Molecular Orbital Theory

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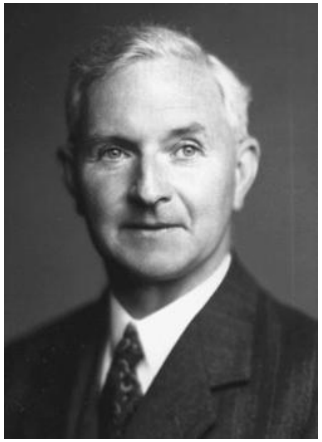
Main Developers of MO Theory:

Robert S. Mulliken
American (1896-1986)
Nobel Prize, 1966

Friedrich H. Hund
German (1896-1997)
No Nobel Prize



John Lennard-Jones
British (1894-1954)
No Nobel Prize

First, a brief look at Quantum Mechanics

Particles behave like waves (Louis de Broglie, 1924; Nobel Prize, 1929)

A particle moving with a momentum p = mv has an associated wave with wavelength λ, given by $\lambda = h/p = h/(mv)$

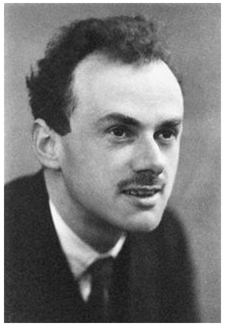
(h is Planck's constant, 6.626×10^{-34} Joule – seconds)

De Broglie's wave follows a wave equation

(Erwin Schrödinger, 1926; Nobel Prize, 1933)

$\hat{H}\psi = E\psi$ or $-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$ for a particle of mass m moving in the x-dimension, subject to a potential energy function V(x).

This gets more complicated for particles moving in more than one dimension, or more than one particle. $\psi(x)^2\,dx$ gives the probability of finding the particle between x and x + dx.



Paul Dirac generalized Schödinger's Equation to obey Einstein's Theory of Special Relativity (1928; Nobel Prize, 1933)

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." (1929)

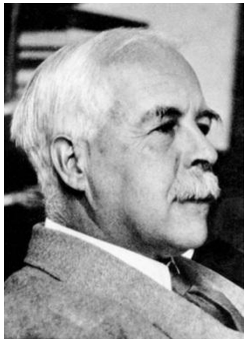
If the equations are too complicated to be soluble, what can we do?

If the equations are too complicated to be soluble, what can we do?

Make approximations!

Valence Bond Theory

[A very atom-based approximation scheme]



Remember Lewis dot structures? (G. N. Lewis, 1916. Sadly – no Nobel Prize, despite being nominated 41 times!)

H· + H· → H:H (a shared electron pair forms a bond)

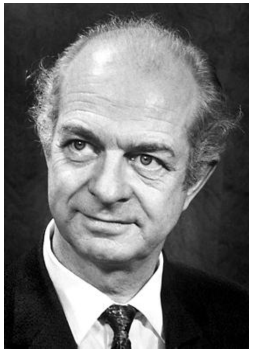
Linus Pauling and Charles Coulson took this idea and formulated it as Valence Bond Theory, where each atom keeps its electron, but the spins are paired:

$$\psi(1,2) = [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] \times [spin - paired\ wavefunction]$$

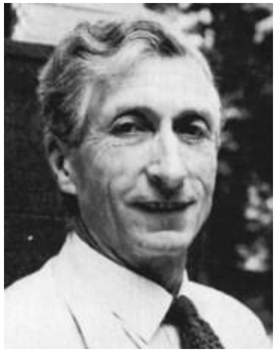
Electron #1 is on nucleus A while electron #2 is on nucleus B

Electron #1 is on nucleus B while electron #2 is on nucleus A

Linus Pauling
Nobel Prize 1954



Charles Coulson
no Nobel Prize



A Different Approximation Scheme: Molecular Orbital Theory

[A very molecule-based approximation scheme]

Instead of keeping the electrons in atomic orbitals, we can place them in molecular orbitals that extend over the entire molecule. This is based on the idea that the electrons are attracted to all the nuclei in the molecule, so we can expect them to extend over the entire molecule.

Note: Either approach is an approximation! But the molecular orbital approach is easier to implement in quantum chemical calculations. It also explains excited states of molecules in a more straightforward way.

For H_2, this approach uses an approximate wavefunction in which each electron is placed in a molecular orbital that extends over the entire molecule:

$$\psi(1,2) = \left[1\sigma_g(1)1\sigma_g(2)\right] \times [spin - paired\ wavefunction]$$

The $1\sigma_g$ orbital is the simplest of the molecular orbitals. It is a wavefunction that extends over both hydrogen nuclei. Just like atomic orbitals, it can hold two electrons, which must have opposite spins.

Linear Combination of Atomic Orbitals – Molecular Orbital Method
LCAO-MO

How can we come up with molecular orbitals? These are functions that depend on the (x, y, z)-coordinates of the electrons, and have a particular value at every point in space. One of the simplest methods is to take them as linear combinations of atomic orbitals. In this approach, the simplest possible LCAO for the $1\sigma_g$ orbital of H_2 is:

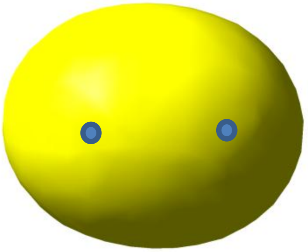
$$1\sigma_g = C\,(\,1s_A + \,1s_B)$$

1s orbital centered on nucleus A

1s orbital centered on nucleus B

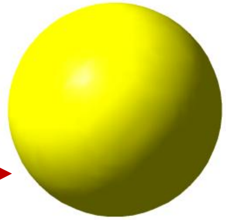
With this combination, an electron in the $1\sigma_g$ orbital is equally likely to be found in the 1s orbital on atom A as on atom B.

$1\sigma_g$ orbital:



In linear molecules, a σ orbital is cylindrically symmetric about the axis of the molecule. Looking down the molecular axis, it looks circular.

Looking down the axis:



This is a bonding orbital, because the atomic orbitals add up in phase between the two atoms, leading to an increase in electron density just where it is needed to hold them together.

Valence Bond vs. Molecular Orbital Theory

In the simplest form of MO theory, we use a wavefunction:

$$\psi(1,2) = 1\sigma_g(1)1\sigma_g(2) \times [spin - paired\ wavefunction]$$

$$= [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \times [spin - paired\ wavefunction]$$

Multiplying this out:

$$= [1s_A(1)1s_A(2) + 1s_B(1)1s_A(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_B(2)] \times [spin - paired\ wavefunction]$$

Rearranging:

$$= [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)] \times [spin - paired\ wavefunction]$$

One electron on each atom – a "covalent structure"

One electron on each atom – a "covalent structure"

Both electrons are on atom A – an "ionic structure" (H^- H^+)

Both electrons are on atom B – another "ionic structure" (H^+ H^-)

MO Theory has equal contributions from "covalent" and "ionic" structures

In the simplest form of VB theory, we use a wavefunction:

$$\psi(1,2) = [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] \times [spin - paired\ wavefunction]$$

This keeps one electron on each atom – it only has contributions from "covalent structures"

Valence Bond vs. Molecular Orbital Theory

Which approximation is better?

The best approximation is somewhere in between,
(both covalent and ionic structures, but mainly covalent)

$$\psi(1,2) = \left\{ \begin{matrix} 0.968[1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] \\ +0.252[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)) \end{matrix} \right\} \times [spin - paired\ wavefunction]$$

Note: the coefficient in front tells the relative importance of that structure
(really c^2 does)

In this case, c^2 for the covalent structures is $(0.968)^2 = 0.937$
c^2 for the ionic structures is $(0.252)^2 = 0.063$

H_2 is 93.7% covalent, 6.3% ionic in character (although both H^- H^+ and H^+ H^- make equal contributions, so there's no net dipole moment). Close enough to call it a covalent molecule. But you all knew that already!

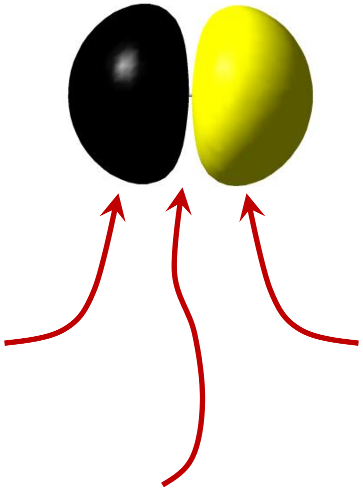
What about molecules with more electrons?

Use the LCAO method to construct higher energy molecular orbitals!

For He_2, we have four electrons altogether. Since the $1\sigma_g$ orbital can only hold 2 electrons, we need another orbital. It turns out there is another way to combine the two 1s orbitals ($1s_A$ and $1s_B$), which is taking the difference:

$$1\sigma_u = 1s_A - 1s_B$$

Pictorially, the $1\sigma_u$ orbital looks like this: (Here different colors correspond to the different signs of the wavefunction; one color is positive, the other negative)



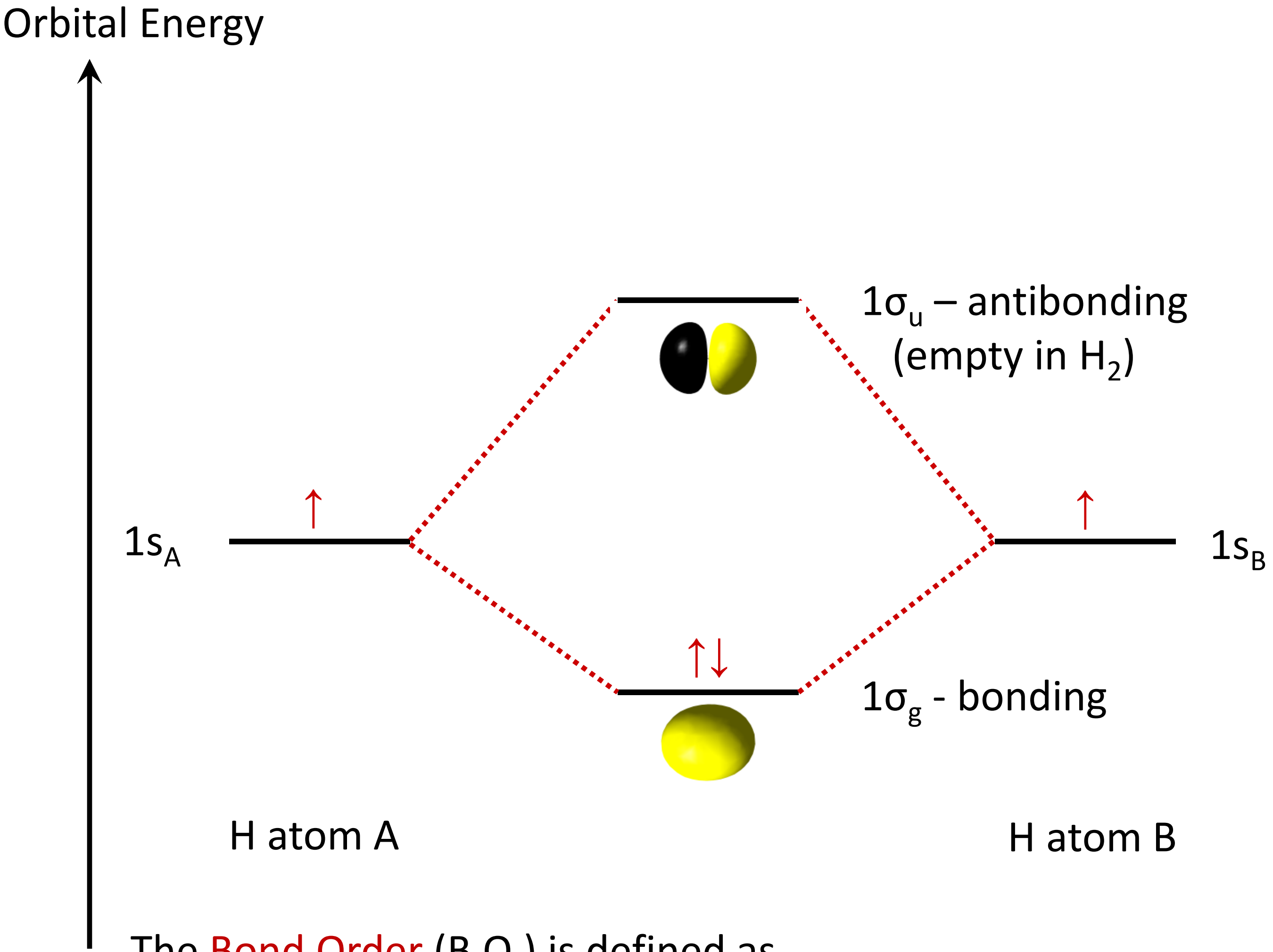
$1s_A$ has a positive sign. The wavefunction has a positive value here

$1s_B$ has a negative sign. The wavefunction has a negative value here

<u>Looking down the axis</u>: Still a σ orbital

Where the wavefunction changes sign is called a <u>node</u> – in this case, it is a planar nodal surface. This depletes electron density between the two nuclei, causing nuclear-repulsion to increase. This makes this an <u>antibonding orbital</u>.

