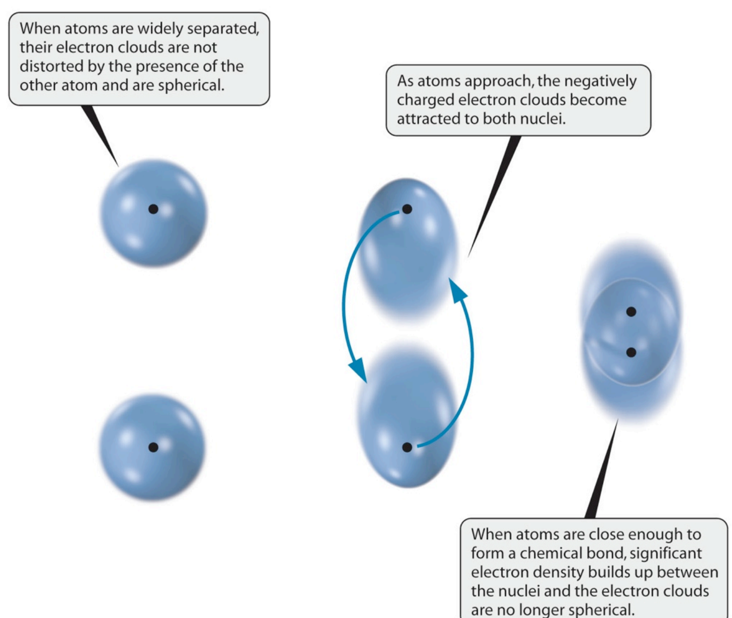
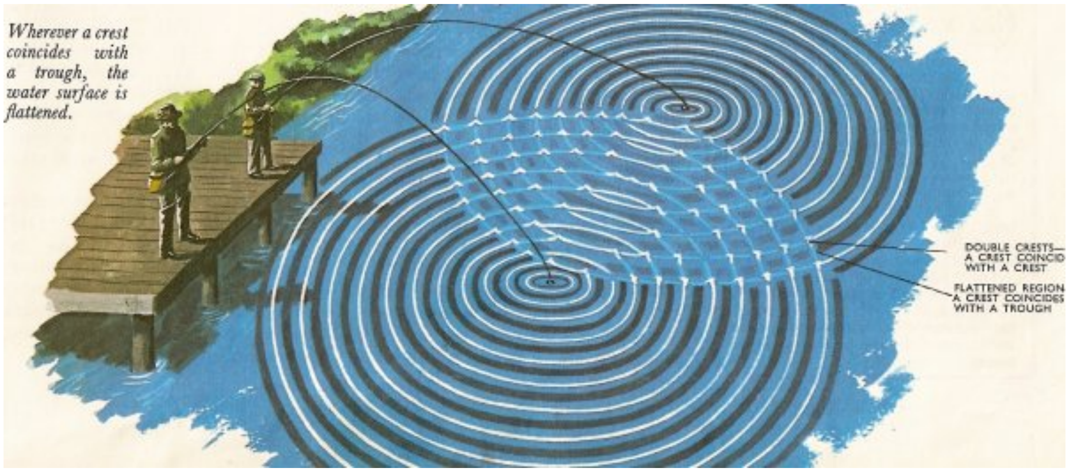


Fig. 7.4;
see 7.12 & 7.13

How do we think about bonding between atoms?

What happens when waves (orbitals) combine?

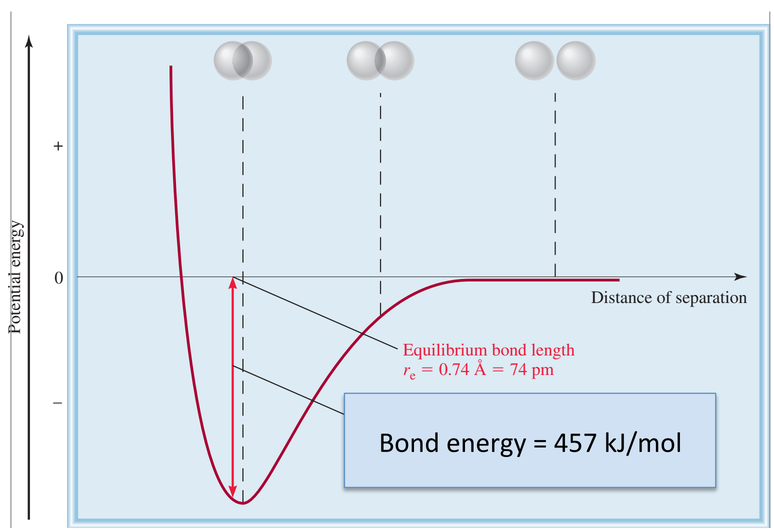


http://www.daviddarling.info/encyclopedia/I/interference.html

in combining waves we have to consider *constructive* and *destructive interference*

