

Quantum Mechanics and Chemical Bonds

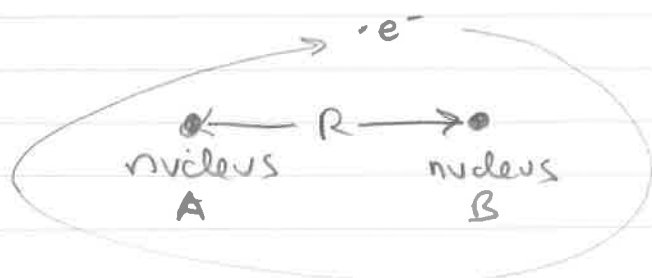
If we want to understand chemical bonding in a molecule using a full quantum mechanical treatment then, once again, we start with

$$\hat{H}\Psi = E\Psi$$

and need to come up with the wavefunction, Ψ , for the molecule, and then we can get the energy.

This is not going to be a simple task, and if we are going to make any headway we need to find some good approximate solutions.

Let's start by considering the hydrogen molecule, H_2 . Better yet, let's start with H_2^+ a hydrogen molecule with only one electron!



The Hamiltonian has 6 terms

$$\begin{aligned} \hat{H}_{H_2^+} = & \hat{T}(A) \leftarrow \text{kinetic energy of nucleus A} \\ & + \hat{T}(B) \leftarrow \text{kinetic energy of nucleus B} \\ & + \hat{T}(e) \leftarrow \text{kinetic energy of electron} \\ & + \frac{Z^2 e^2}{4\pi\epsilon_0 R} \leftarrow \text{nucleus-nucleus potential energy} \\ & - \frac{Z e^2}{4\pi\epsilon_0 r_{1A}} \leftarrow \text{electron-nucleus A potential energy} \\ & - \frac{Z e^2}{4\pi\epsilon_0 r_{1B}} \leftarrow \text{electron-nucleus B potential energy} \end{aligned}$$

Our 1st approximation is to neglect nuclear motion and assume the nuclei are fixed in space. This is called the BORN - OPPENHEIMER approximation.

Then the Hamiltonian is

$$\hat{H}_{H_2^+} = T(1) + V(1A) + V(1B) + V(R)$$

\uparrow \uparrow \uparrow \uparrow
 e^- kinetic e^- -A e^- -B A-B
 energy attraction attraction repulsion.

It is possible to solve the Schrödinger Eq exactly with this Hamiltonian, but the solution is not helpful for later when we look at multi-electron molecules.

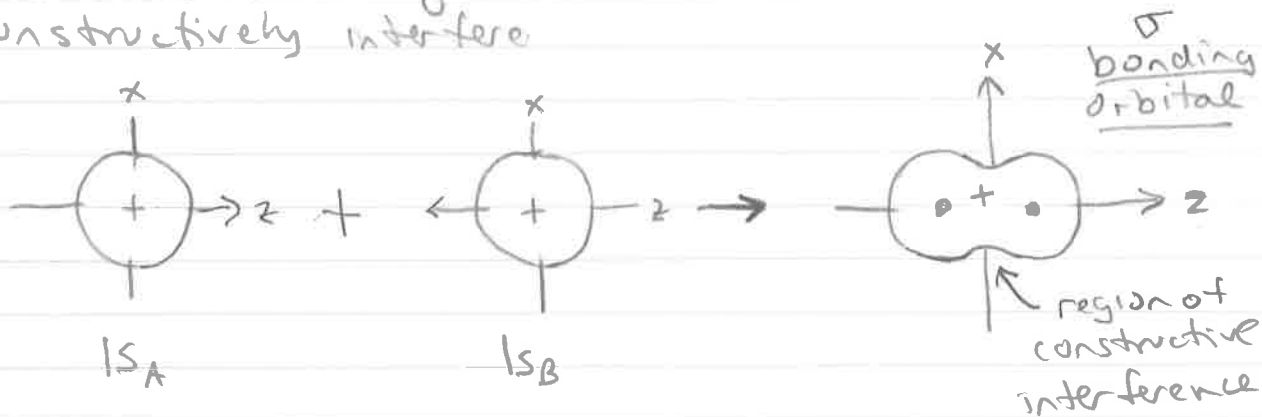
Molecular Orbital Theory (MO Theory)

In MO Theory, the molecular wavefunction is proposed to be a linear combination of atomic orbitals. In our H_2^+ case, we would propose

$$\text{molecular orbital} \rightarrow \Psi_{MO} = \Psi_{A1s} + \Psi_{B1s}$$

\uparrow \uparrow
 1s orbital 1s orbital
 centered on A centered on B

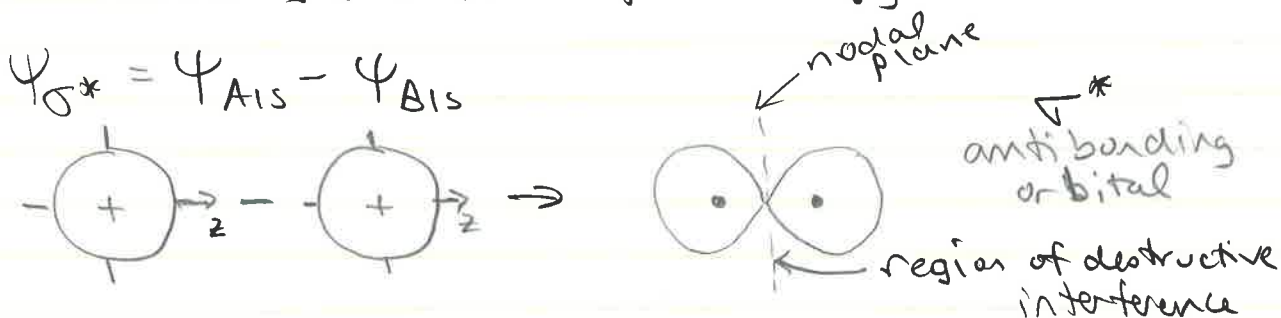
To visualize this molecular orbital imagine bringing two 1s orbitals together and have their wavefunctions constructively interfere



