

Chemistry 1B

Fall 2016

Topics ~~Lectures~~ 13-14

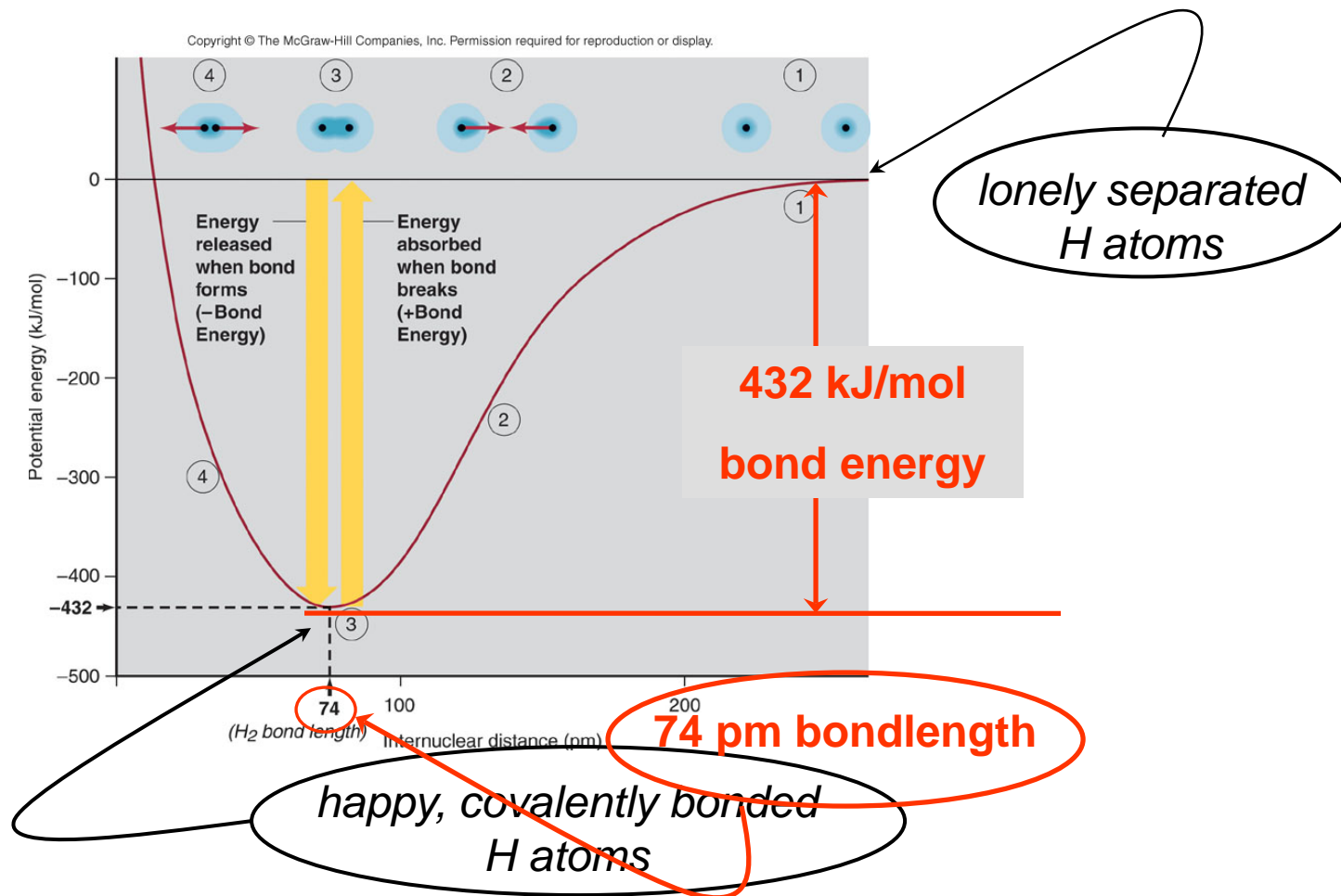
Quantum Mechanics of the Covalent Bond

for chapter 14 animations and links see:

http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/WWW_other_links/Ch14_links.htm