Molecular orbital diagram for H_2



Orbital Energy

$1\sigma_u$ – antibonding (empty in H_2)

$1s_A$ $\uparrow$

$\uparrow$ $1s_B$

$\uparrow\downarrow$

$1\sigma_g$ - bonding

H atom A

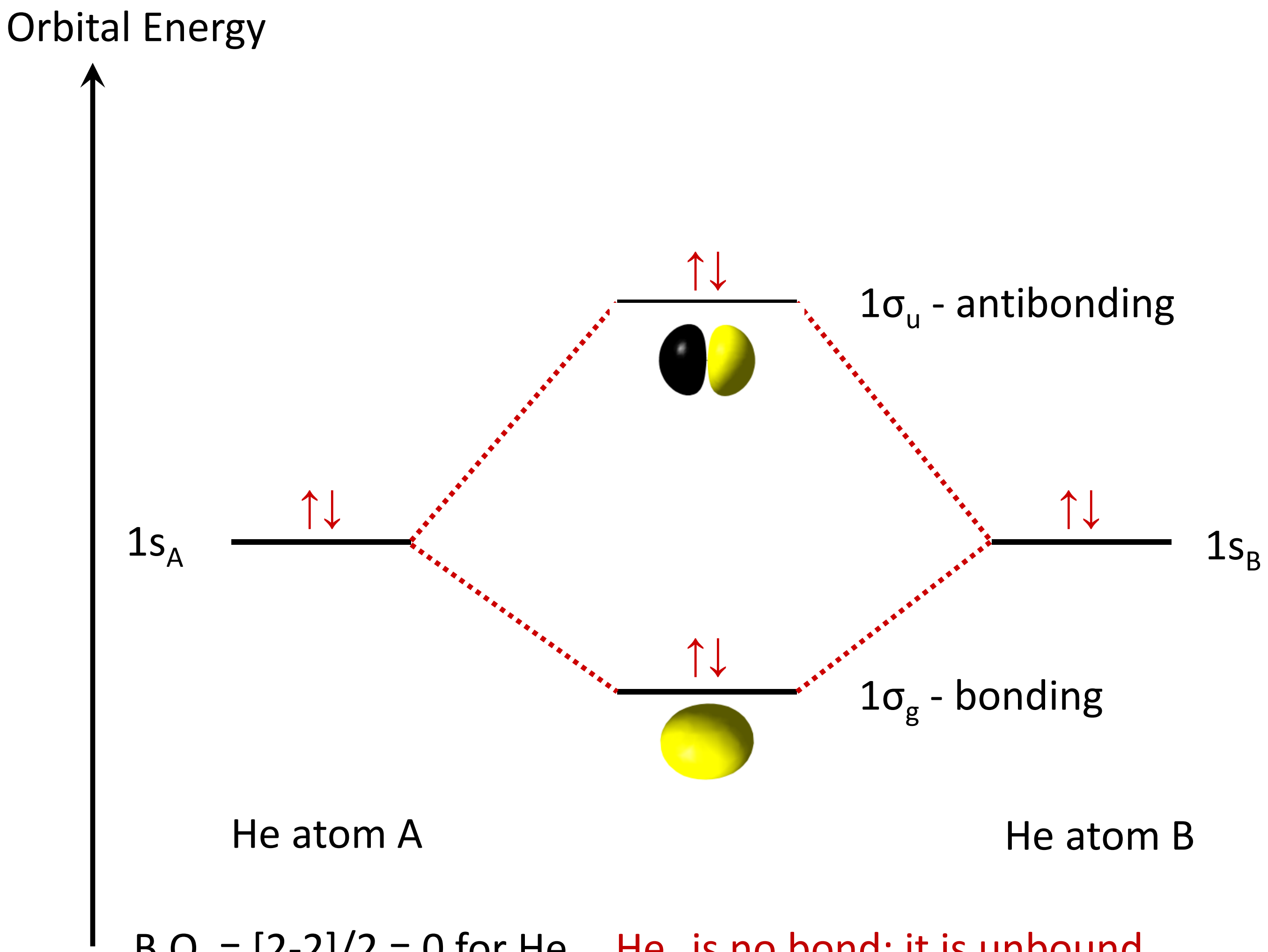
H atom B

The Bond Order (B.O.) is defined as

B.O.=[(# of electrons in bonding orbitals) – (# of electrons in antibonding orbitals)]/2

B.O. = [2-0]/2 = 1 for H_2. H_2 has a single bond.

Molecular orbital diagram for He_2



Orbital Energy

↑↓

$1\sigma_u$ - antibonding

$1s_A$ ↑↓

↑↓ $1s_B$

↑↓

$1\sigma_g$ - bonding

He atom A

He atom B

Note: The antibonding orbital goes up in energy more than the bonding orbital goes down! As a result, there is no net bonding in He_2, and helium exists as a monatomic gas.

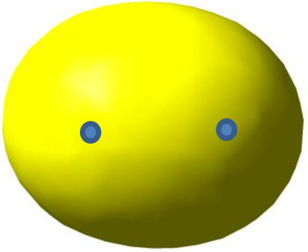
B.O. = [2-2]/2 = 0 for He_2. He_2 is no bond; it is unbound.

A brief note: What does g/u mean?

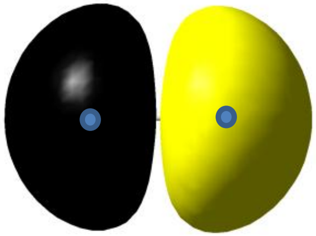
These crazy subscripts tell whether the wavefunction stays the same when the electron is moved through the center to the opposite side, changing (x, y, z) to (-x, -y, -z), or if it changes sign.

If it stays the same, it is "g", or "gerade" (from the German word for "even")

If it changes sign, it is "u", or "ungerade" (from the German word for "odd")

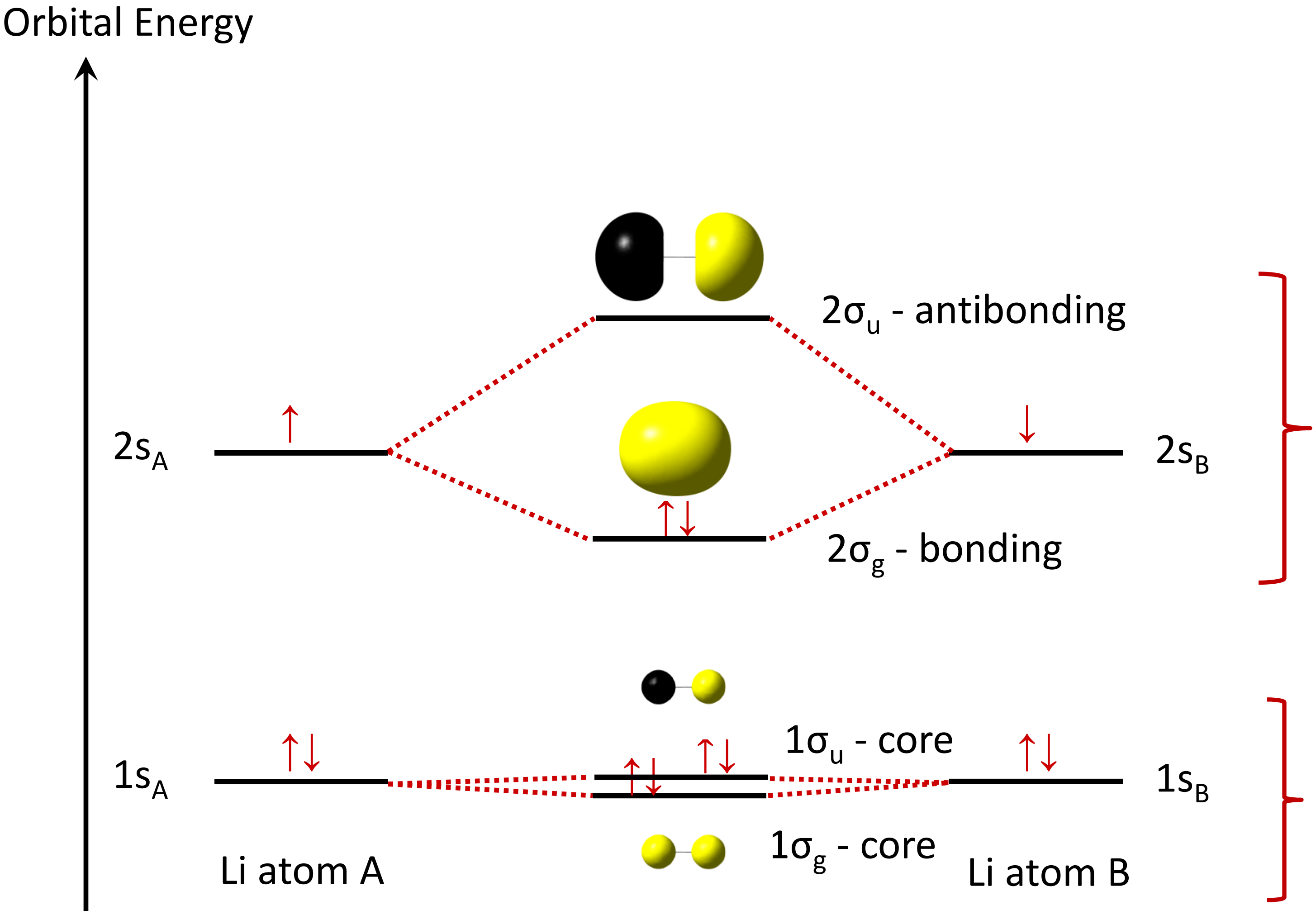


$1\sigma_g$ orbital – stays the same



$1\sigma_u$ orbital – changes sign

Molecular orbital diagram for Li_2

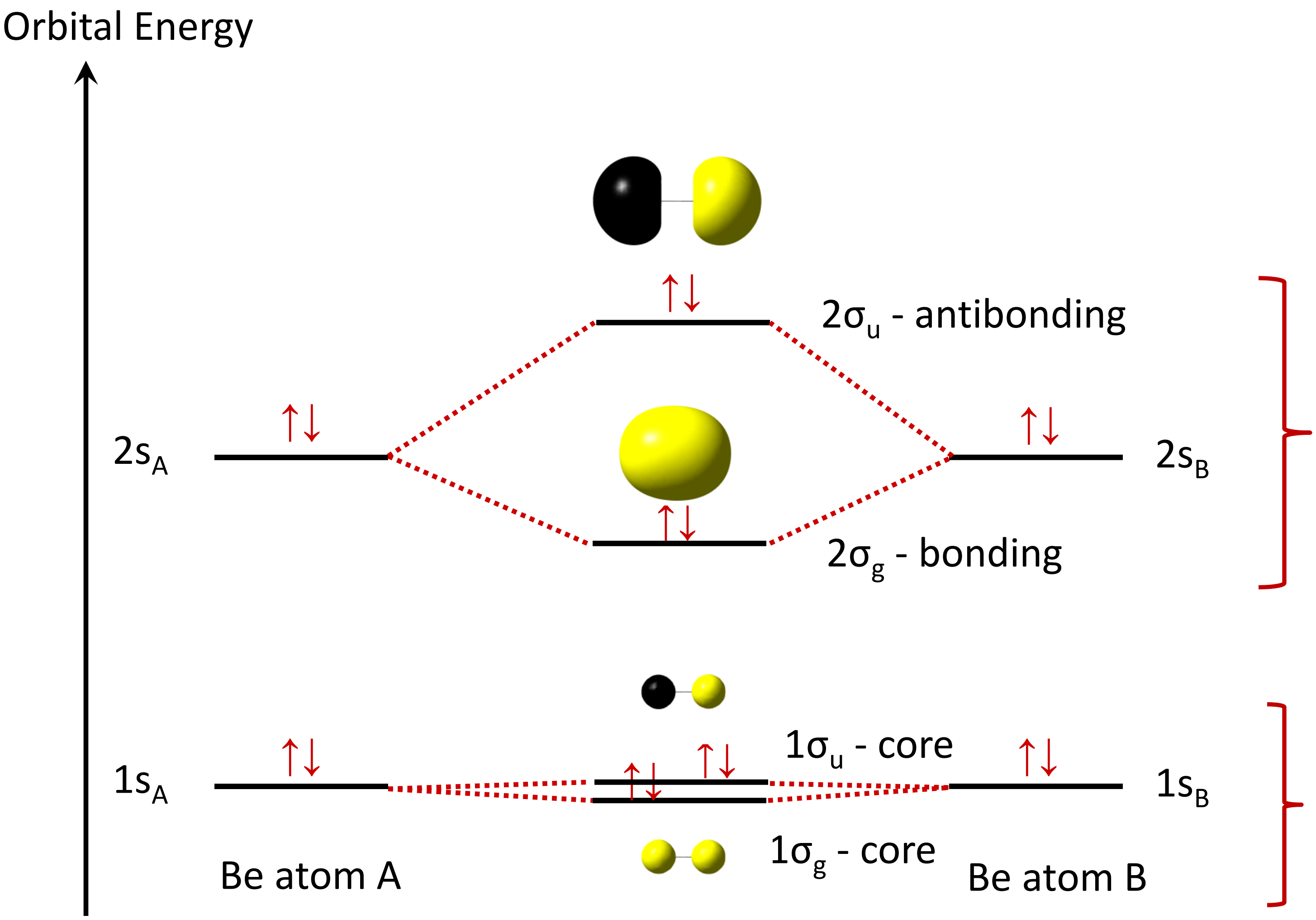


Valence orbitals- Responsible for chemical bonds.

Core orbitals- No overlap, too close to the nucleus; no contribution to bonding. **Much lower in energy than shown!**

B.O. = [2-0]/2 = 1 for Li_2. Li_2 has a single bond (MUCH weaker than H_2, though).

Molecular orbital diagram for Be_2



Orbital Energy

$2\sigma_u$ - antibonding

$2s_A$

$2s_B$

$2\sigma_g$ - bonding

$1s_A$

$1\sigma_u$ - core

$1s_B$

$1\sigma_g$ - core

Be atom A

Be atom B

Valence orbitals- Responsible for chemical bonds.

Core orbitals- No overlap, too close to the nucleus; no contribution to bonding. Much lower in energy than shown!

B.O. = [2-2]/2 = 0 for Be_2. Be_2 has a bond order of 0 and should be unbound. This is oversimplified, and it is very weakly bound.

When p orbitals get involved, the shapes get more interesting!

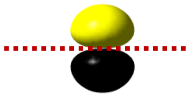
With p orbitals, you can get two different types of bonds:
σ bonds and π bonds.