Chemical bonding in H_2

Let's examine the energy of interaction between two H atoms as the bond is formed

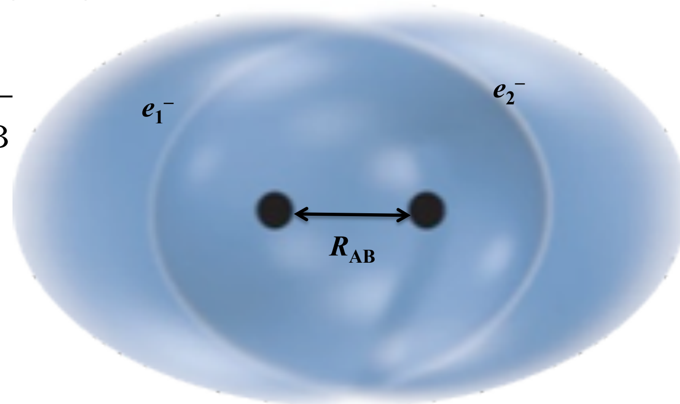


(Similar to Figs. 7.3 & 7.4)

What holds H_2 together

$$V^{\text{nuclear}}_{\text{repulsion}} = \frac{e^2}{4\pi\epsilon_0 R_{\text{AB}}}$$

$$V^{\text{electron}}_{\text{repulsion}} = \frac{e^2}{4\pi\epsilon_0 R_{\text{ee}}}$$



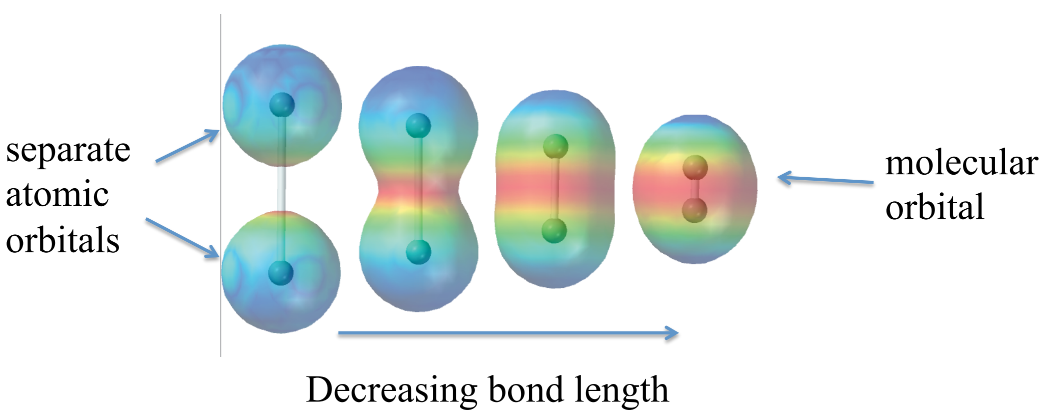
$$V_{\text{attraction}} = V_{e_1\text{A}} + V_{e_1\text{B}} + V_{e_1\text{A}} + V_{e_1\text{A}}$$

$$\boxed{\text{Energy} = V^{\text{nuclear}}_{\text{repulsion}} + V^{\text{electron}}_{\text{repulsion}} + V_{\text{attraction}} + \text{electron KE}}$$

When the orbitals overlap, they merge to form a *molecular orbital* and each electron can access the entire MO – decreasing its kinetic energy

(Similar to Figs. 7.3 & 7.4)

What holds H_2 together

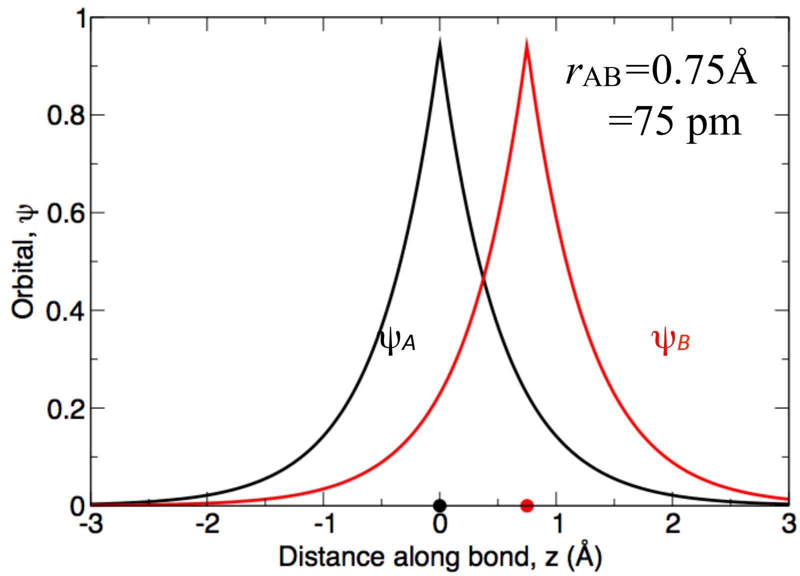


When the orbitals overlap, they merge to form a *molecular orbital* and each electron can access the entire MO