- WE WILL BE COVERING SECOND PART OF CHAPTER 14 (pp 676-688) **FIRST**
- You will go **CRAZY** unless you concentrate on the material presented in lecture and homework

why do atoms form bonds to become molecules?



full quantum mechanical treatment 'solving the Schrödinger equation'

	experiment	theory
bond length:	74 pm	74 pm
bond energy:	432 kJ/mol	431.679 kJ/mol

QM rules !!!

molecular orbital (mo approximation)

- the orbitals for electrons in molecules are described by combinations of atomic orbitals (a.o.s) on the atoms involved in the bond
- these orbitals (wavefunctions) are called molecular orbitals (m.o.s)
- our **MISSION** will be to:
 - ✓ understand the nature of the m.o.'s , their energies and their electron densities (ρ^2)
 - ✓ fill the m.o.'s with covalent bonding electrons to give ground and excited configurations (states)
 - ✓ understand the properties of diatomic molecules (bond strength, bond length, and magnetic properties) in terms of these electron configurations and orbital properties



atomic orbitals [*waves*] on the atoms involved in a bond can interact [*wave interference*] in two ways:

- add (**constructive** interference)
- subtract (**destructive** interference)

constructive interference of ao's



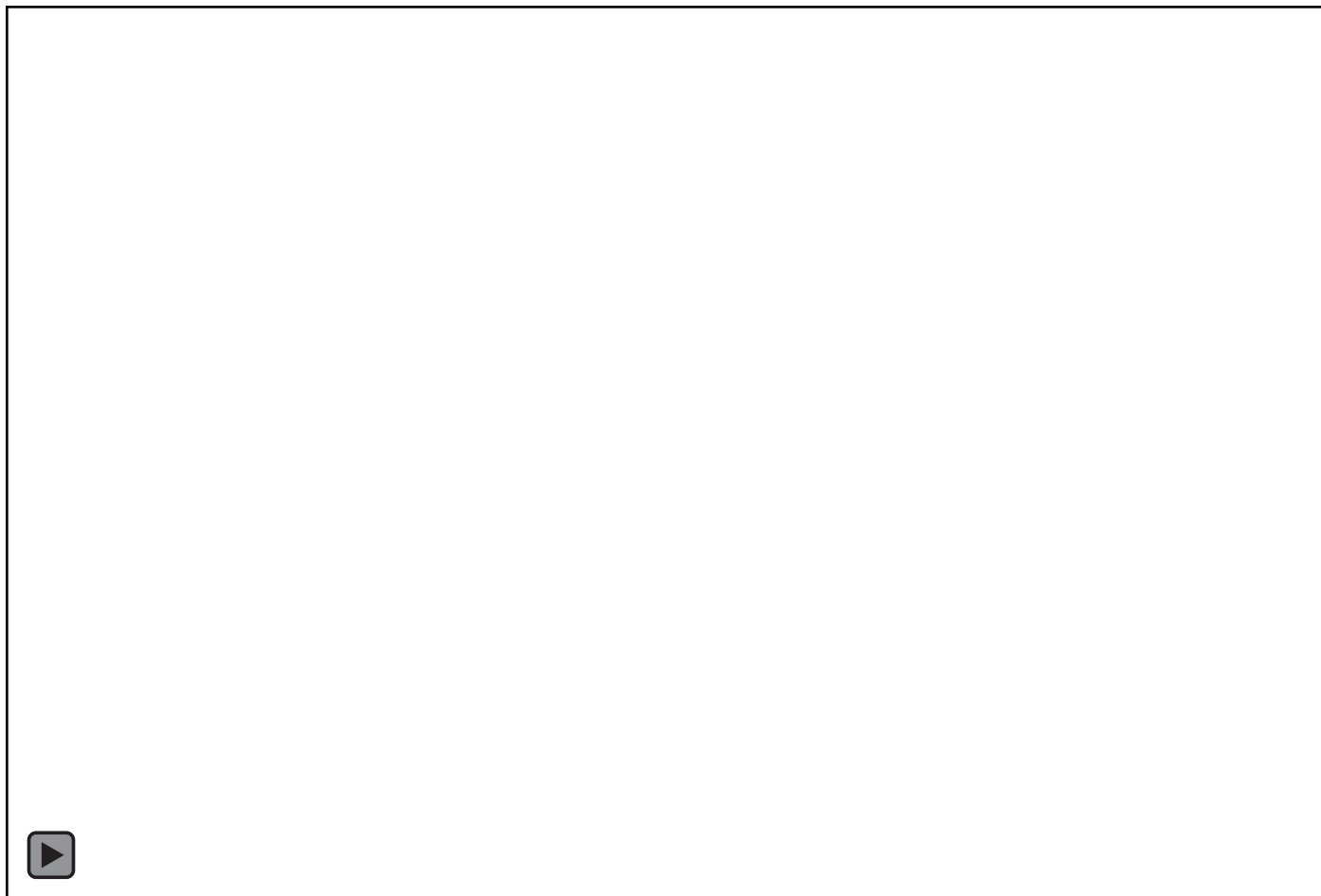
originally from:
<http://www.wellesley.edu/Chemistry/chem120/mo1.html>