This is called a sigma orbital because of cylindrical symmetry when rotated about the internuclear axis



In M.O. Theory the next highest energy molecular orbital is



The σ^* orbital also has cylindrical symmetry. Because it is higher energy we label it σ^*

$\Psi_{\sigma_{1s}} = \Psi_{A1s} + \Psi_{B1s}$ $\Psi_{\sigma_{1s}^*} = \Psi_{A1s} - \Psi_{B1s}$

If we calculate the probability density we find:

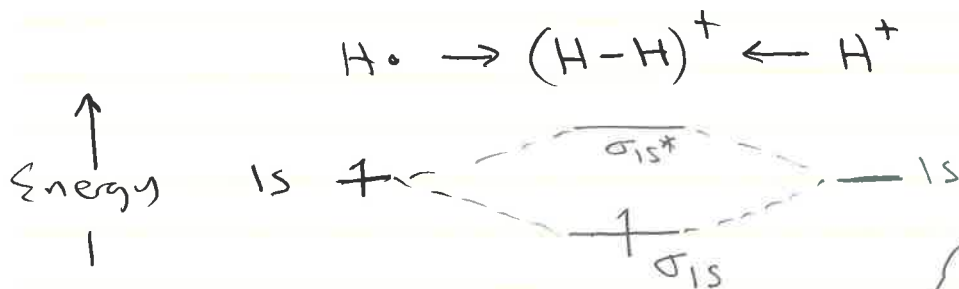
$|\Psi_{\sigma_{1s}}|^2 = \Psi_{A1s}\Psi_{A1s}^* + \Psi_{B1s}\Psi_{B1s}^* + (\Psi_{A1s}\Psi_{B1s}^* + \Psi_{A1s}^*\Psi_{B1s})$

↑ constructive ← interference term

$|\Psi_{\sigma_{1s}^*}|^2 = \Psi_{A1s}\Psi_{A1s}^* + \Psi_{B1s}\Psi_{B1s}^* - (\Psi_{A1s}\Psi_{B1s}^* + \Psi_{A1s}^*\Psi_{B1s})$

↑ destructive ←

The greater the overlap the lower the energy compared to original atomic orbital.



The bond energy of H_2^+ is 255 kJ/mole

electron configuration: $(\sigma_{1s})^1$

energy difference between bonding and anti bonding increases with increasing orbital overlap

What about MULTIElectron molecules?

We make the same approximation we made for multi-electron atoms: we ignore $e^- - e^-$ repulsions. This assumption would make the energies more negative than they actually are, but we can similarly adjust, for example, by introducing effective nuclear charges.

For H_2 with 2 electrons, we write the wavefunction as the product of single electron wavefunctions

$$\Psi = \Psi(1)\Psi(2)$$

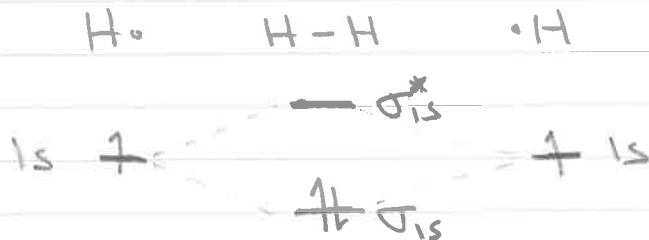
And since the Pauli exclusion principle still applies, we can build up our multi-electron molecule by filling molecular orbitals starting with the lowest energy orbitals and working our way up.

For a ground state H_2 molecule the wavefunction is

$$\Psi = \Psi_{\sigma_{1s}}(1)\Psi_{\sigma_{1s}}(2)$$

remember the electron spin quantum number have to be different.

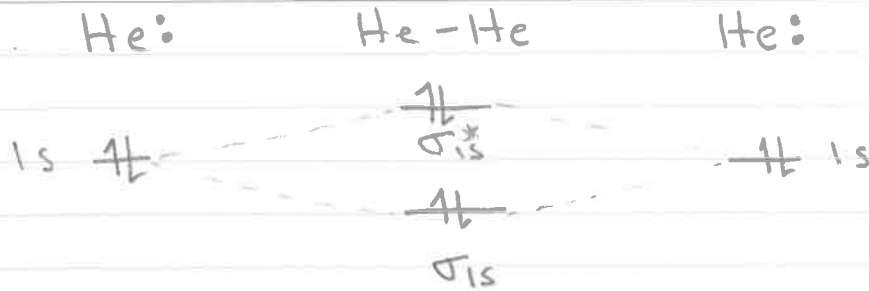
On an energy level diagram we show



and write the electron configuration as $(\sigma_{1s})^2$

The bond energy of H_2 is 431 kJ/mole

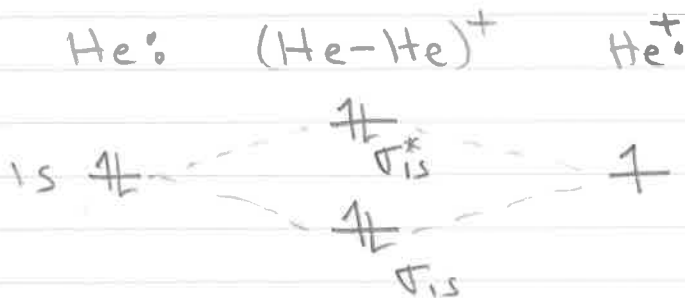
Using this approach let's move on to Helium...
What happens if two helium atoms tried to get together and form He_2 ?