Bonding Molecular Orbitals H_2

To form the bonding molecular orbital – the atomic orbitals are added constructively

(Fig. 7.4)

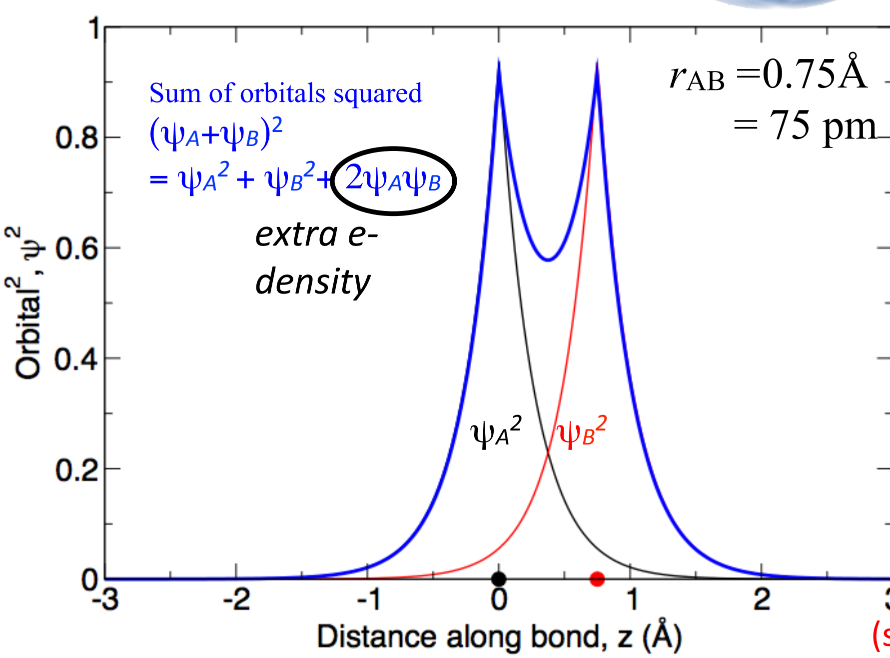


(see Fig. 7.13)

Bonding Molecular Orbitals H_2

To get the electron probability density we need to square the MO wavefunction

(Fig. 7.4)

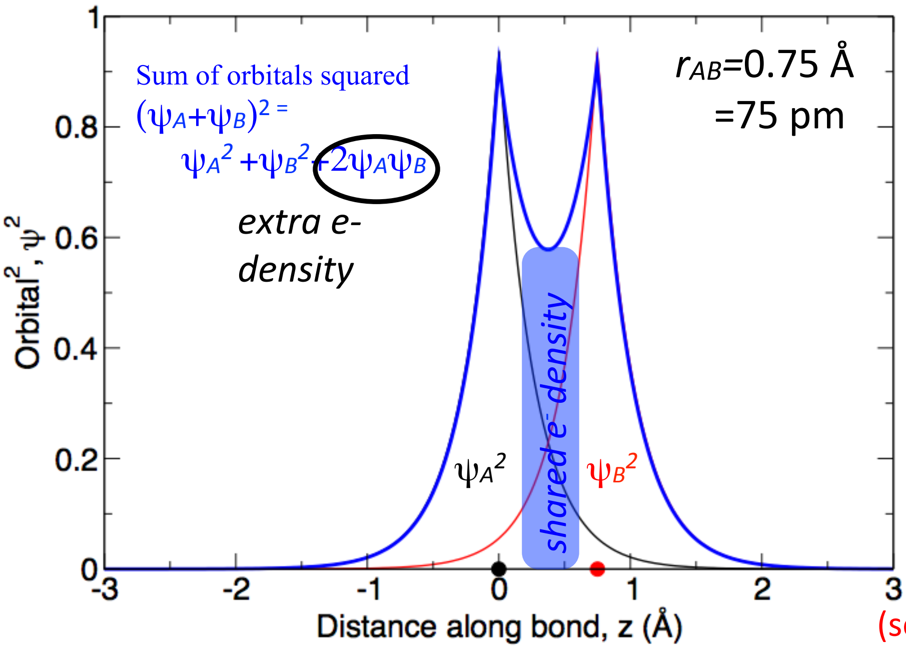


(see Fig. 7.13)