σ orbitals have cylindrical symmetry about the molecular axis, no nodal planes containing the axis

π orbitals have one nodal plane containing the axis

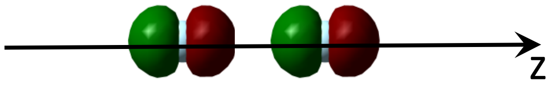
Looking down the axis:

Cylindrical Symmetry, no nodal planes: σ orbital



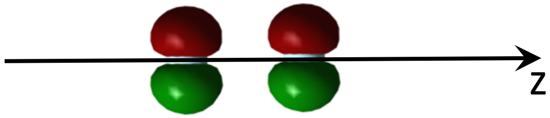
One nodal plane: π orbital

σ interaction of 2p orbitals:



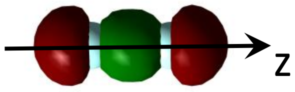
Atom A   Atom B

π interaction of 2p orbitals:

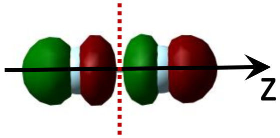


Atom A   Atom B

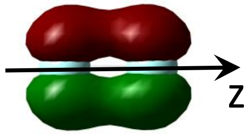
In each orientation, the orbitals can approach so they overlap constructively to form bonding orbitals, or destructively to form antibonding orbitals.



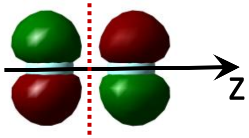
$-2p_{zA} + 2p_{zB}$
$3\sigma_g$
Bonding



$2p_{zA} + 2p_{zB}$
$3\sigma_u{}^*$
Antibonding

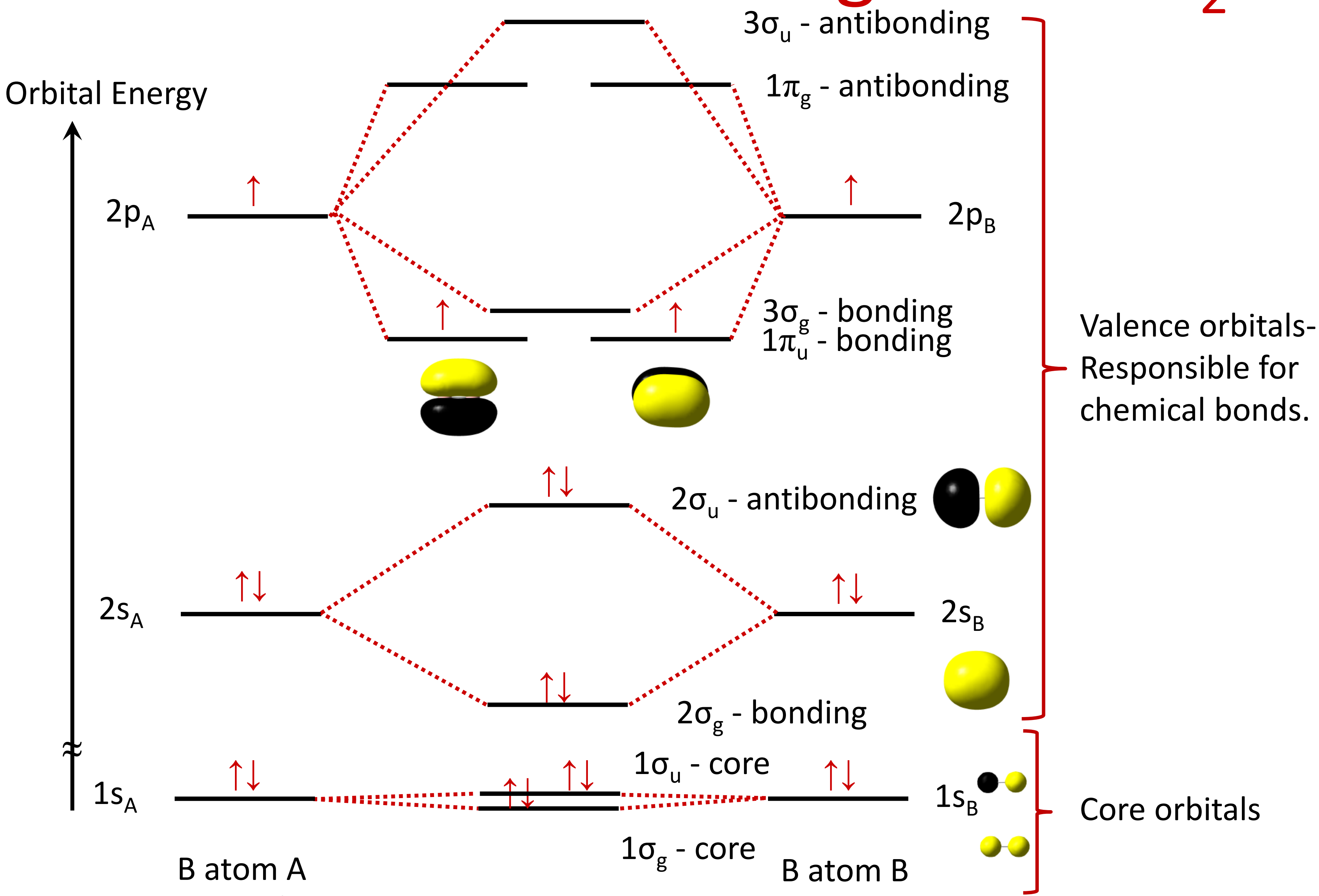


$2p_{xA} + 2p_{xB}$
$1\pi_u$
Bonding



$-2p_{xA} + 2p_{xB}$
$1\pi_g{}^*$
Antibonding

Molecular orbital diagram for B_2



Orbital Energy

$3\sigma_u$ - antibonding

$1\pi_g$ - antibonding

$2p_A$

$2p_B$

$3\sigma_g$ - bonding

$1\pi_u$ - bonding

Valence orbitals-
Responsible for
chemical bonds.

$2\sigma_u$ - antibonding

$2s_A$

$2s_B$

$2\sigma_g$ - bonding

$1\sigma_u$ - core

$1s_A$

$1s_B$

Core orbitals

$1\sigma_g$ - core

B atom A

B atom B

B.O. = [4-2]/2 = 1 for B_2. B_2 has a bond order of 1.

Ground state electronic configurations of diatomic molecules

			Bond energy
H_2	$1\sigma_g^2$	BO = 1	4.478 eV
He_2	$1\sigma_g^2\ 1\sigma_u^2$	BO = 0	0.00000008 eV
Li_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2$	BO = 1	1.05 eV
Be_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2$	BO = 0	0.1 eV
B_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^2$	BO = 1	3.05 eV
C_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4$	BO = 2	6.25 eV
N_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2$	BO = 3	9.71 eV (Strong bond!)
O_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2$	BO = 2	5.12 eV
F_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4$	BO = 1	1.63 eV
Ne_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\sigma_u^2$	BO = 0	0.002 eV

FYI: 1 eV = 23.061 kcal/mol = 96.485 kJ/mol

Bond energy sort of tracks the bond order, but all bonds are not created equal!
The single bonds of H_2, Li_2, B_2, and F_2 have bond energies of 4.478, 1.05, 3.05, and 1.63 eV, respectively!

This has a lot to do with how well the orbitals overlap – good overlap means a strong bond.
The 2s orbital of Li is too large and fluffy for good overlap. It’s even worse in Na_2, K_2, *etc.*

Between N_2 and O_2 the orbital ordering changes. Why?

H_2	$1\sigma_g^2$	
He_2	$1\sigma_g^2\ 1\sigma_u^2$	
Li_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2$	
Be_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2$	$1\pi_u$ lies below $3\sigma_g$
B_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^2$	
C_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4$	
N_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2$	
O_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2$	$3\sigma_g$ lies below $1\pi_u$
F_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4$	
Ne_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\sigma_u^2$	

This has to do with how well the 2s and 2p orbitals can mix. If they can mix, it is really good for bonding. What happens if they mix?

Between N_2 and O_2 the orbital ordering changes. Why?

H_2	$1\sigma_g^2$
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B_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^2$
C_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4$
N_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2$
O_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2$
F_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4$
Ne_2	$[1\sigma_g^2\ 1\sigma_u^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\sigma_u^2$

$1\pi_u$ lies below $3\sigma_g$

$3\sigma_g$ lies below $1\pi_u$

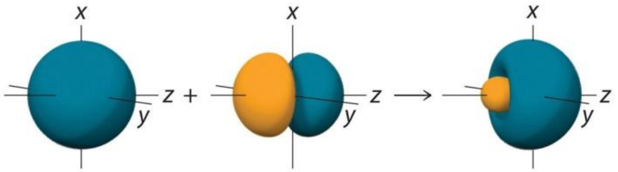
This has to do with how well the 2s and 2p orbitals can mix. If they can mix, it is really good for bonding. What happens if they mix?

s-p hybrid orbitals!

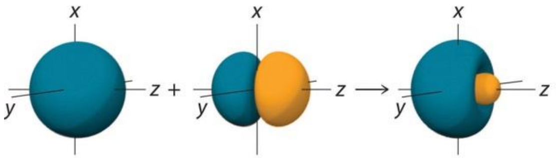
sp-hybrid orbitals

sp-hybrids are formed by first adding (or subtracting) the 2p orbital to the 2s orbital. Since two atomic orbitals are combined in this way, two hybrid orbitals are obtained.

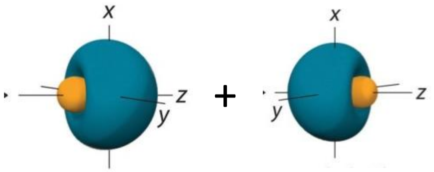
Adding the $2s + 2p_z$ gives
an orbital pointed toward +z:



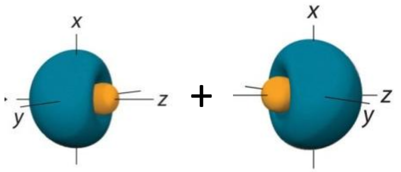
Subtracting $2s - 2p_z$ gives
an orbital pointed toward –z:



If you form sp-hybrids on both atoms, you get 4 orbitals that can be combined to form a really good bonding orbital and a really bad bonding orbital,
along with two antibonding orbitals:

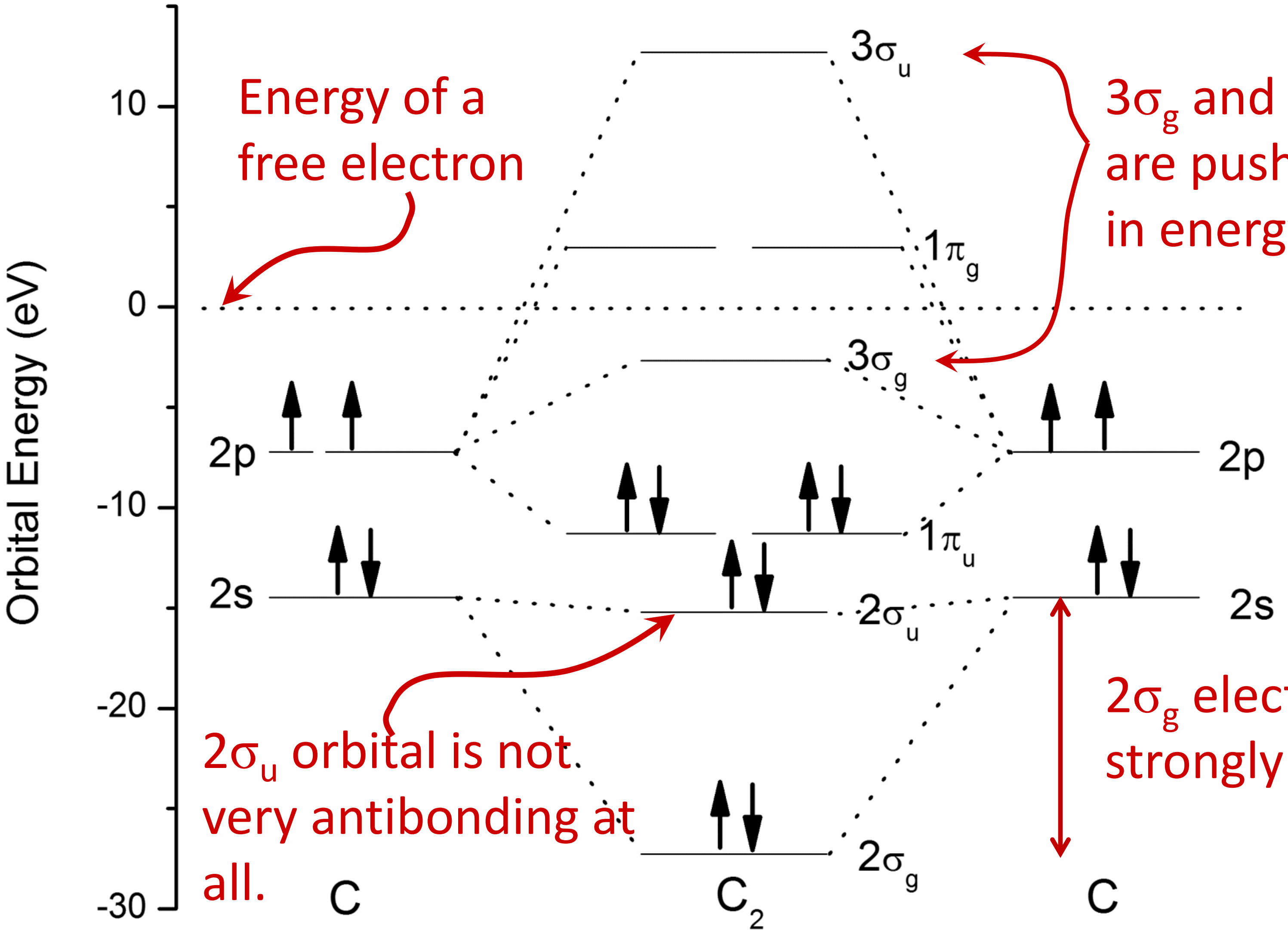


great overlap → good bonding orbital
hybridization lowers the energy of $2\sigma_g$



poor overlap → poor bonding orbital
hybridization increases the energy of $3\sigma_g$, so it lies above the $1\pi_u$ orbital in B_2, C_2, and N_2