The anti bonding orbitals are higher in energy than the 1s orbitals. So the stabilization of 2 e⁻ in the σ_{1s} orbital is lost when 2 e⁻ go into the σ_{1s}^* orbital.

He₂ doesn't exist.

This picture suggests, however, that He₂⁺ should exist, since there is a net lowering in energy compared to separated He and He⁺.



He₂⁺ exists and has a bond energy of 251 kJ/mole

electron configuration: $(\sigma_{1s})^2 (\sigma_{1s}^*)^1$

In Lewis structures we had single, double, & triple bonds. In M.O. theory we can similarly define bond order as

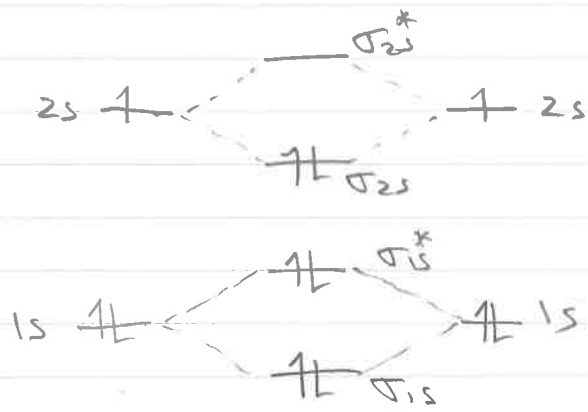
$$\text{Bond Order} = \frac{1}{2} (n_e - n_e^*)$$

\uparrow \uparrow
 # e⁻ in bonding orbitals # e⁻ in anti-bonding orbitals

Bond	Bond order
H ₂ ⁺	1/2
H ₂	1
He ₂ ⁺	1/2
He ₂	0

To a 1st approximation only atomic orbitals with similar energies can combine to form molecular orbitals.

Li₂ has 3+3 = 6e⁻



Bond energy of Li₂ is 105 kJ/mol

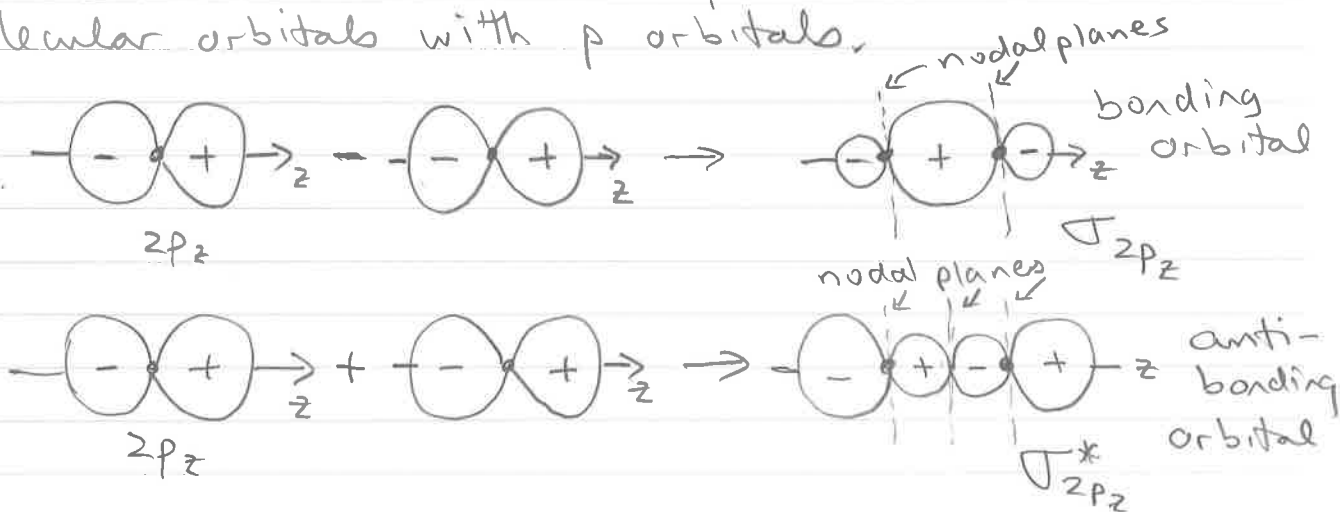
Bond order is 1

Bond length 267 pm

Electron configuration: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2$
filled shell