Covalent Bonding in H_2

A bond formed by electron sharing in an MO is called a *covalent bond*

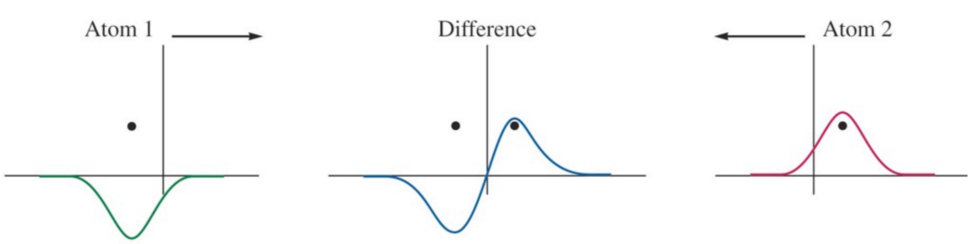
(Fig. 7.4)



(see Fig. 7.13)

What about *destructive* interference

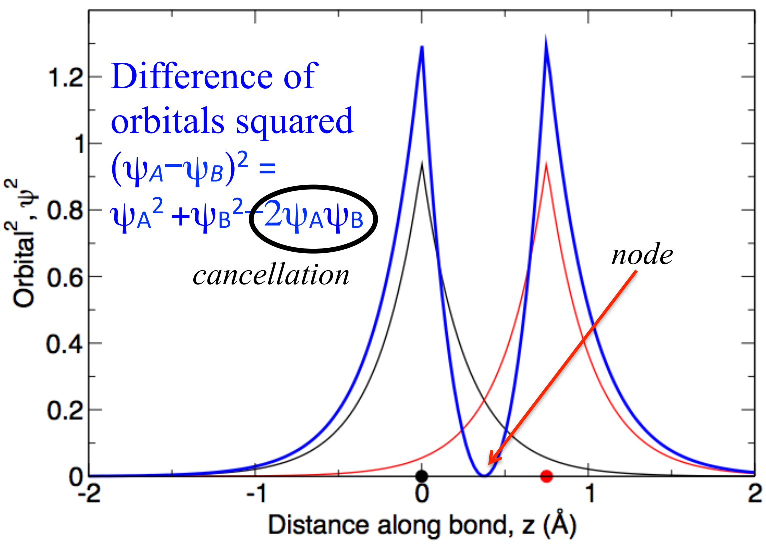
The bonding MO was formed by adding together H atom wavefunctions (orbitals) constructively. We can also add them *destructively* to form another type of MO



Destructive interference of two waves gives a node between the nuclei.

An MO with a node between the two atoms is called an *"anti-bonding" orbital*

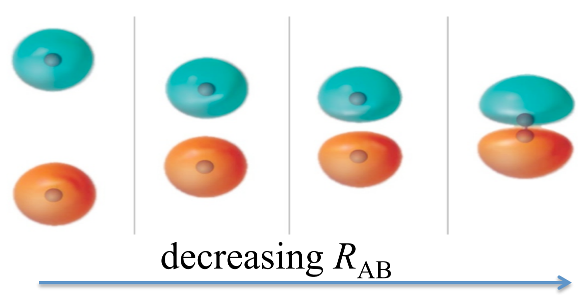
Antibonding orbitals in H_2



because the electron-nuclear attraction is less in the antibonding orbital, its energy is higher than a bonding MO