Calculated MO diagram for C_2



Energy of a free electron

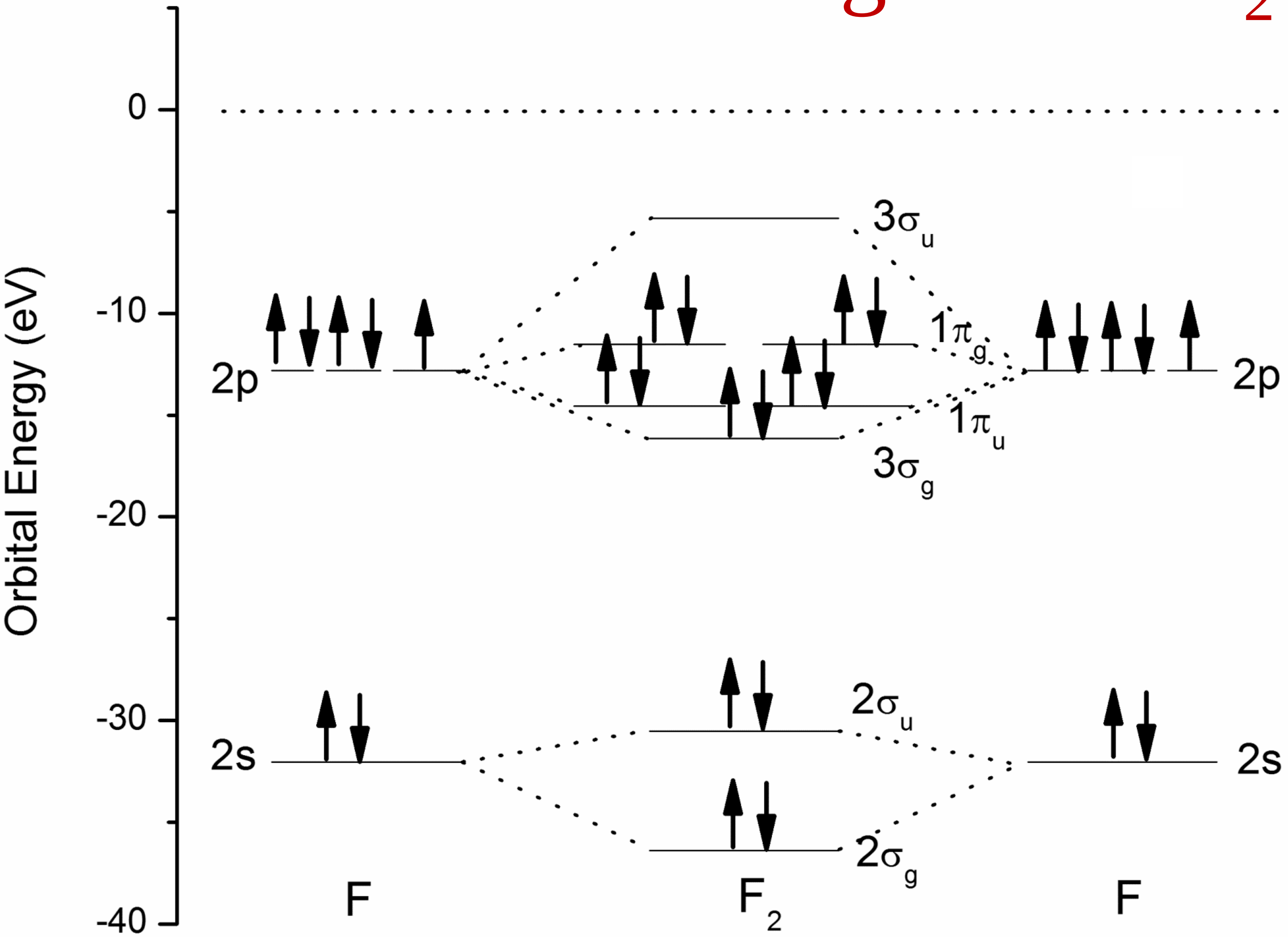
$3\sigma_g$ and $3\sigma_u$ orbitals are pushed way up in energy

$2\sigma_u$ orbital is not very antibonding at all.

$2\sigma_g$ electrons are strongly bonding

2s-2p mixing works well in C because the 2s and 2p orbitals are close in energy.

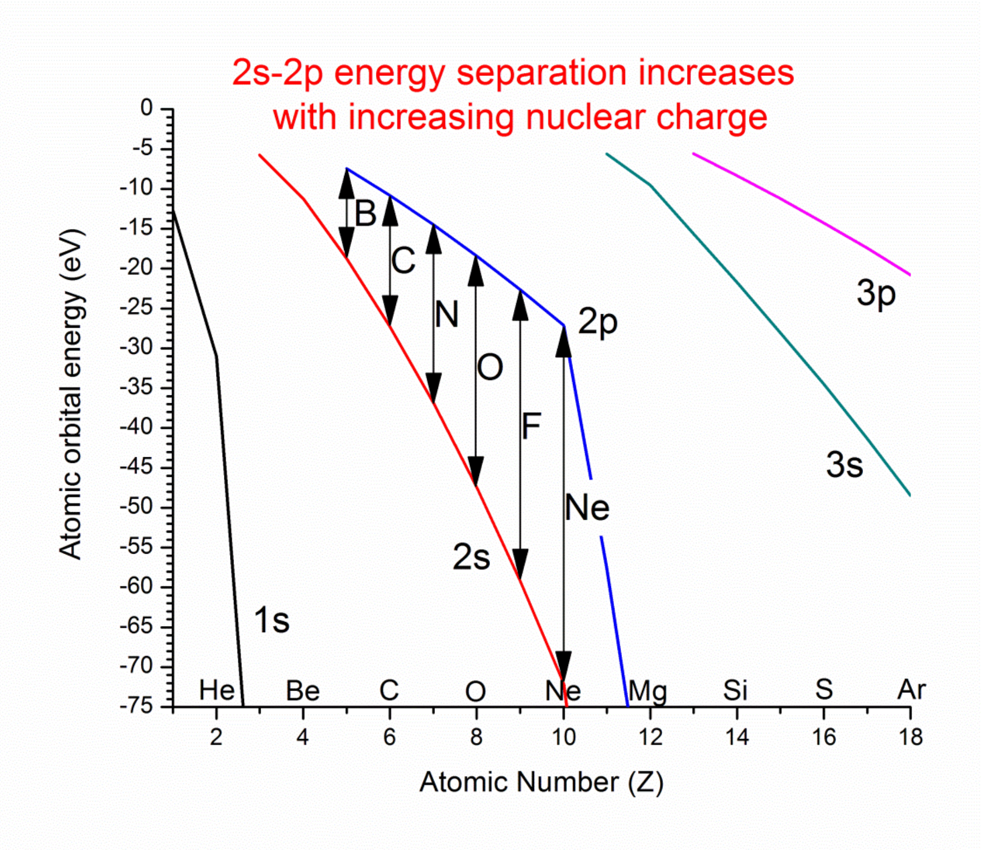
A calculated MO diagram for F_2



2s-2p mixing works badly in F because the 2s and 2p orbitals are far apart in energy.

Why does s-p hybridization change as you go across the p block?

As you go across the series, you're adding charge to the nucleus, so the electrons are held more and more tightly, until you have to go to the next subshell. The orbitals just keep dropping in energy as you go across. Also, the 2s drops faster than the 2p.

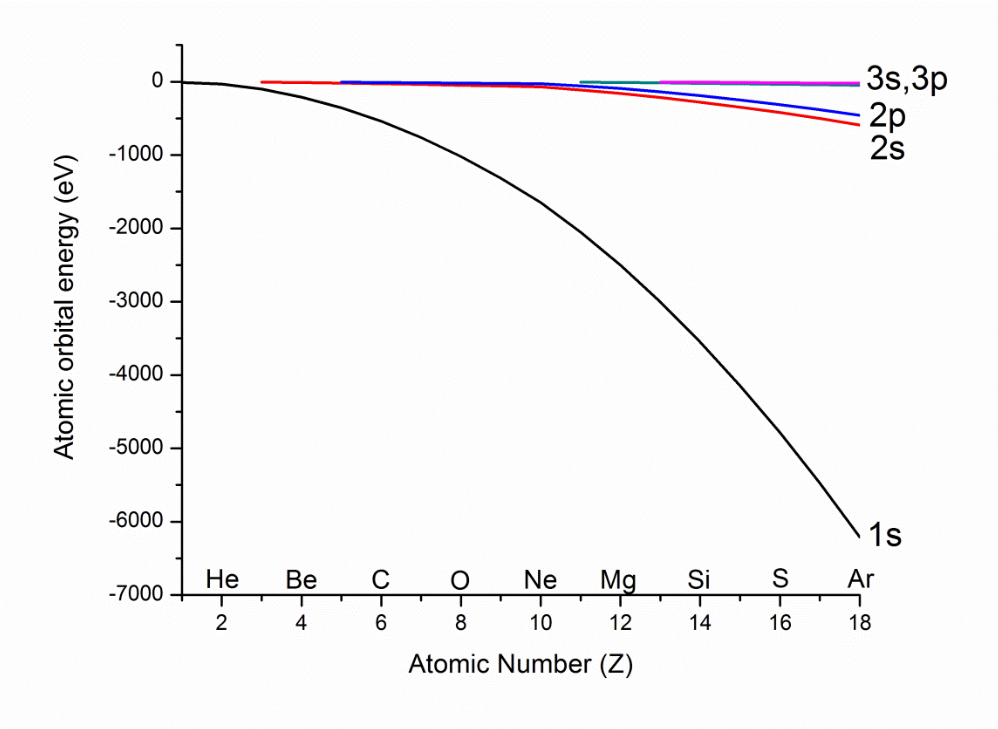


In B_2, C_2, and N_2, the 2s and 2p orbitals are close enough in energy that they can mix to form 2s-2p hybrids. In the process the $2\sigma_g$ (which is no longer purely 2s) becomes a better bonding orbital and the $3\sigma_g$ (which is also no longer purely 2p) becomes a worse bonding orbital.

This interaction is strong enough to reverse the order of the $3\sigma_g$ and $1\pi_u$ orbitals between B, C, and N, where the 2s and 2p are close in energy and the $1\pi_u$ lies lower, and O, F, and Ne, where the $3\sigma_g$ lies lower.

Where are the $1\sigma_g$ and $1\sigma_u$ orbitals in C_2 and F_2?

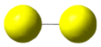
If we look at the atomic orbital energies as a function of atomic number, the energies drop very rapidly:



As they drop, they get much smaller too:

H_2 $1\sigma_g$

Li_2 $1\sigma_g$



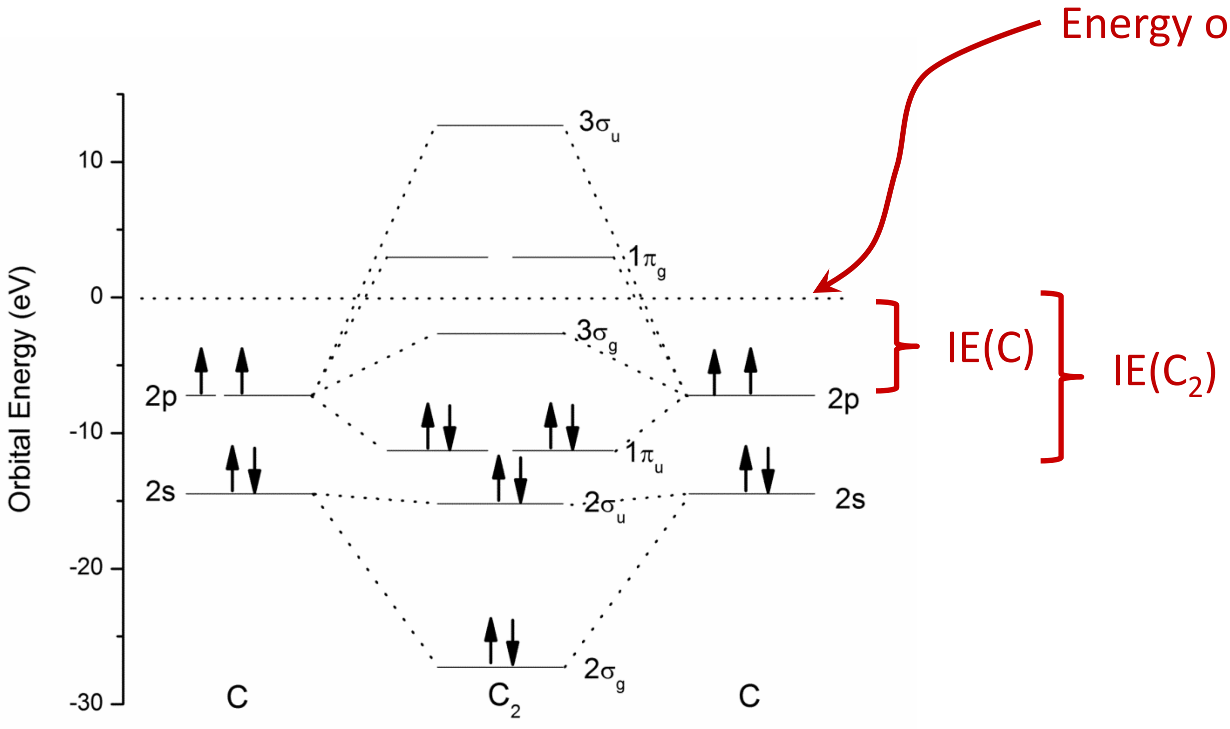
No orbital overlap implies a core orbital, not a valence orbital.

In C_2 and F_2, the ($1\sigma_g$, $1\sigma_u$) orbitals have dropped out of sight: -309 eV and -675 eV!!

Homonuclear Diatomic Molecules

<u>QUESTIONS FOR AP STUDENTS</u>:

1. Is the ionization energy of X_2 greater than that of the atom, or less than that of the atom? Let's compare C_2 and F_2.