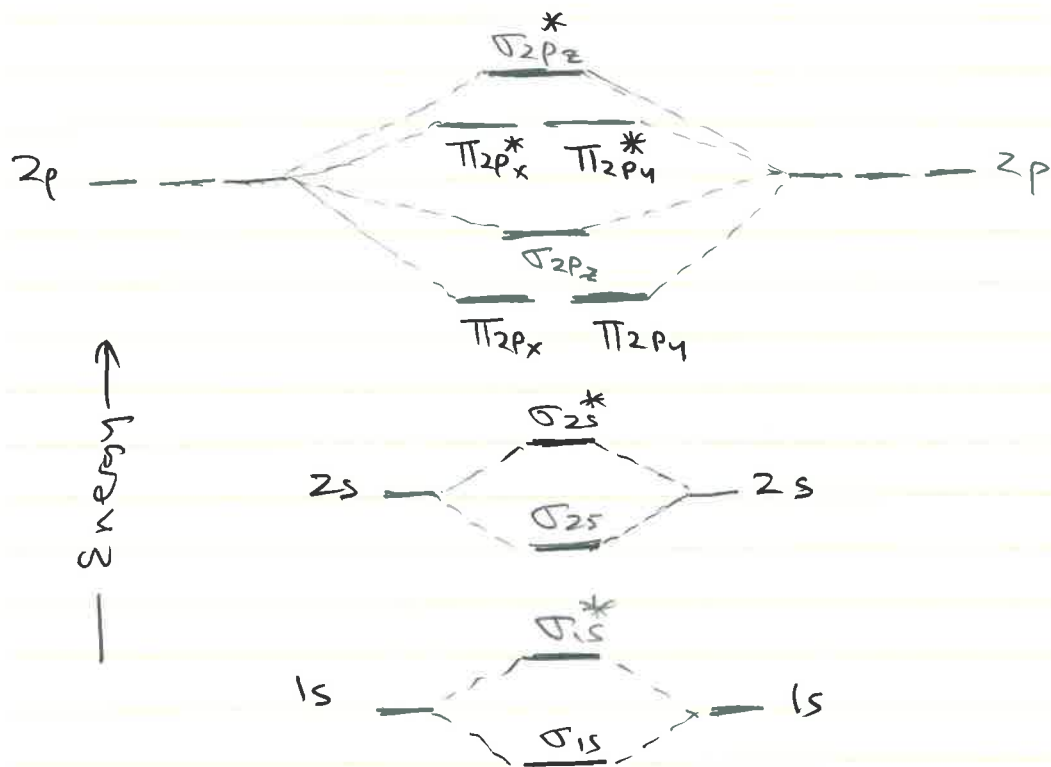
Be₂ has 4+4 = 8e⁻ and is not observed

at B₂ we see that it is also possible to form molecular orbitals with p orbitals.



Using p orbitals a second type of orbital called the π orbital can be formed...

When the shielding, σ , is smaller, such as B_2, C_2, N_2 , the atomic s and p subshells are closer in energy. This causes a slightly different molecular orbital energy ordering, shown below:



So, for B_2 , with $10e^-$, or 6 valence e^- , the MO diagram is

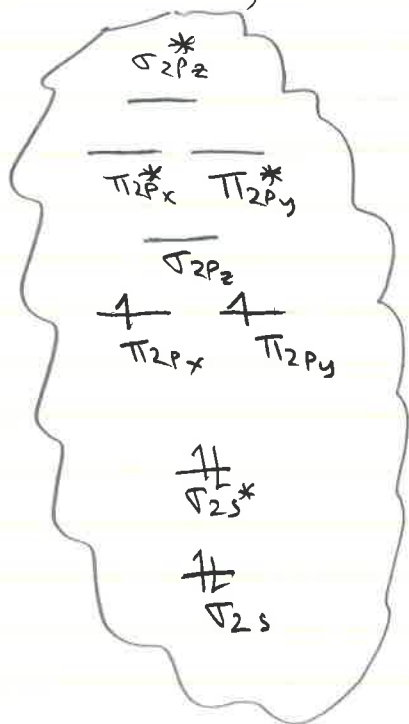
Bond Order is

$$\frac{1}{2}(2-2+2) = 1$$

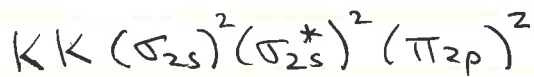
Single Bond.

Bond Energy
289 kJ/mol

Bond length
159 pm



The electronic configuration is

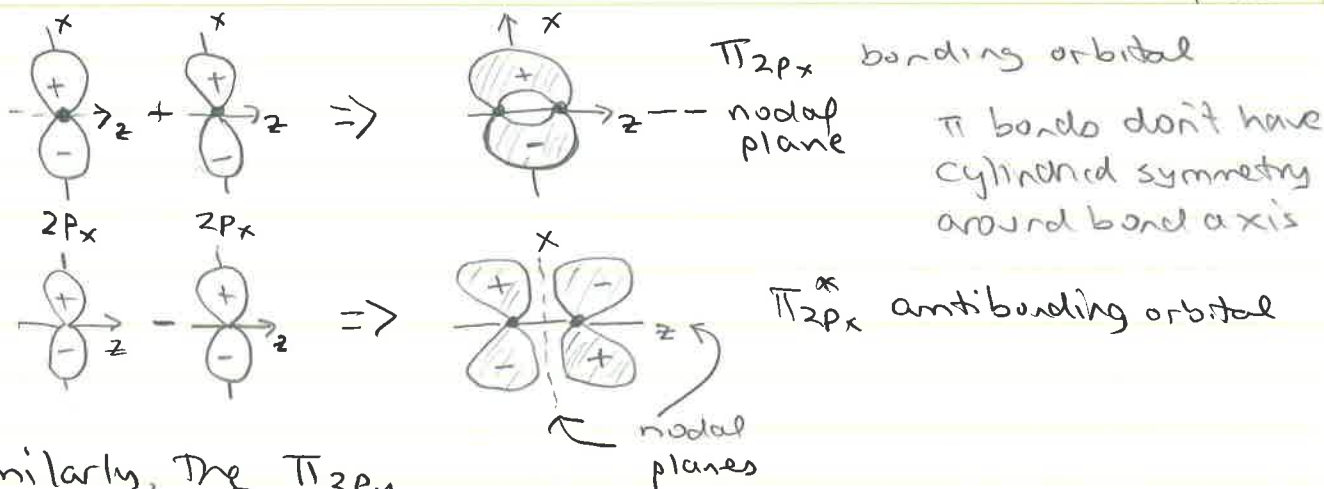


↑↑
Filled shell on each B atom

↑
Highest occupied molecular orbital (HOMO)