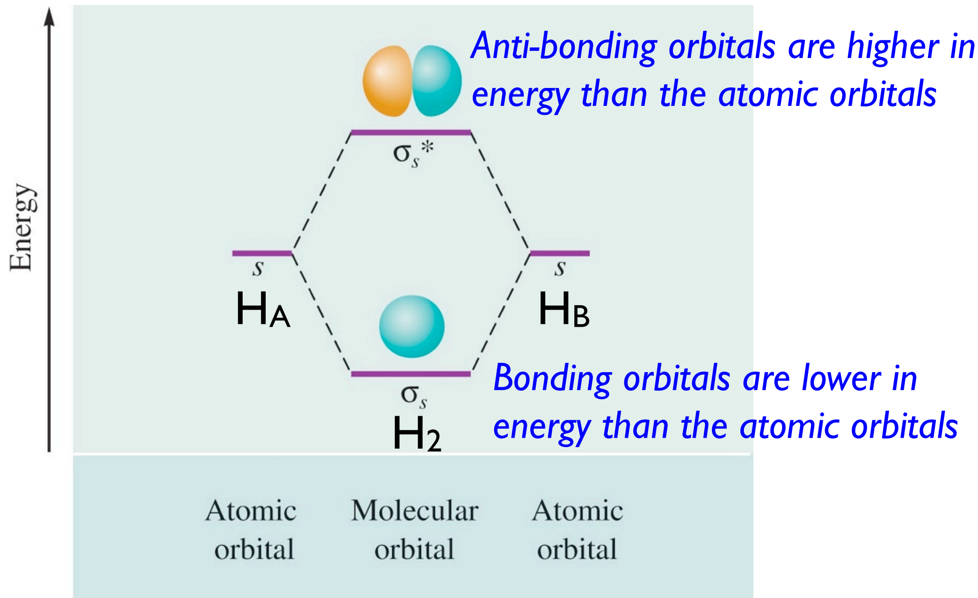
Antibonding orbitals in H_2

"Anti-bonding" results from destructive cancellation between the atomic orbitals



We see that combining two atomic orbitals we can form two types of molecular orbitals – *bonding* and *antibonding* – depending upon whether we have constructive or destructive interference

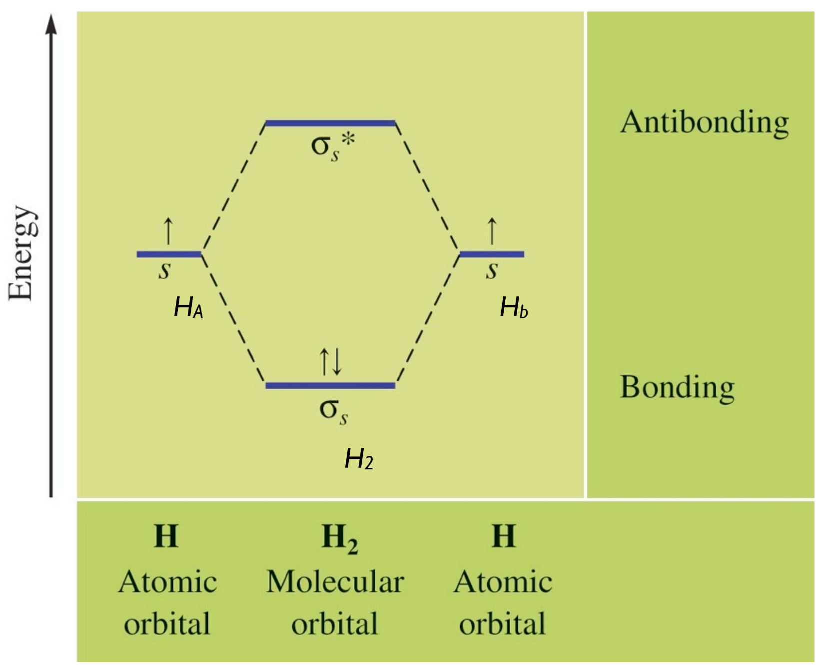
Bonding in H_2: Molecular Orbital Diagrams



whether a molecule is stable or not is determined by the number of bonding vs. anti-bonding electrons

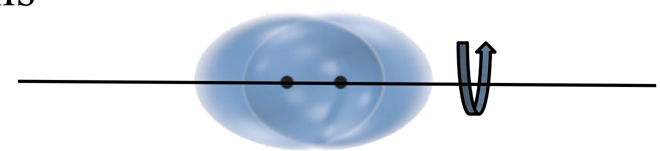
Molecular Orbital Diagram for H_2

whether a molecule is stable or not is determined by the number of bonding vs. anti-bonding electrons



What do we mean by σ?

Both the bonding and antibonding molecular orbitals formed from the 1s atomic orbitals are symmetric with respect to rotation around the bond axis



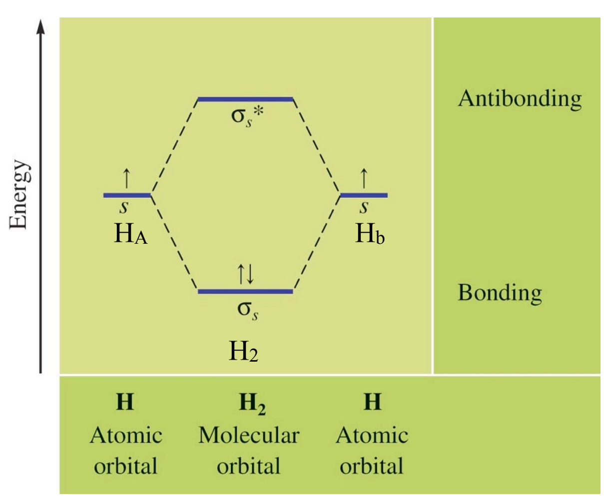
Any MO with this property is called a *sigma* MO and the bond is called a *sigma bond*