Energy of a free electron

IE(C)

IE(C_2)

Because the HOMO of the C_2 molecule is a bonding orbital, that electron is held more tightly than it is in the atom. Thus, we expect IE(C_2) > IE(C).

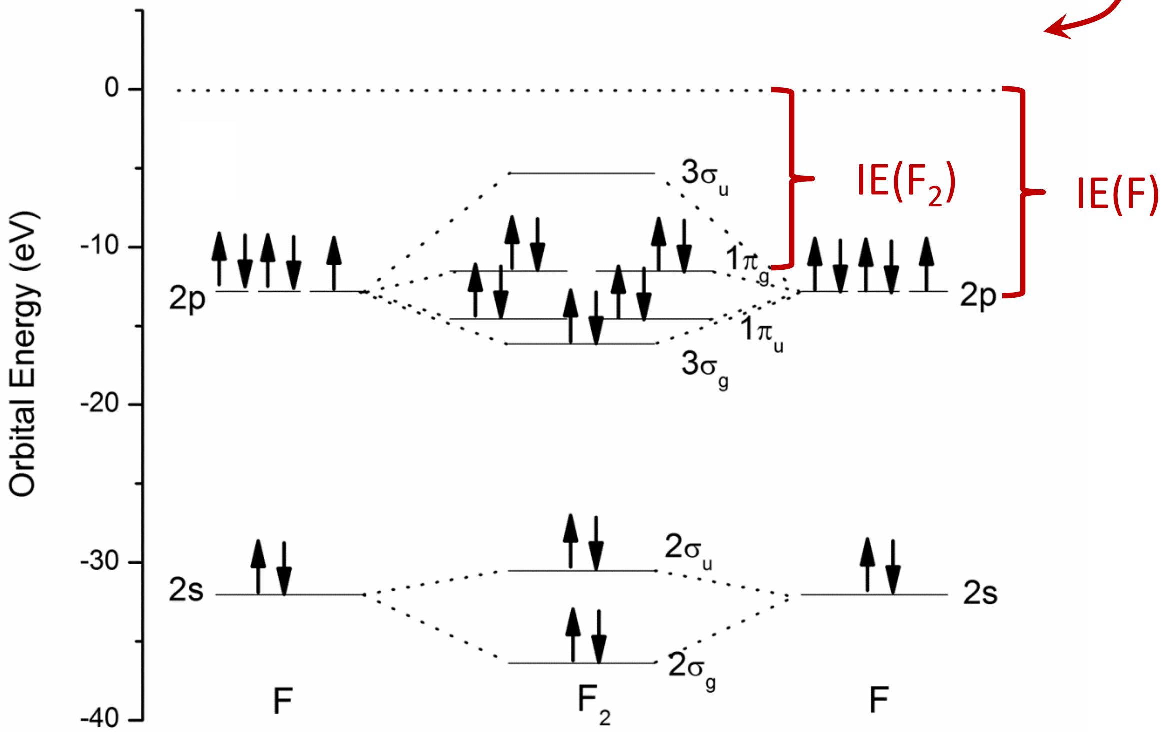
Experimentally:
IE(C_2) = 11.866 eV
IE(C) = 11.260 eV
YES! Just as we predicted.

Homonuclear Diatomic Molecules

QUESTIONS FOR AP STUDENTS:

1. Is the ionization energy of X_2 greater than that of the atom, or less than that of the atom? Let's compare C_2 and F_2.

Energy of a free electron



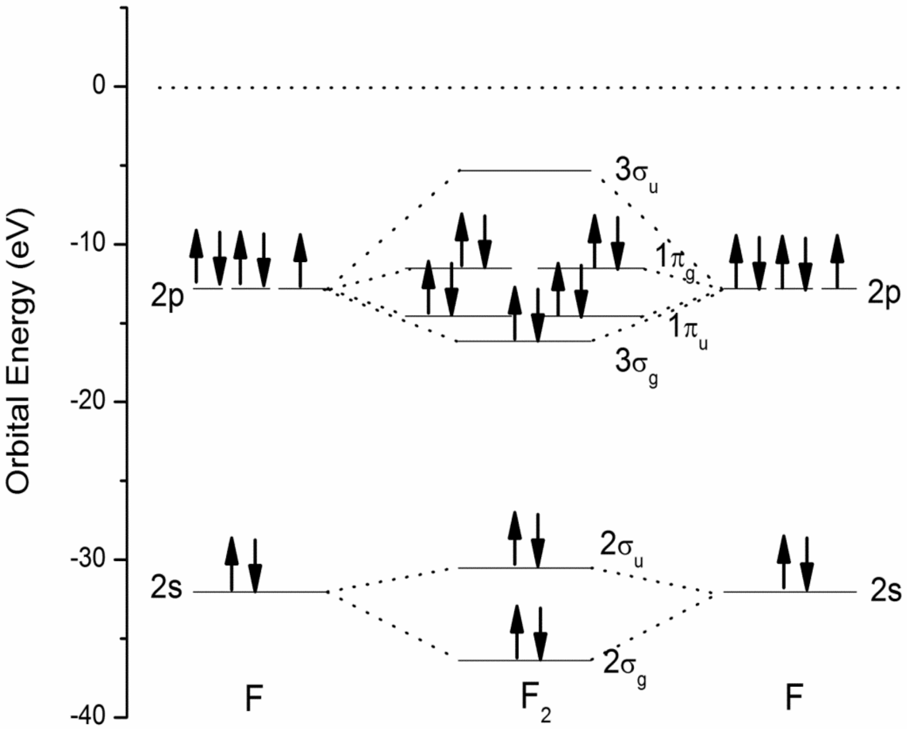
Because the HOMO of the F_2 molecule is an antibonding orbital, that electron is held less tightly than it is in the atom. Thus, we expect IE(F_2) < IE(F).

Experimentally:
IE(F_2) = 15.70 eV
IE(F) = 17.42 eV
YES! Just as we predicted.

Homonuclear Diatomic Molecules

QUESTIONS FOR AP STUDENTS:

2. Is the bond energy of X_2 greater than that of X_2^+, or less? Let's compare F_2 and F_2^+.



For F_2, the bond order is 1, because there are 8 bonding electrons and 6 antibonding electrons. When it is ionized, we remove an antibonding electron, so the bond order of F_2^+ is 1.5.

The bond dissociation energy of F_2^+ should be greater than that of F_2.

Experimentally, the bond energies are:

F_2	$D_0(F_2) = 1.63$ eV
F_2^+	$D_0(F_2^+) = 3.35$ eV

EXACTLY AS EXPECTED!

These quantities are linked by a thermochemical cycle: $D_0(X_2) + IE(X) = IE(X_2) + D_0(X_2^+)$

Homonuclear Diatomic Molecules

QUESTIONS FOR AP STUDENTS:

3. Is X_2 diamagnetic (weakly repelled by a magnetic field) or paramagnetic (attracted into a magnetic field).

This is just a hidden way of asking if the molecule has unpaired electrons. If it has unpaired electrons, the unpaired spin causes it to be paramagnetic.

Examples of paramagnetic molecules that are stable [ignoring core electrons]:

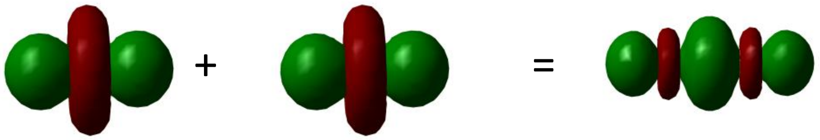
O_2 $2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2$ (Here the last two $1\pi_g$ electrons go into the $1\pi_g$ orbitals with parallel spins, causing O_2 to be a high spin molecule that is attracted into a magnetic field.)

NO $3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi^4\ 2\pi^1$ (Here there is only one unpaired electron, but that is enough! NO is a paramagnetic molecule.)

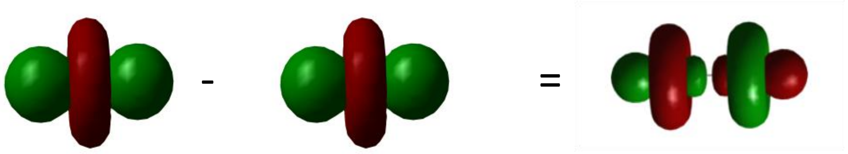
All radicals (molecules with unpaired spins) are paramagnetic.

d-orbital bonding

If the bonding is between transition metals, you can get d-orbital bonding.
For the internuclear axis defined as the z-axis, you can combine the d_{z^2} orbtals to get bonding and antibonding dσ orbitals:



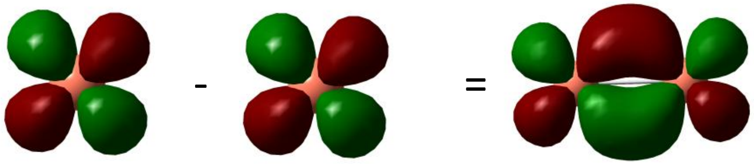
dσ bonding orbital



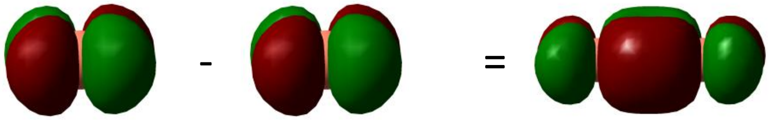
dσ* antibonding orbital

d-orbital bonding

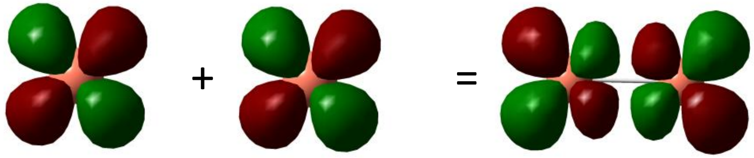
If you combine the d_{xz} orbitals (or the d_{yz} orbitals), you can get dπ bonding and antibonding orbitals.



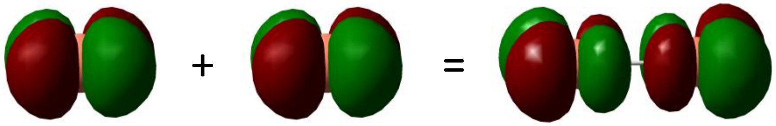
dπ bonding orbital



dπ bonding orbital



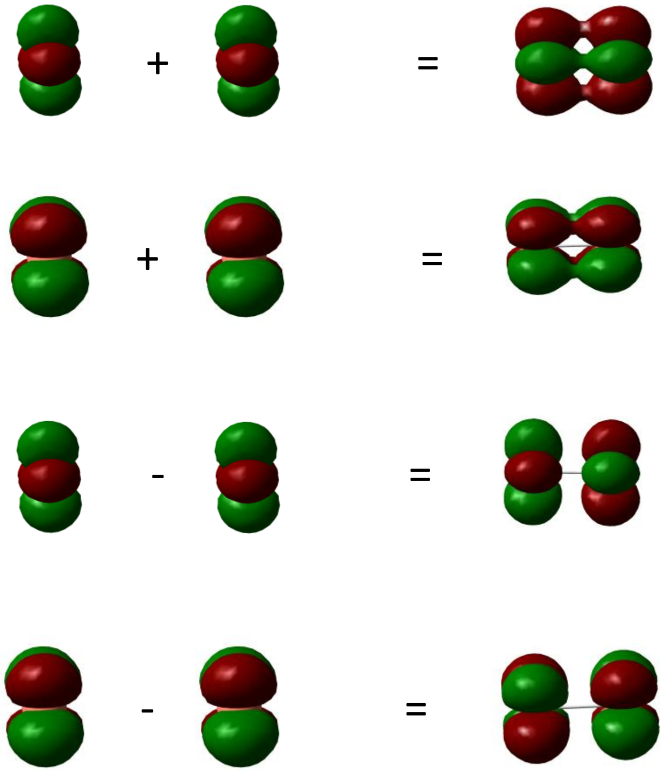
dπ* antibonding orbital



dπ* antibonding orbital

d-orbital bonding

If you combine the d_{xy} orbitals (or the d_{x2-y2} orbitals), you can get dδ bonding and antibonding orbitals.