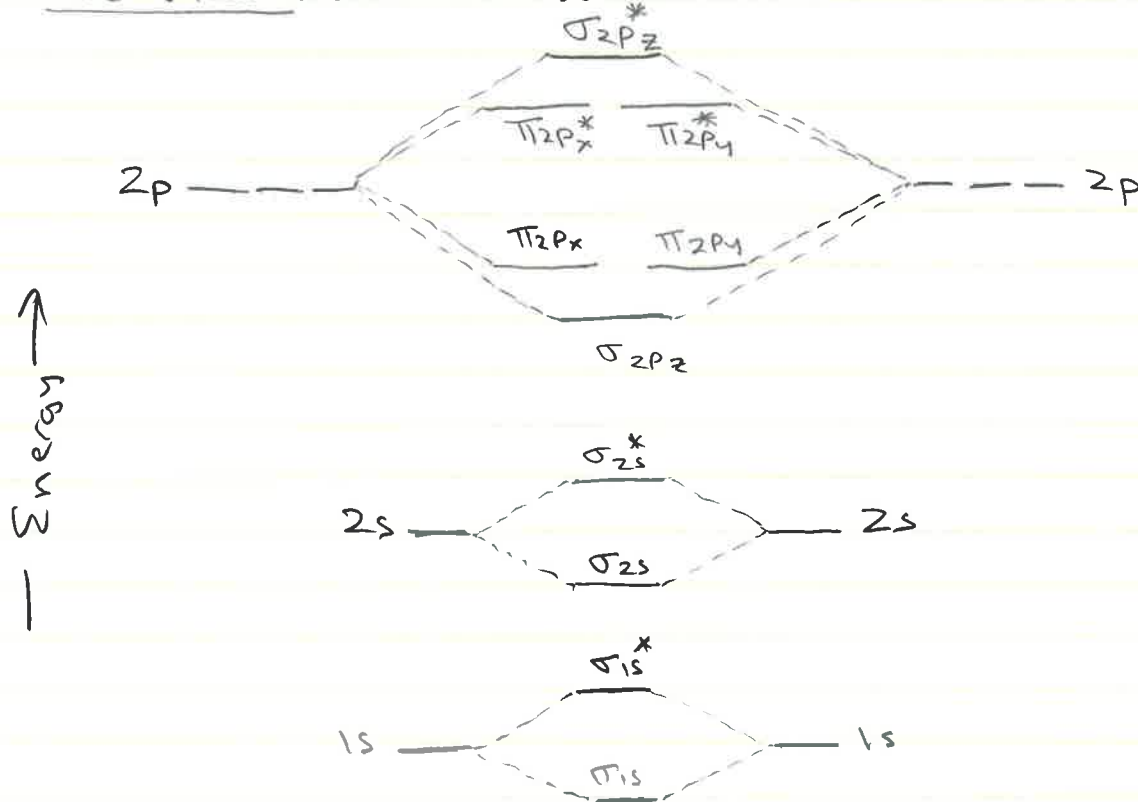
$\sigma_{2pz} \Rightarrow$ Lowest Unoccupied molecular orbital (LUMO)

for B_2



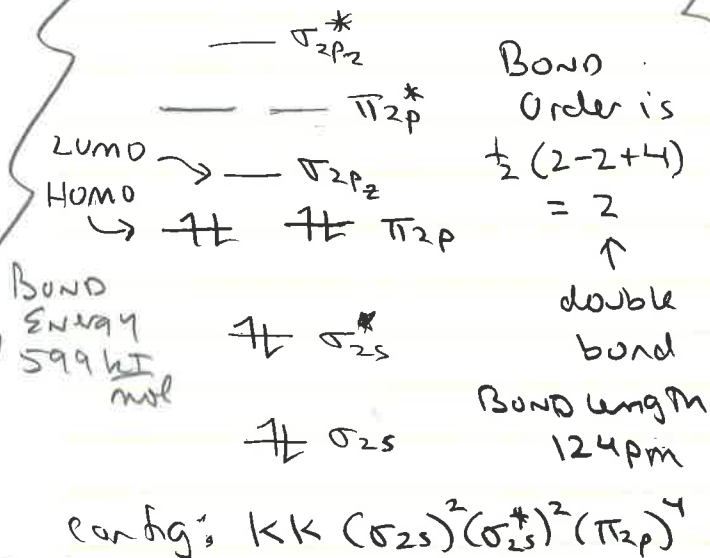
Similarly, the π_{2p_y} and $\pi_{2p_y}^*$ orbitals are formed.

The larger the difference between atomic orbital energies
The smaller the overlap for making a molecular orbital.
When the atomic s and p subshell energy differences are large, then the molecular orbital energy levels are ordered as shown below!

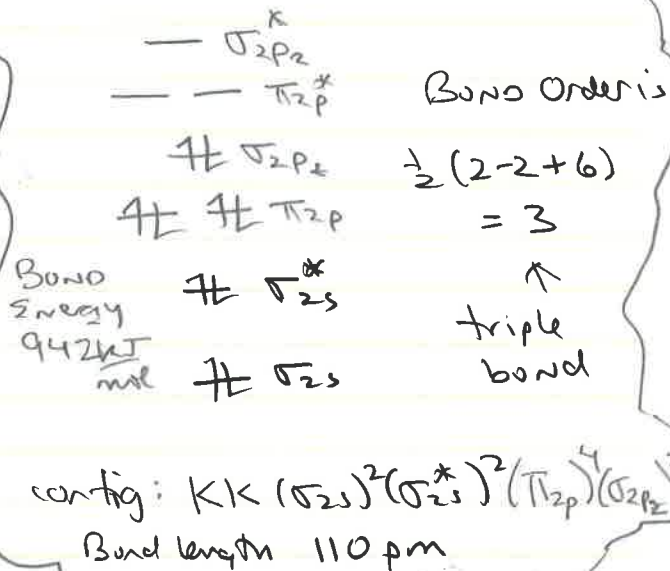


This ordering of energy occurs with the shielding, σ , is large enough that 2s and 2p are widely separated in energy, such as O_2 and F_2 , where σ is large.