The electron configuration of H_2 is σ_{1s}^2

Bond Order

The bond order of a bond is defined as

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

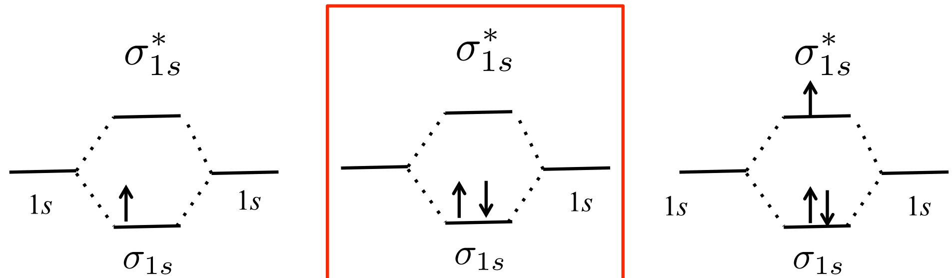


BO for H_2 = (2 – 0)/2
= 1

We say that H_2 has a single bond: H–H

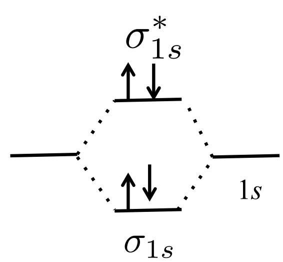
Stability of a bond is related to Bond Order

Let’s compare the molecular orbital diagrams (and properties for H_2^+, H_2^+ and He_2^+



	H_2^+	H_2	He_2^+
Bond Order	½	1	1/2
		More Stable!	
Bond Energy	268 kJ/mol mole	457 kJ/mol	241 kJ/
Bond Length	106 pm 108 pm	74 pm	

Molecular Orbital Analysis predicts (correctly) that He_2 is unstable



He_2

Bond Order $= 0$

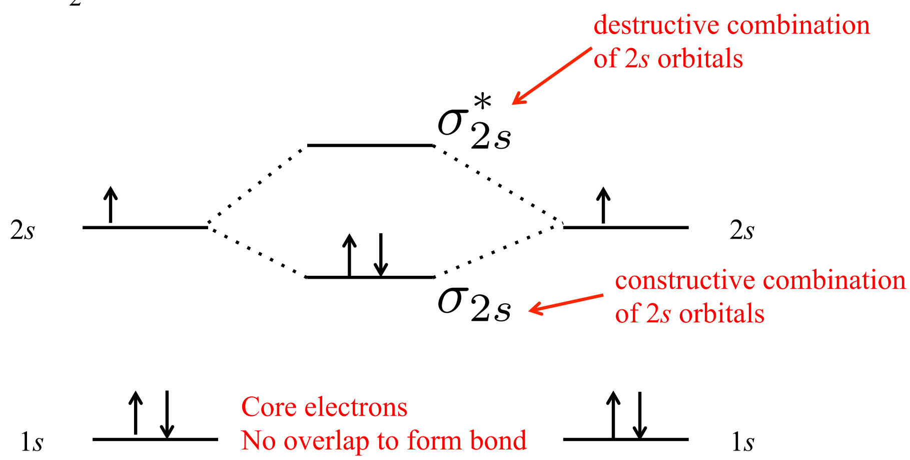
The number of bonding electrons is equal to the number of anti-bonding electrons in He_2

He$_2$ is not a stable molecule – its bond energy is < 1 kJ/mol

How do we go beyond Hydrogen and Helium?

In bonding, generally only the valence electrons take part.

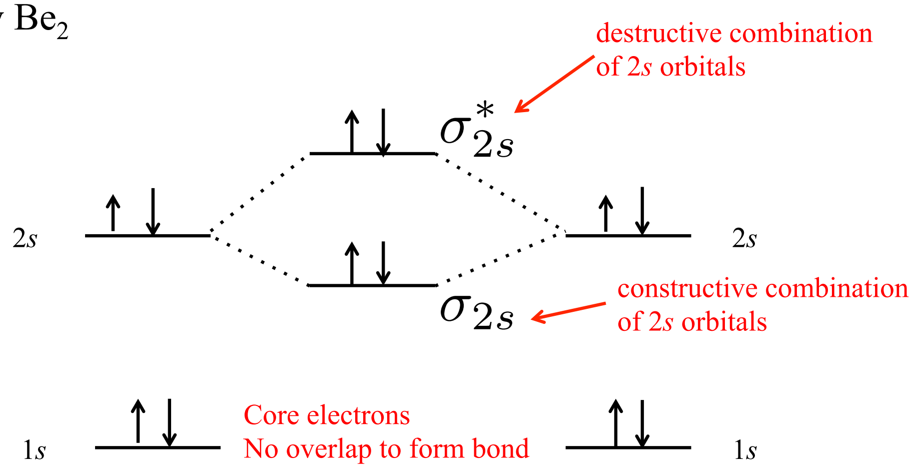
Look at Li_2



Configuration: $(\sigma_{2s})^2$ Bond Order = 1

How do we go beyond Hydrogen and Helium?