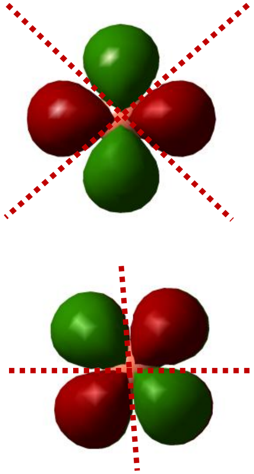
$d\delta_g$ bonding orbital

$d\delta_g$ bonding orbital

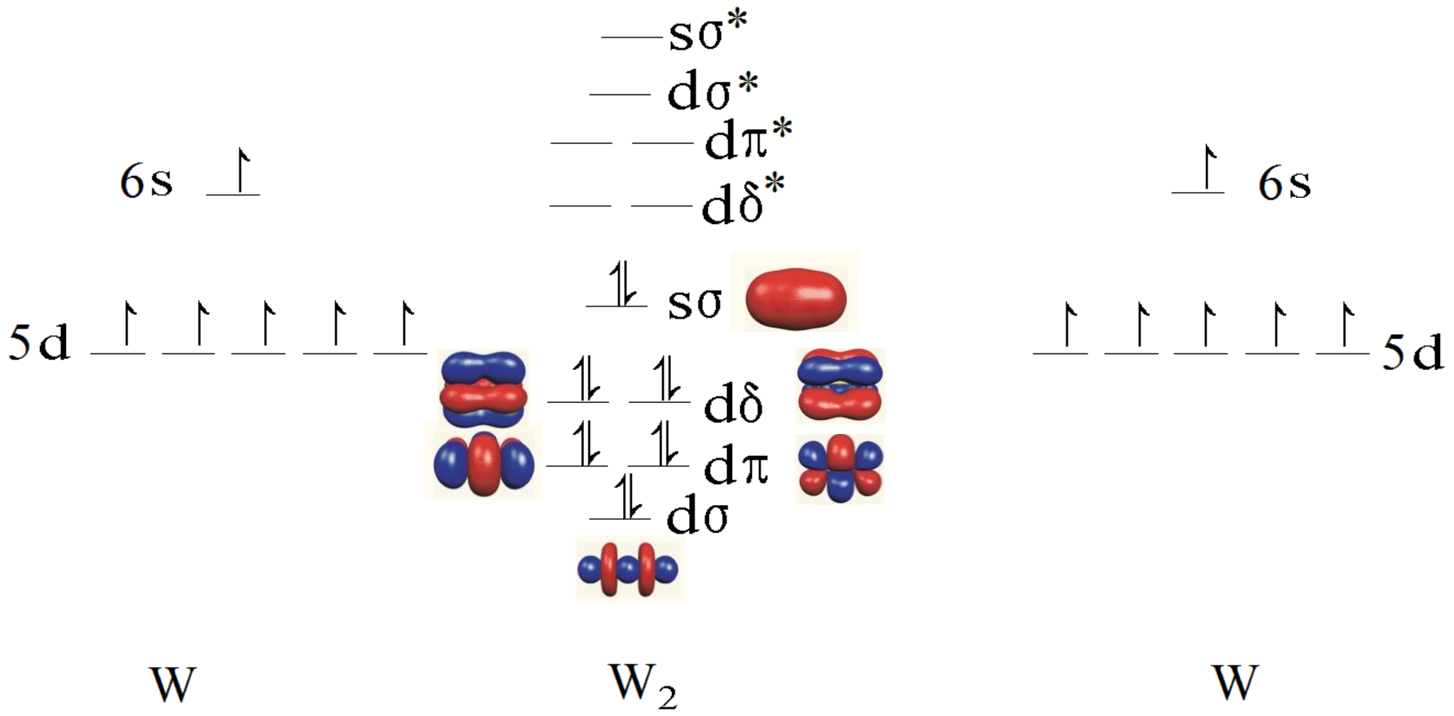
$d\delta_u$ antibonding orbital

$d\delta_u$ antibonding orbital

Looking down the axis: Two nodal planes make these δ orbitals

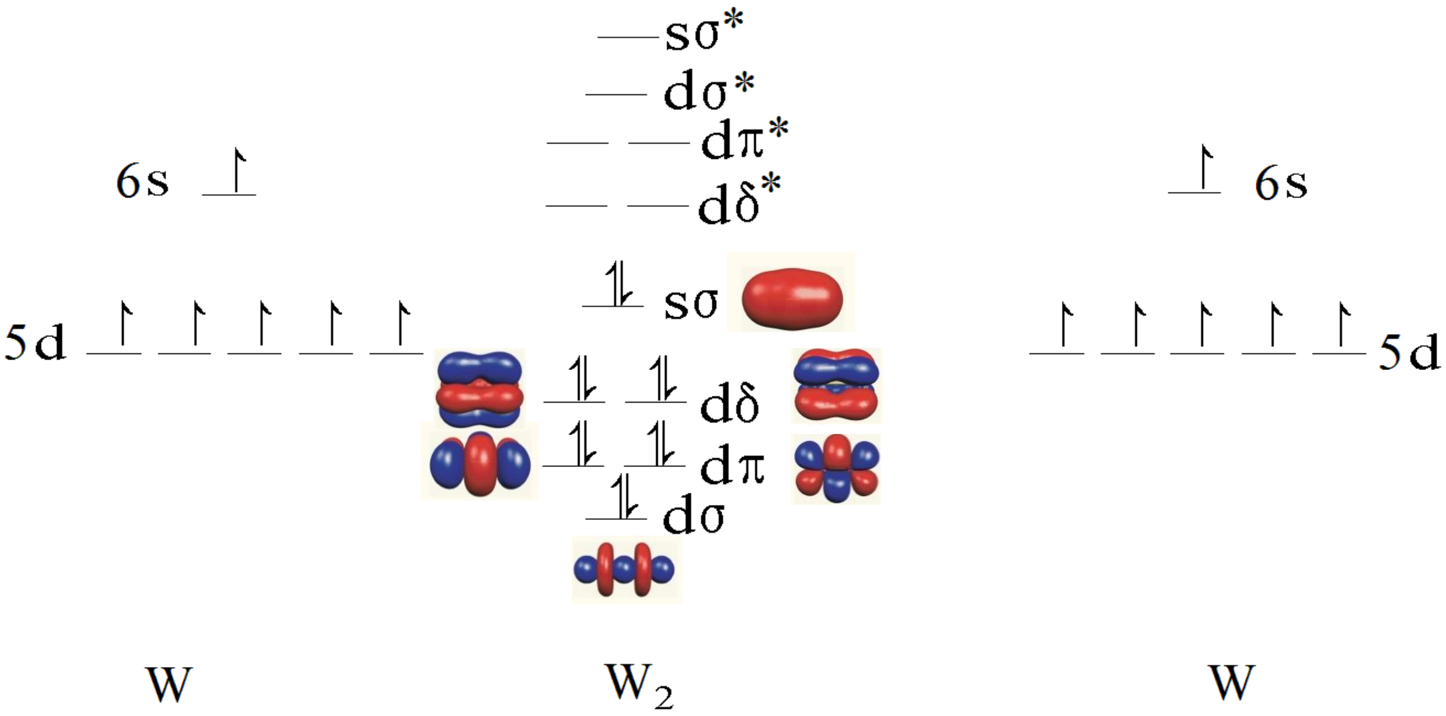


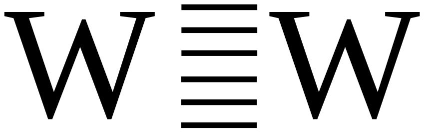
d-orbital bonding in W_2



Tungsten dimer has a sextuple bond!

d-orbital bonding in W_2



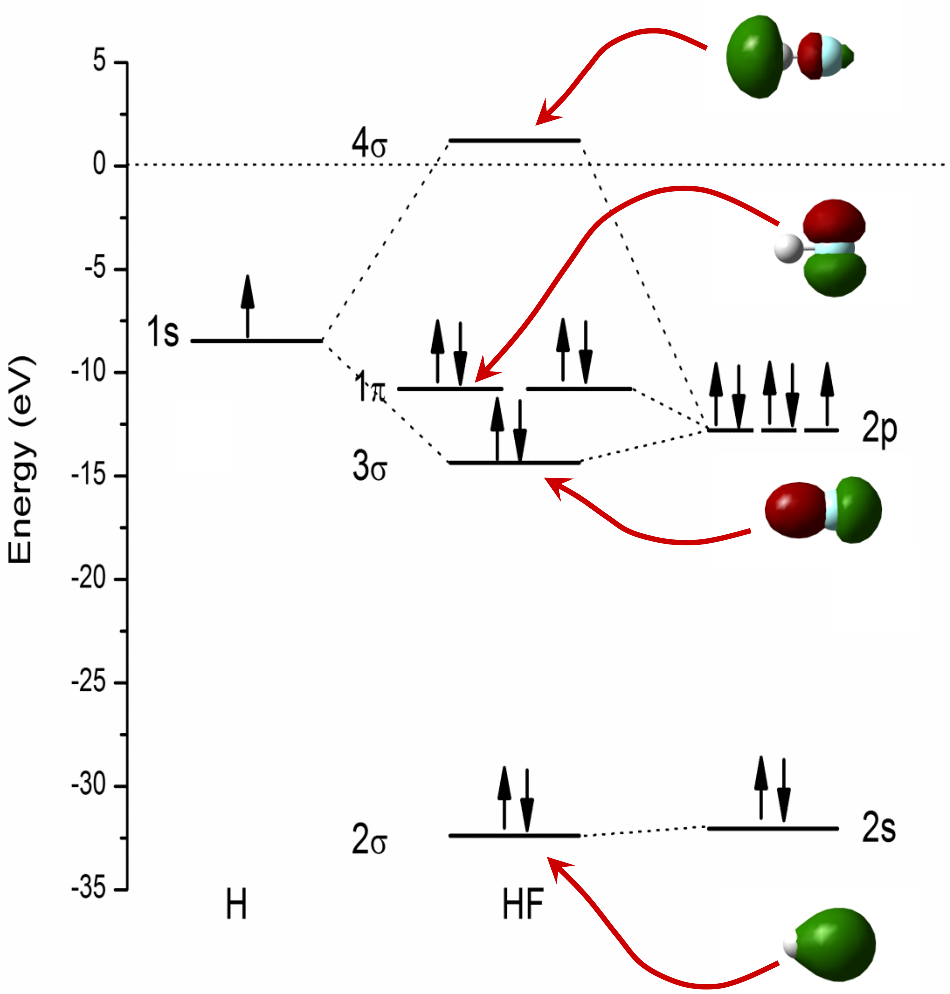


Rules for combining atomic orbitals:

1. Orbitals must be relatively close in energy
2. Orbitals must overlap significantly
3. Orbitals must have the same symmetry

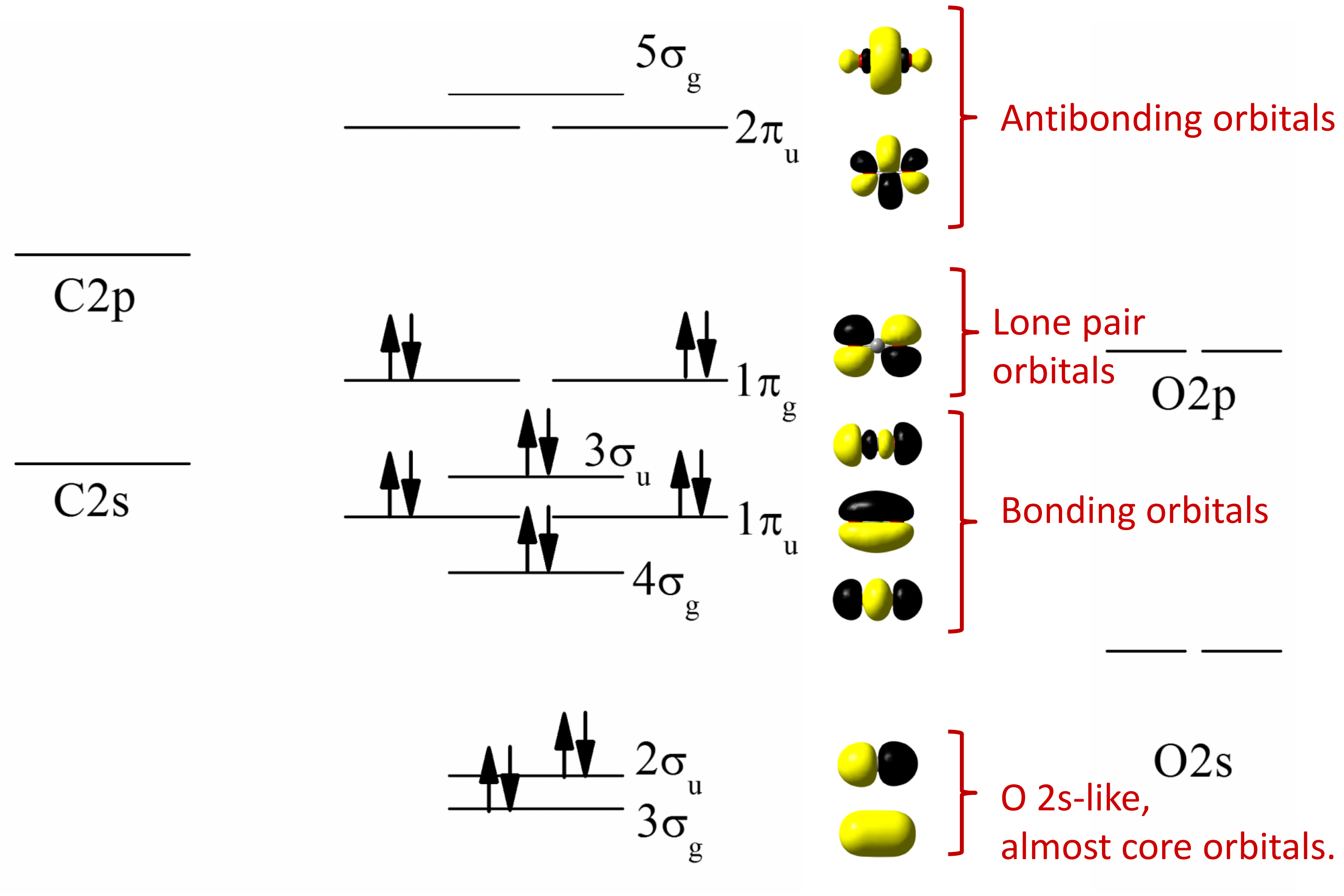
That’s it.

Heteronuclear Diatomic Molecules: HF



- In HF, the 2s orbital of F is so low in energy it barely combines with anything. (Rule1)
  As a result, the 2σ orbital is nearly purely $2s_F$ in character.
- Likewise, the $2p_x$ and $2p_y$ orbitals on F have π symmetry (one nodal plane). The nearest orbital on H with π symmetry is very high in energy (coming from H 2p), and can't combine. The 1π orbital of HF is almost purely $2p_F$ in character.
- The bond is formed from the 1s of H interacting with the $2p_z$ of fluorine, forming bonding (3σ) and antibonding (4σ) orbitals. No g/u designations here, because there's no center of symmetry.