C₂ (8 valence e⁻s)

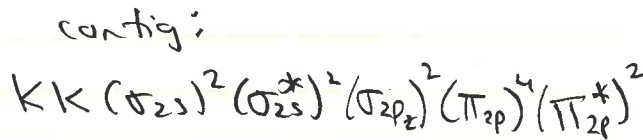
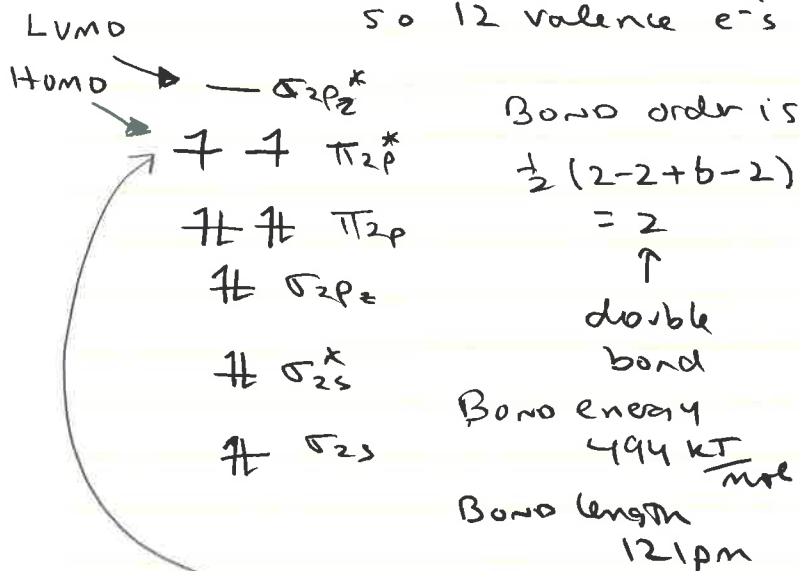


N₂ (10 valence e⁻)



For O₂, the M.O. energy ordering changes,

so 12 valence e⁻s are distributed as



Lewis structure $\langle O=O \rangle$ correctly predicts double bond, but fails to predict unpaired electrons

MO diagram predicts that O₂ has unpaired electrons, so it will be paramagnetic, i.e., sticks to magnets.

What is the bond order for F₂?

Is F₂ paramagnetic?

What is the electronic configuration and bond order for CO?

CO has 4+6=10 valence e⁻s. it is isoelectronic w/ N₂.

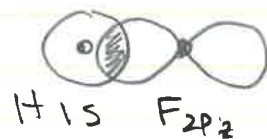
$KK (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p_z})^2$ Bond order = 3, Bond length = 113 pm
Bond energy = 1071 kJ/mol

We can use the MO theory for more polar diatomics like HF, but we must remember that the atomic orbitals that are closest in energy are the ones that overlap most when forming molecular orbitals.

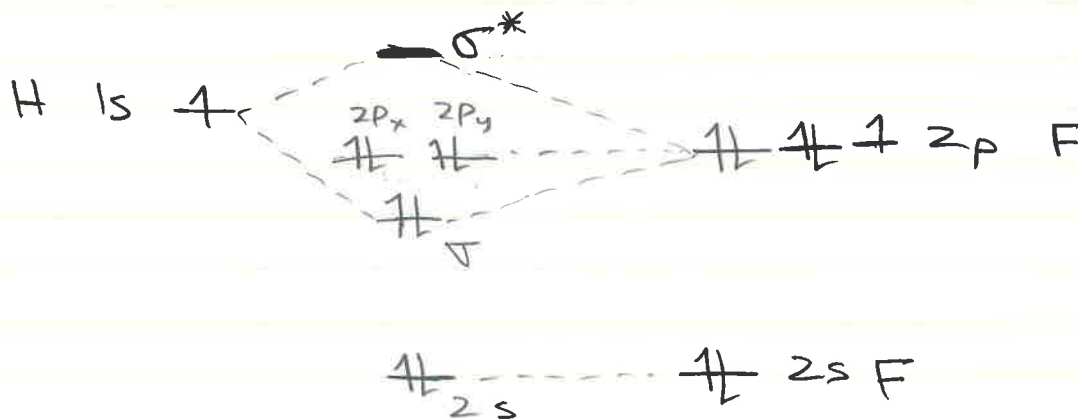
In HF, the Fluorine nucleus has a much higher charge than the hydrogen nucleus. So, the F 1s orbital is much lower in energy than the H 1s orbital.

Even the F 2s orbital is lower in energy than the H 1s orbital.

The F 2p orbital is closest, so the MO is formed between H 1s and F 2p_z.



The MO energy level diagram is



Bond order: $\frac{2 - 0}{2} = 1$ single bond

MO Theory, Valence Bond Theory, and Lewis Structures

For a 2 electron molecule like H_2 the MO Theory wavefunction is given by

$$\Psi_{MO} = \Psi_{\sigma_{1s}}(1) \Psi_{\sigma_{1s}}(2) \quad \text{Ground State}$$

and remember that the one electron molecular orbitals are proposed to be a linear combination of atomic orbitals

$$\Psi_{\sigma_{1s}} = \Psi_{A_{1s}} + \Psi_{B_{1s}}$$

Let's write out Ψ_{MO} in terms of the atomic orbitals

$$\begin{aligned} \Psi_{MO} &= (\Psi_{A_{1s}}(1) + \Psi_{B_{1s}}(1)) (\Psi_{A_{1s}}(2) + \Psi_{B_{1s}}(2)) \\ &= \left. \begin{aligned} &\Psi_{A_{1s}}(1) \Psi_{B_{1s}}(2) \\ &+ \Psi_{B_{1s}}(1) \Psi_{A_{1s}}(2) \end{aligned} \right\} H_A^- H_B^+ \text{ or } H_B^- H_A^+ \\ &+ \Psi_{A_{1s}}(1) \Psi_{A_{1s}}(2) \rightarrow H_A^- H_B^+ \\ &+ \Psi_{B_{1s}}(1) \Psi_{B_{1s}}(2) \rightarrow H_A^+ H_B^- \end{aligned}$$

We can imagine each of these four products as representing a Lewis structure resonance form for H_2 .