Now Be_2

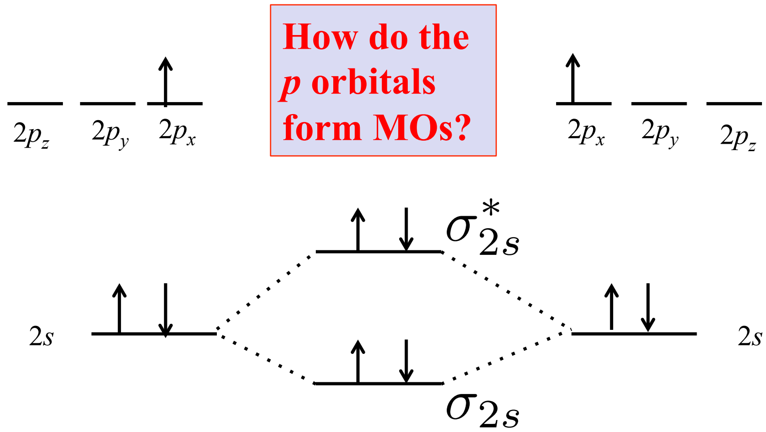


Be_2: Configuration: $(\sigma_{2s})^2(\sigma^*_{2s})^2$ Bond Order = 0 $E_{\text{bond}} <$ 10 kJ/mol

Li_2 Configuration: $(\sigma_{2s})^2$ Bond Order = 1 E_{bond} = 110 kJ/mol

Bonding with *p* Orbitals

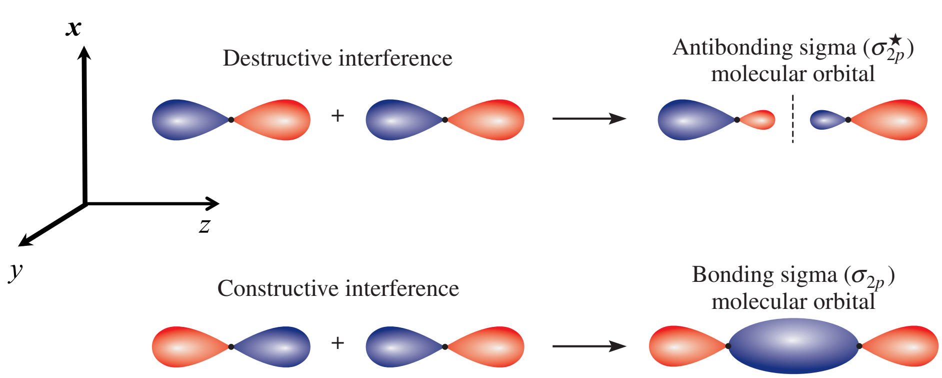
Let's look now at B_2



We can create MOs from two *p* orbitals in two ways

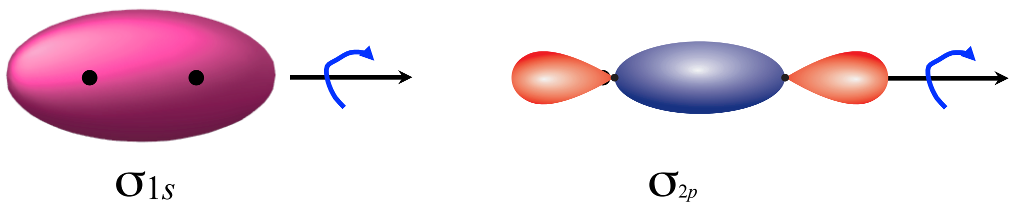
There are 3 2*p* orbitals – oriented along each Cartesian direction: *x, y* and *z*

Let's take the bond axis to be the *z* axis. The $2p_z$ orbitals of the two B atoms are oriented head on. We can combine them constructively or destructively…..