Polyatomic Molecules: CO_2



Antibonding orbitals

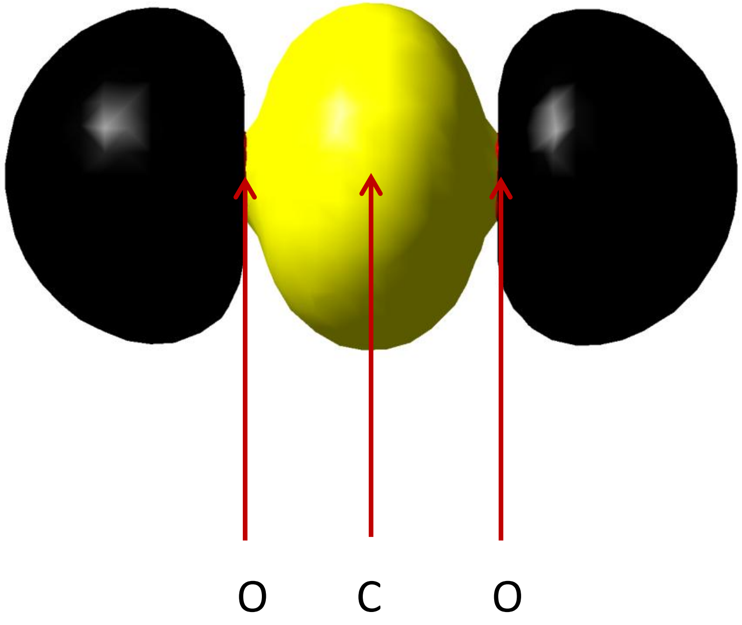
Lone pair orbitals

Bonding orbitals

O 2s-like,
almost core orbitals.

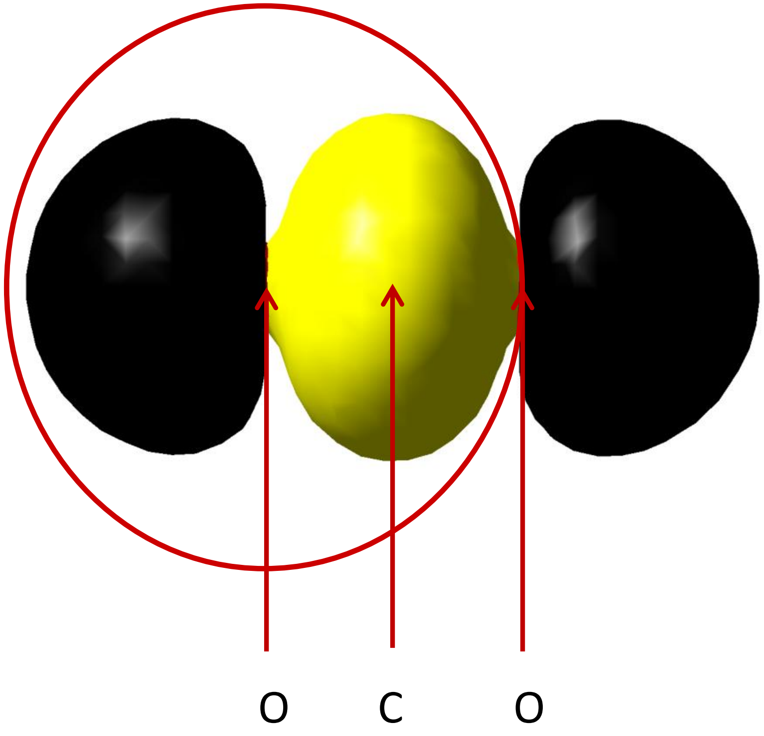
The 1s orbitals are extremely low in energy, way down in the basement!

Let's examine some of these to understand their bonding/nonbonding/antibonding character: $4\sigma_g$ orbital



What atomic orbitals have been used to make this molecular orbital?

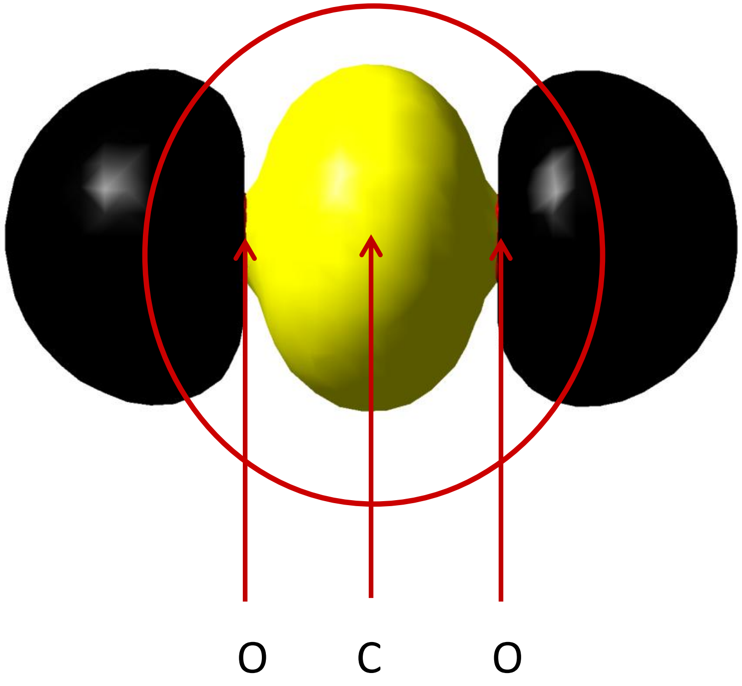
Let’s examine some of these to understand their bonding/nonbonding/antibonding character: $4\sigma_g$ orbital



What atomic orbitals have been used to make this molecular orbital?

Around the O atoms, the orbital looks like a $2p_z$ atomic orbital.

Let's examine some of these to understand their bonding/nonbonding/antibonding character: $4\sigma_g$ orbital

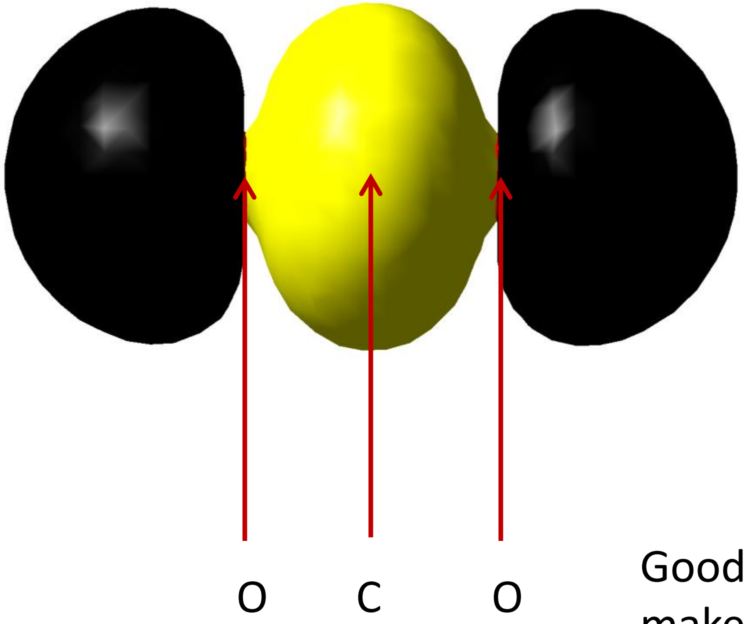


What atomic orbitals have been used to make this molecular orbital?

Around the C atom, the orbital looks like a 2s atomic orbital.

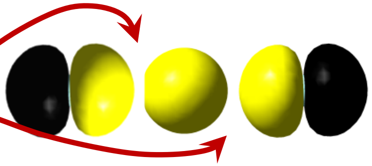
Let’s examine some of these to understand their bonding/nonbonding/antibonding character:

$4\sigma_g$ orbital



Overall, it looks like a combination of two O $2p_z$ orbitals and a C 2s orbital:

Exploded view

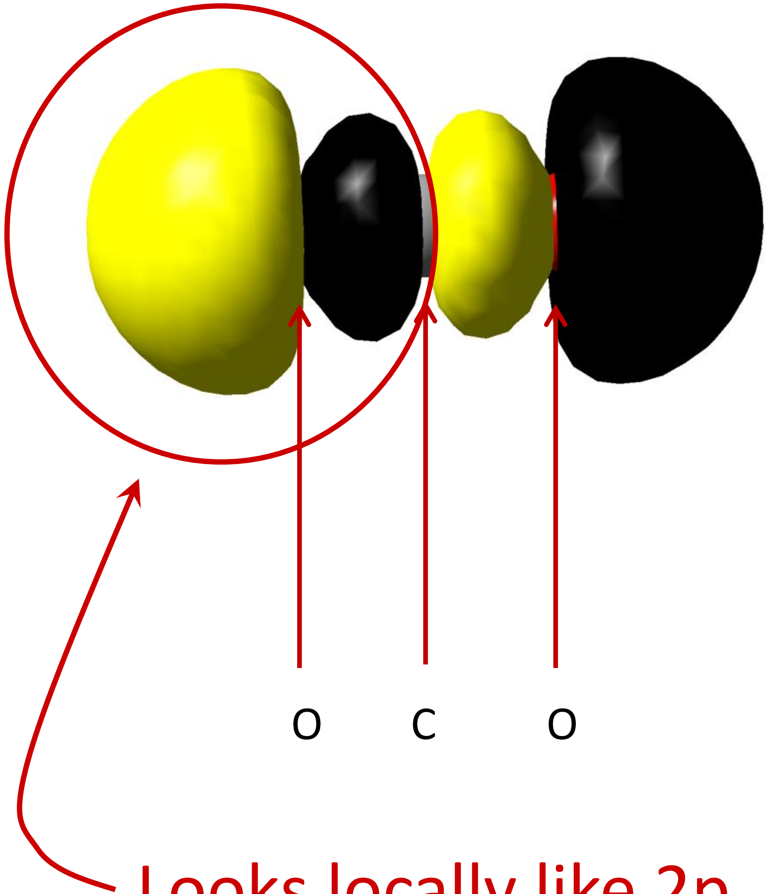


Good overlap makes this a good bonding orbital!

Bringing the atoms together

Fully overlapped and bonded

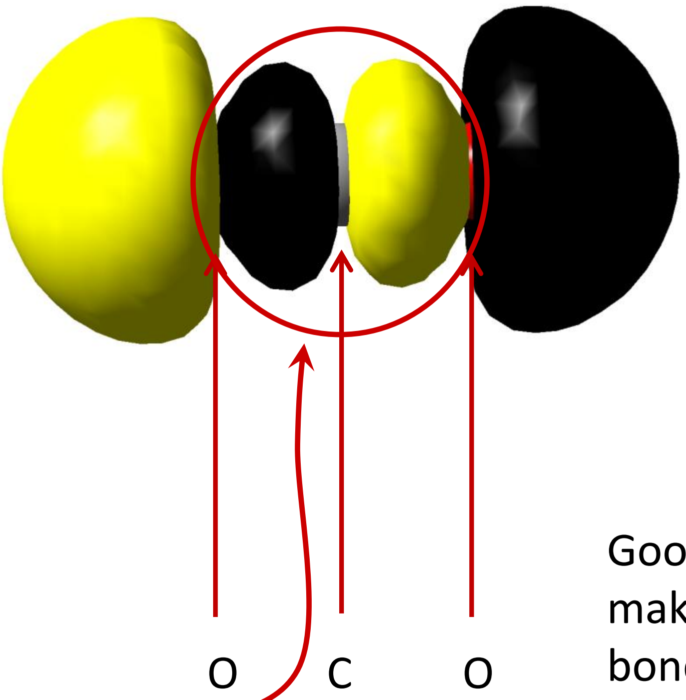
What about the $3\sigma_u$ orbital?



Looking closely at this, this orbital looks like a combination of $2p_z$ orbitals on all three atoms.

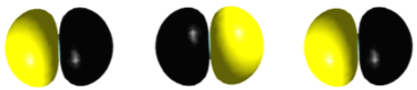
Looks locally like $2p_z$ around the O atom.

What about the $3\sigma_u$ orbital?



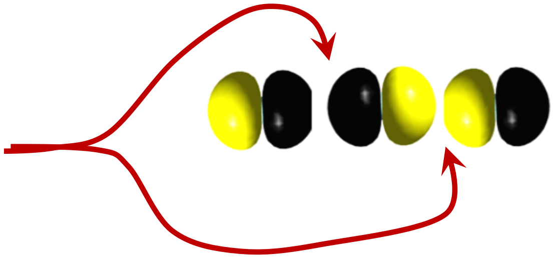
Looks locally like $2p_z$ around the C atom, too.

A combination of $2p_z$ orbitals on all three atoms.

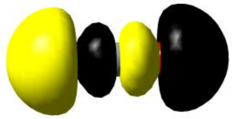


Exploded view

Good overlap makes this a good bonding orbital!

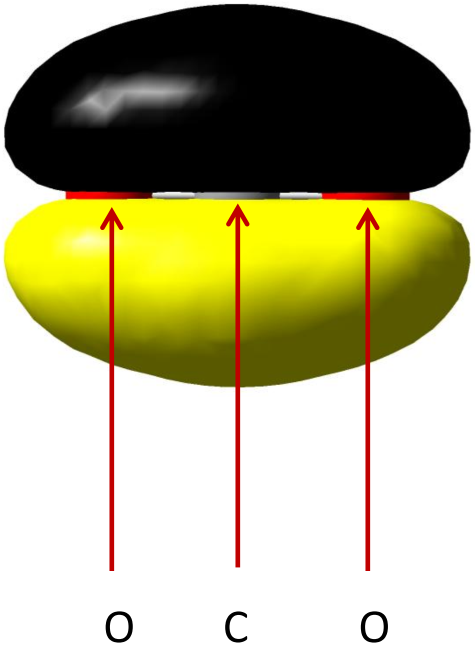


Bringing the atoms together

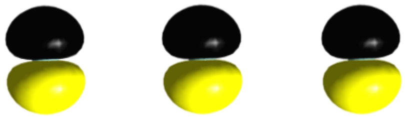


Fully overlapped and bonded

What about the $1\pi_u$ orbital?