The 1st and 2nd are identical, but the 3rd and 4th represent resonance forms when H_2 has ionic bonding, what!

A problem with MO Theory is that it includes these unlikely resonance forms. An alternative to MO Theory is Valence Bond Theory. It says ignore the last two terms and write the wavefunction as

$$\Psi_{VB} = \Psi_{A_{1s}}(1) \Psi_{B_{1s}}(2) + \Psi_{B_{1s}}(1) \Psi_{A_{1s}}(2)$$

That makes sense for a molecule like H_2 , but in molecules like CO or HF you might expect a little ionic contribution to be important.

You can think of MO Theory as VB Theory with ionic terms.

$$\Psi_{MO} = \Psi_{VB} + \Psi_{ionic}$$

The problem is that MO Theory over emphasizes ionic bonding and valence bond Theory underemphasizes (ignores) it.

As an intermediate approach Ψ could be

$$\Psi = c_1 \Psi_{VB} + c_2 \Psi_{ionic}$$

and weighting factors c_1 & c_2 can be adjusted to get the right mix.

Atomic Orbital Hybridization

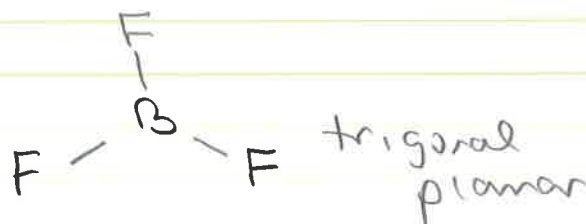
We've just learned about two types of bonds: σ & π .

You might expect for polyatomic molecules that you can put the atoms of the molecule around each central atom and work out what σ and π bonds will form.

We know from VSEPR what geometries will form.

The problem is that for most molecular geometries the atomic orbitals on the central atom don't point in the right direction to form a strong σ or π bond.

Let's look at BF_3



If all the valence electrons on B were in the $2s$, $2p_x$, $2p_y$, & $2p_z$ orbitals you wouldn't be able to form 3 equivalent σ or π bonds.

We know the B-F bonds are all equivalent because they all have the same bond dissociation energy.

Our linear combination of one atomic orbital from each atom to make a molecular orbital is not versatile enough to handle our BF_3 example.

A simple extension is to make a linear combination of many atomic orbitals from each atom to make a molecular orbital.

$$\psi_{\text{MO}} = \underbrace{(a\psi_{A2s} + b\psi_{A2p_x} + c\psi_{A2p_y} + d\psi_{A2p_z})}_{\text{hybrid orbital on A}} + \underbrace{(a'\psi_{B2s} + b'\psi_{B2p_x} + c'\psi_{B2p_y} + d'\psi_{B2p_z})}_{\text{hybrid orbital on B}}$$

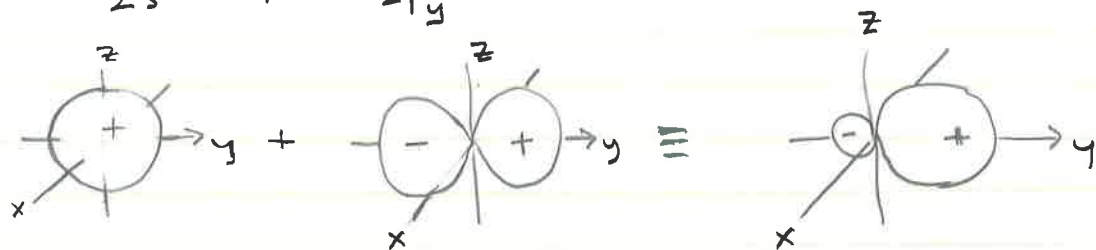
it's the same approach as before

$$\begin{array}{ccc} \psi_{\text{MO}} = & \psi_{\text{A hybrid}} & + & \psi_{\text{B hybrid}} \\ \nearrow & \uparrow & & \uparrow \\ \text{molecular} & \text{hybrid} & & \text{hybrid} \\ \text{orbital} & \text{orbital} & & \text{orbital} \\ & \text{centered} & & \text{centered} \\ & \text{on A} & & \text{on B} \end{array}$$

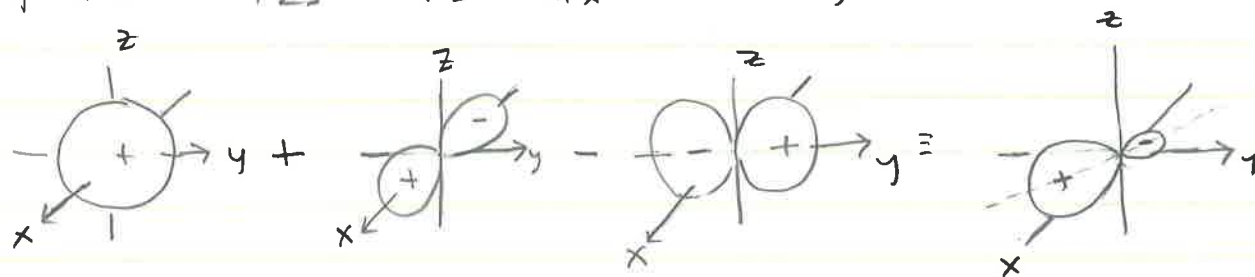
except we have to "invent" hybrid orbitals that form better σ bonds.

In the case of BF_3 , we need 3 hybrid orbitals centered on B that give strong overlap in a σ bond with F.