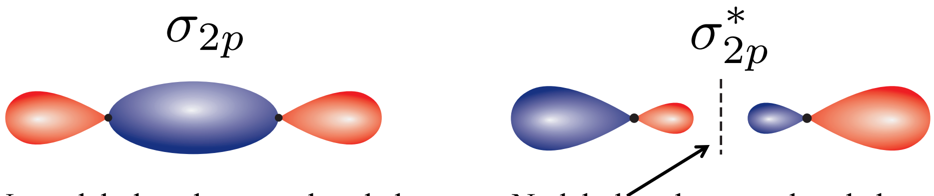


Remember the definition of a σ orbital?

Electron density is cylindrically symmetric about the bond axis



How do you tell if it is bonding or antibonding?

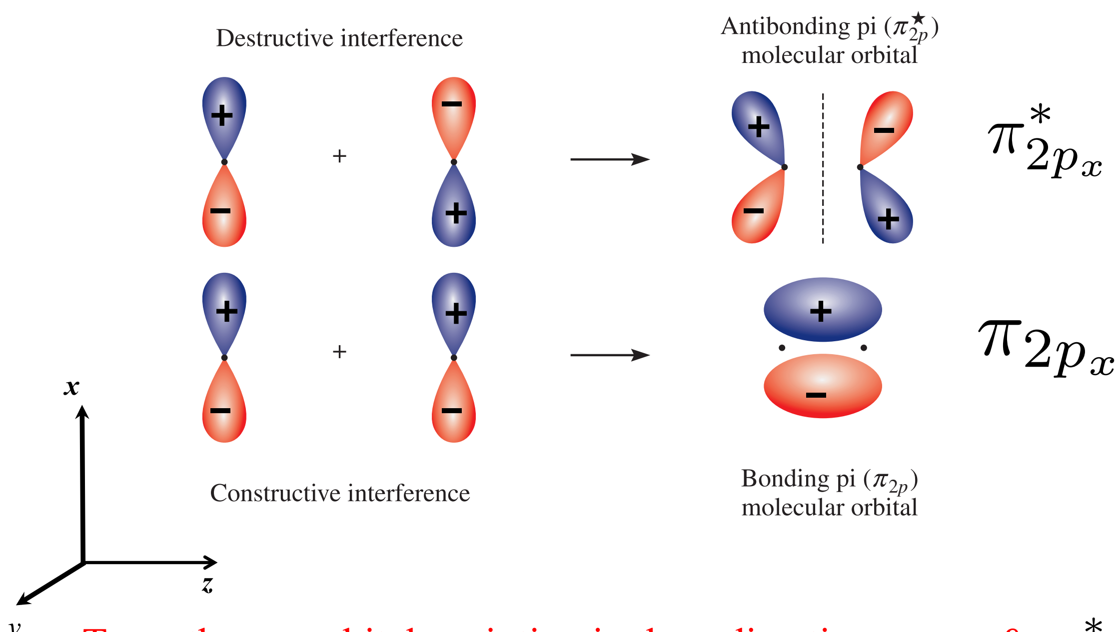


No nodal plane between bonded atoms → ***bonding orbital***

Nodal plane between bonded atoms → ***antibonding orbital***

Bonding with *p* Orbitals

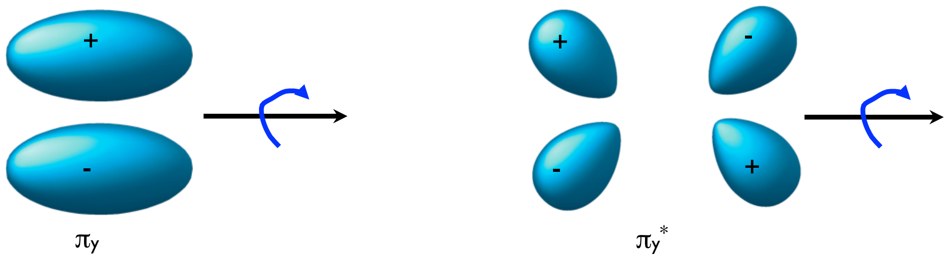
The other two *p* orbitals are perpendicular to bond axis



Two other π_p orbitals pointing in the *y* direction: π_{2p_y} & $\pi^*_{2p_y}$

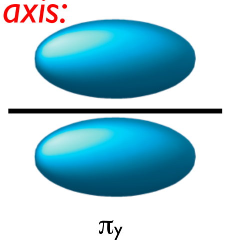
What is π orbital?

Orbital changes sign when rotated by 180º about bond axis

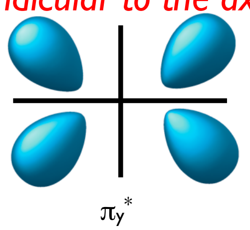


Rotate about the axis → *orbital rotates (not symmetric)*

Nodal plane parallel to the axis:



*Nodal planes parallel **and** perpendicular to the axis:*



Bonding with π orbitals