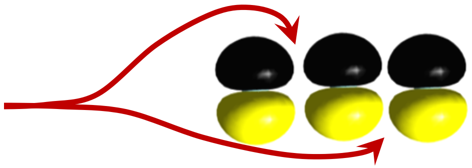


Obviously, this is a combination of all three $2p_x$ orbitals in phase



Exploded view

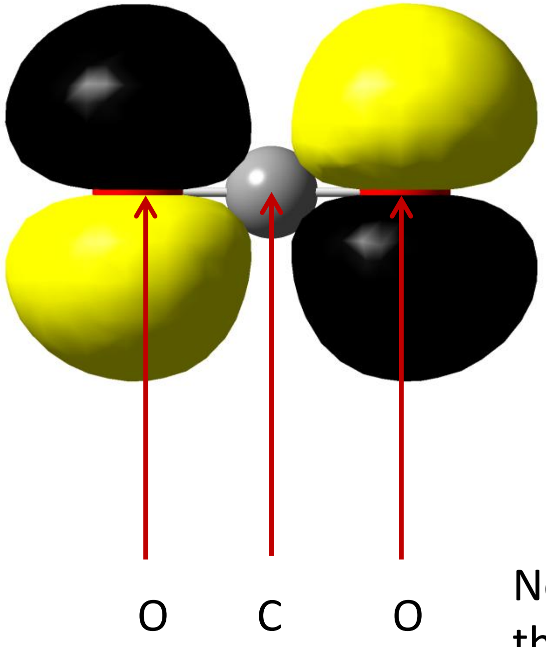
Good overlap makes this a good bonding orbital!



Bringing the atoms together

Fully overlapped and bonded

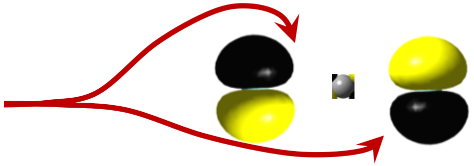
What about the $1\pi_g$ orbital?



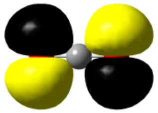
Again, a combination of $2p_x$ orbitals, but only on the O atoms

Exploded view

No contribution on the C atom, means no interaction. This is a nonbonding orbital.

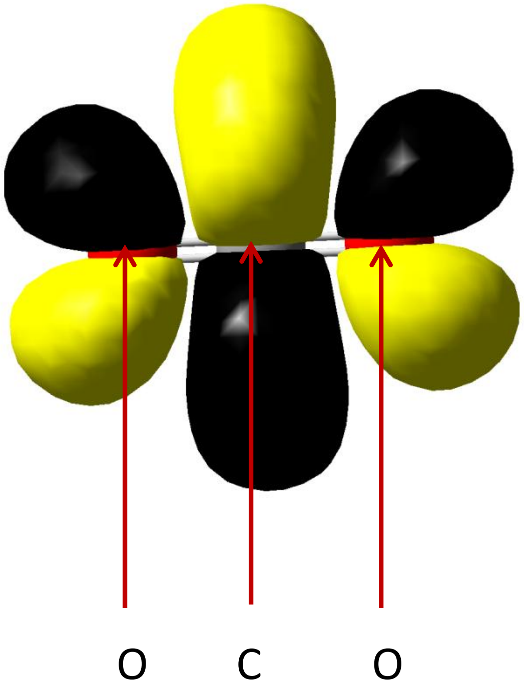


Bringing the atoms together

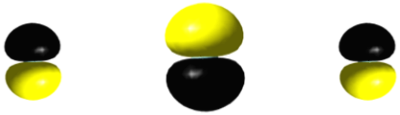


Fully overlapped and bonded

What about the $2\pi_u$ orbital?

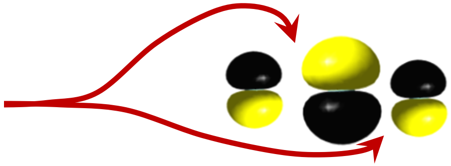


Again, a combination of $2p_x$ orbitals, on all three atoms



Exploded view

Uh-oh! The wavefunction changes sign between the atoms! This is an antibonding orbital.

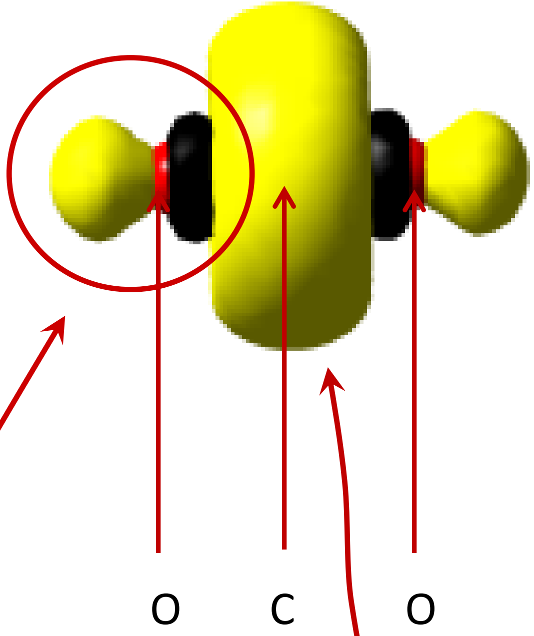


Bringing the atoms together

Fully overlapped

What about the $5\sigma_u$ orbital?

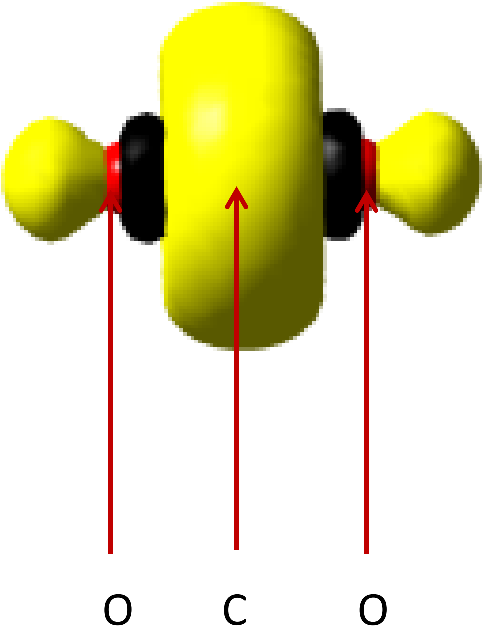
Looks like a combination of $2p_z$ orbitals on the O atoms and a 2s orbital on the C atom.



Looks like 2s on the C atom.

Looks locally like $2p_z$ around the O atom.

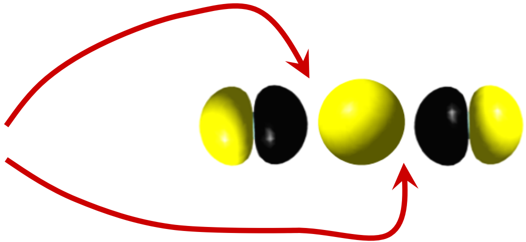
What about the $5\sigma_u$ orbital?



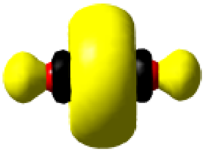
Looks like a combination of $2p_z$ orbitals on the O atoms and a 2s orbital on the C atom.

Exploded view

This is an antibonding orbital.



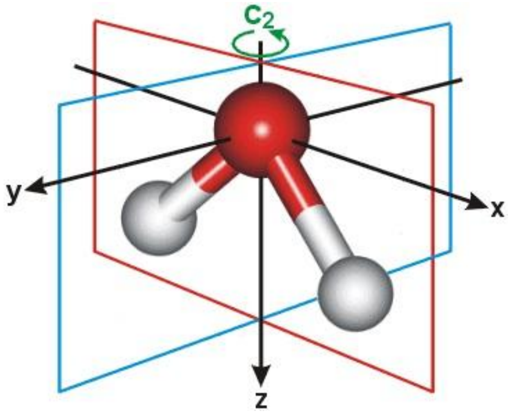
Bringing the atoms together



Fully overlapped and bonded

Molecular Orbitals Display the Symmetry of the Molecule

For example, water has two mirror planes (the xz plane and the yz plane) and a two-fold axis of rotation. All of the molecular orbitals of water are either symmetric (stay the same) or antisymmetric (change sign) when you apply these symmetries to them.

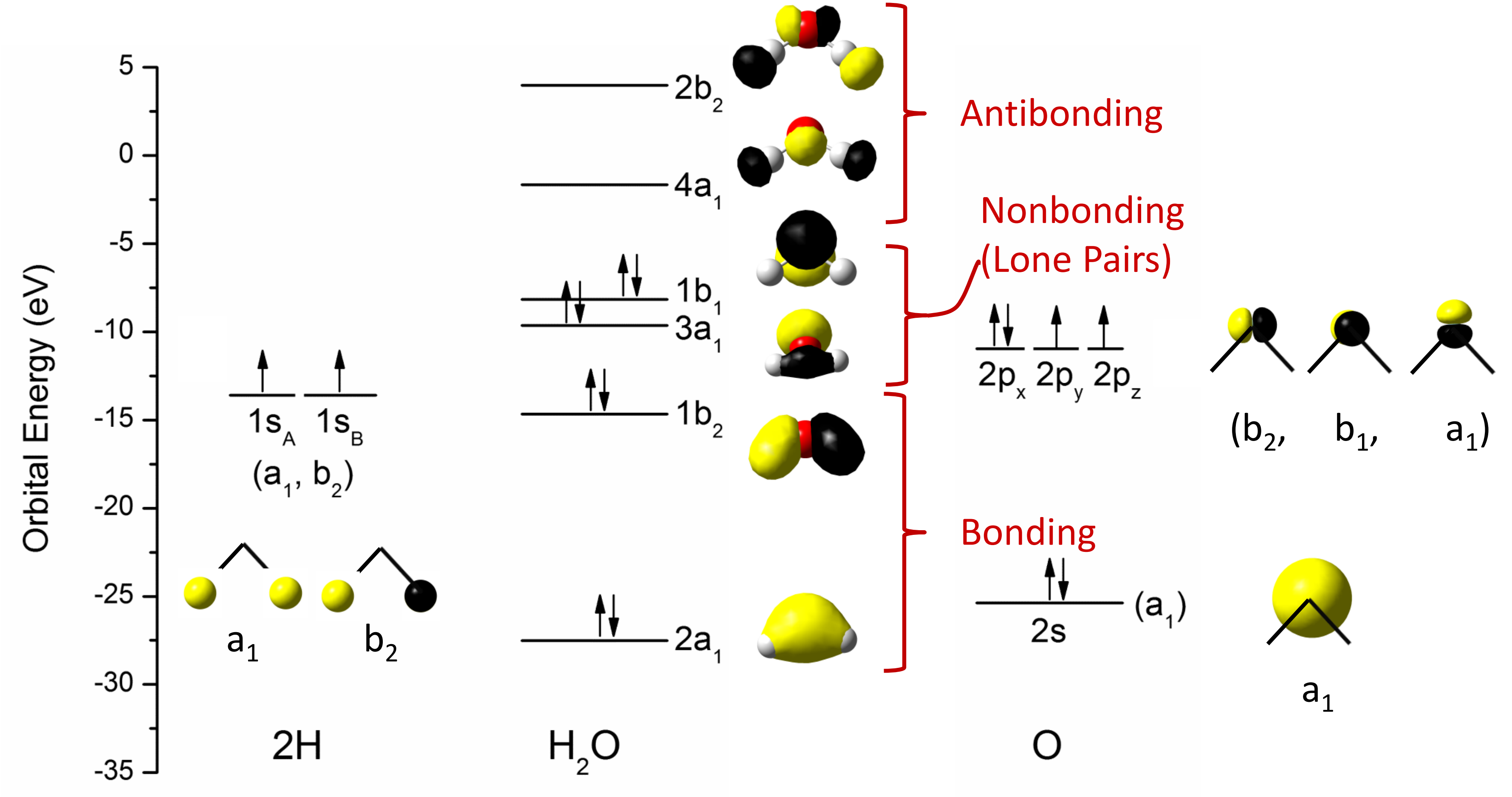


Possible Symmetry Types:

Label	Rotation	xz-plane	yz-plane
A_1	Symmetric	Symmetric	Symmetric
A_2	Symmetric	Antisymmetric	Antisymmetric
B_1	Antisymmetric	Symmetric	Antisymmetric
B_2	Antisymmetric	Antisymmetric	Symmetric

So what do the MOs of water look like?

Polyatomic Molecules: H_2O



The $1a_1$ orbital is a nearly pure O 1s orbital, way in the basement! (-520 eV)

More nodes means higher energy:

Consider the polyacetylene: $HC_{20}H$

H-C≡C-C≡C-C≡C-C≡C-C≡C-C≡C-C≡C-C≡C-C≡C-C≡C-H

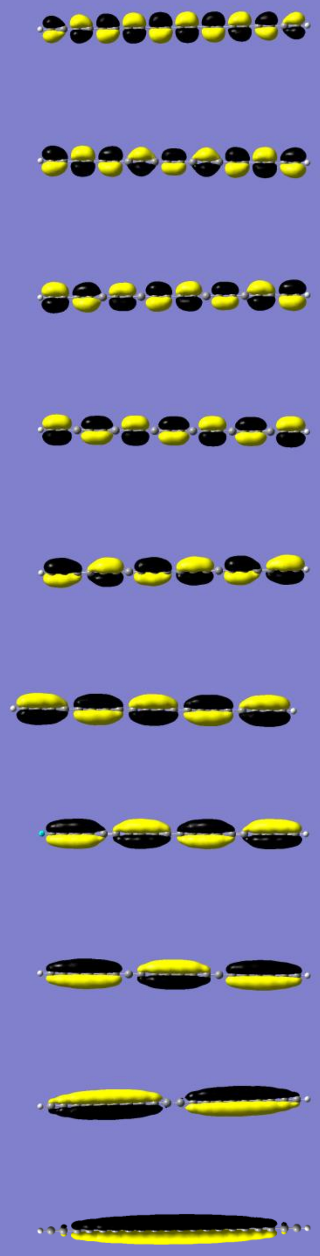
Remember De Broglie's waves?

$$p = \frac{h}{\lambda}$$

Shorter wavelengths, λ, mean higher momentum, p. This means higher kinetic energy because

$$KE = \frac{p^2}{2m}$$

These orbitals move to higher energy as their de Broglie wavelength gets shorter!



Thanks to all of you for listening!

All molecular orbital calculations were done using the computational chemistry software purchased from Gaussian, Inc.

Gaussian, Inc.
Wallingford, Connecticut