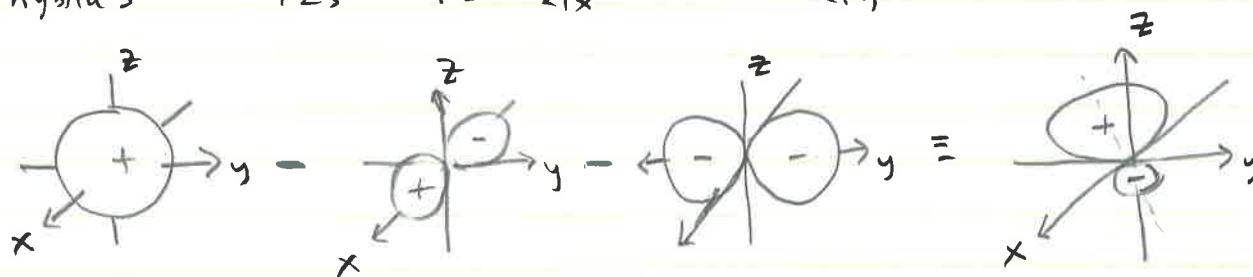
$$\Psi_{\text{hybrid 1}} = \Psi_{2s} + \sqrt{2} \Psi_{2p_y}$$



$$\Psi_{\text{hybrid 2}} = \Psi_{2s} + \sqrt{\frac{3}{2}} \Psi_{2p_x} - \sqrt{\frac{1}{2}} \Psi_{2p_y}$$



$$\Psi_{\text{hybrid 3}} = \Psi_{2s} - \sqrt{\frac{3}{2}} \Psi_{2p_x} - \sqrt{\frac{1}{2}} \Psi_{2p_y}$$

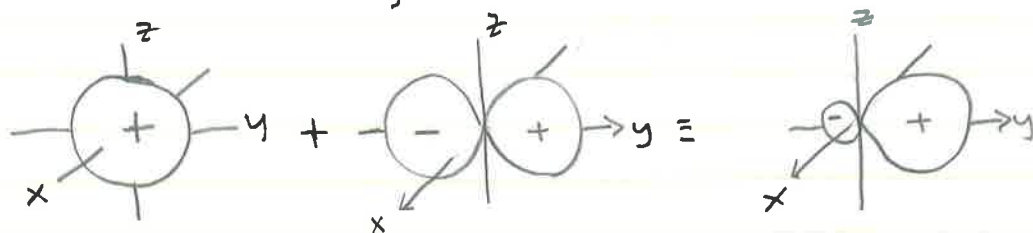


Here, we combine s, p_x, p_y to form 3 hybrid orbitals that have large positive wavefunctions pointing 120° apart and in the $x-y$ plane.

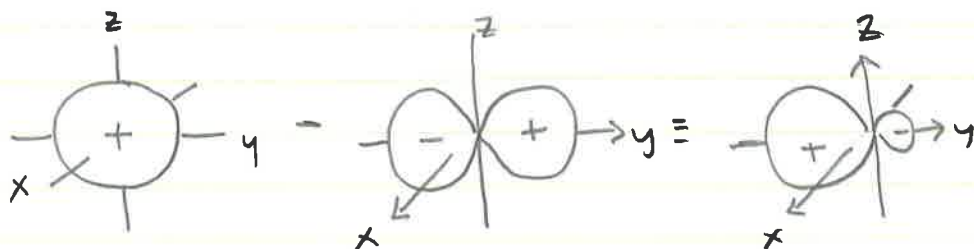
Because these were constructed from one s and two p orbitals they are called sp^2 hybrid orbitals.

Consider another example, BeF_2 , we know is linear. We need two hybrid orbitals on Be that point 180° apart.

$$\Psi_{\text{hybrid 1}}^{(sp)} = \Psi_{2s} + \Psi_{2p_y}$$



$$\Psi_{\text{hybrid 2}}^{(sp)} = \Psi_{2s} - \Psi_{2p_y}$$



These two hybrid orbitals are constructed from one s and one p orbital, and are called sp hybrid orbitals.

For a tetrahedral arrangement, like CH_4 , or NH_3 , we can hybridize one s and three p orbitals to get sp^3 hybrid orbitals which adopt the tetrahedral structure and are 109.5° away from each other.

$$\Psi_1^{(sp^3)} = \Psi_{2s} + \Psi_{2p_x} + \Psi_{2p_y} + \Psi_{2p_z}$$

$$\Psi_2^{(sp^3)} = \Psi_{2s} - \Psi_{2p_x} - \Psi_{2p_y} + \Psi_{2p_z}$$

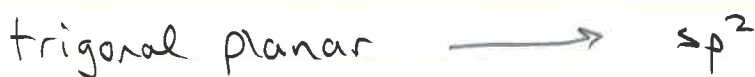
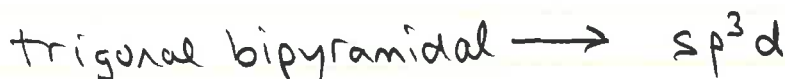
$$\Psi_3^{(sp^3)} = \Psi_{2s} + \Psi_{2p_x} - \Psi_{2p_y} - \Psi_{2p_z}$$

$$\Psi_4^{(sp^3)} = \Psi_{2s} - \Psi_{2p_x} + \Psi_{2p_y} - \Psi_{2p_z}$$

For molecules when a central atom gets more than an octet of electrons I said the extra e^- s went into d-orbitals.

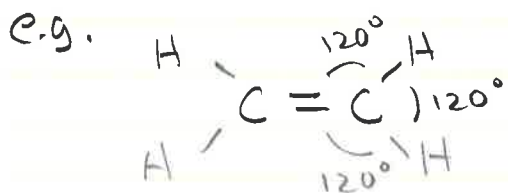


This is treated with hybrid orbitals that combine s, p, and d-orbitals.



Generally, hybrid atomic orbitals are formed to make better sigma bonds.

π bonds can still occur between p orbitals



C atoms are sp^2 hybridized
double bond consists of one sigma bond and one π bond

σ bond between sp^2 hybrid orbitals on each C

π bond between p orbital on each C