constructive interference of ao's



<http://www.ck12.org/ck12-physics-audio-visuals/ck12-physics-audio-visuals>

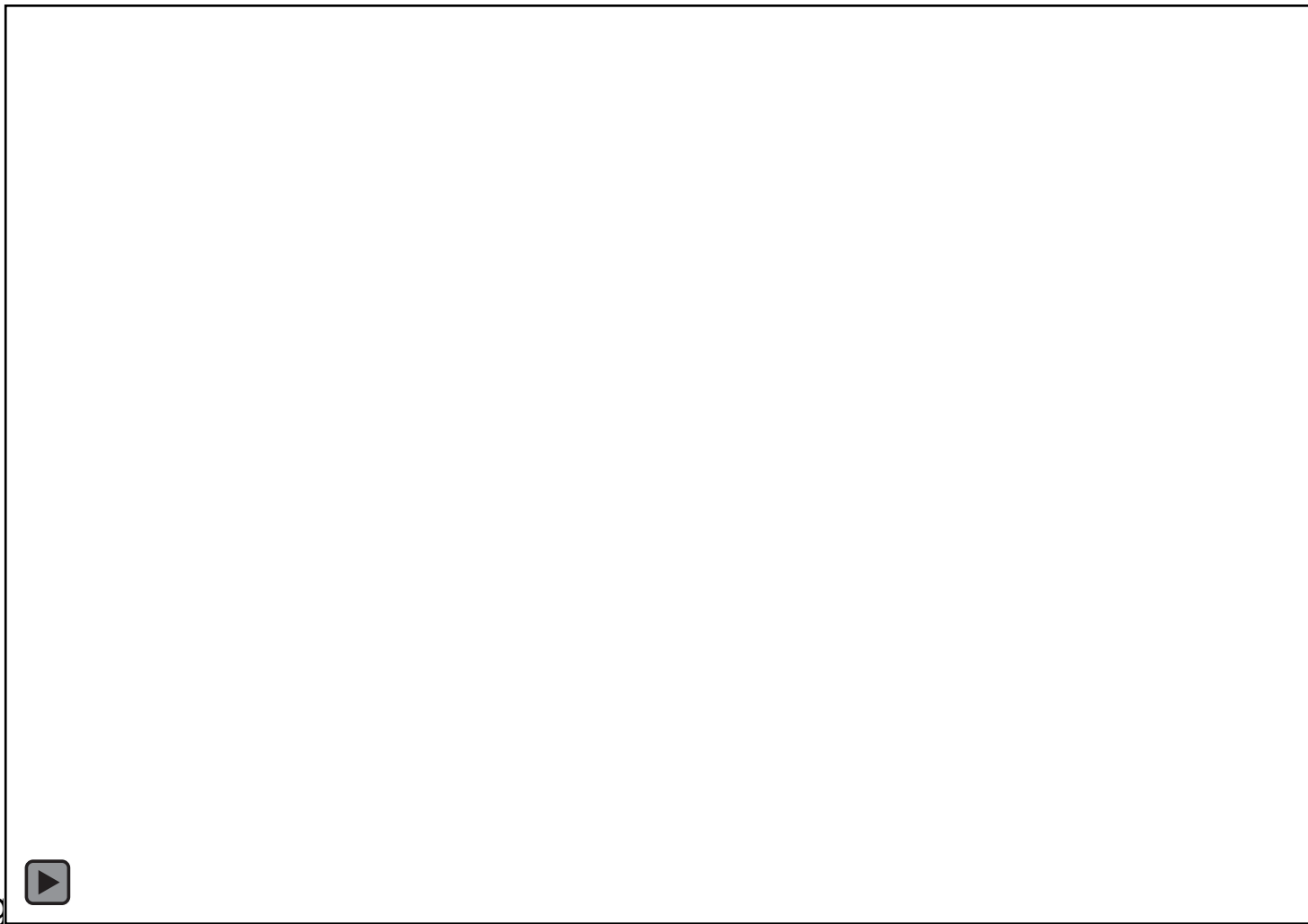
destructive interference of ao's



originally from:

<http://www.wellesley.edu/Chemistry/chem120/mo1.html>

destructive interference of ao's



orig



<http://www.wellesley.edu/Chemistry/chem120/mo1.html>

constructive interference to form bonding molecular orbital

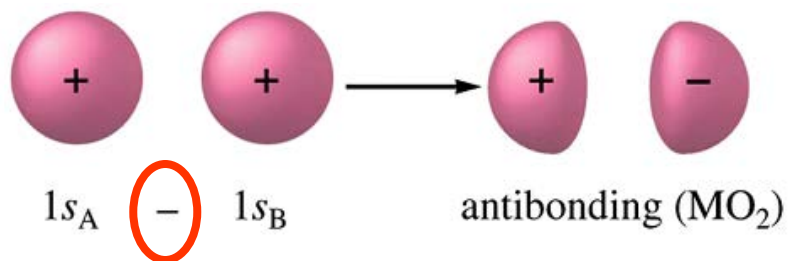
- The atomic orbitals can add (*constructive interference*) to form a **bonding** molecular orbital.
- Properties of bonding orbital (from constructive interference of a.o.s)
 - *the bonding molecular orbital has a **lower energy** than the two contributing atomic orbitals*
 - *the electron probability cloud (Ψ^2) has a **greater electron density** between the nuclei than would non-interacting atoms*

destructive interference to form antibonding molecular orbital

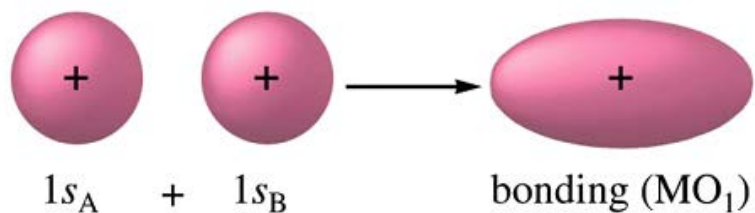
- The atomic orbitals can subtract (*destructive interference*) to form an **antibonding** molecular orbital.
- Properties of antibonding orbital (from destructive interference of a.o.s)
 - *the antibonding molecular orbital has a **higher energy** than the two contributing atomic orbitals*
 - *the electron probability cloud (Ψ^2) has a **lower electron density** between the nuclei than would non-interacting atoms (notice node)*

constructive and destructive interference of 1s orbital “waves”

Figure 14.25

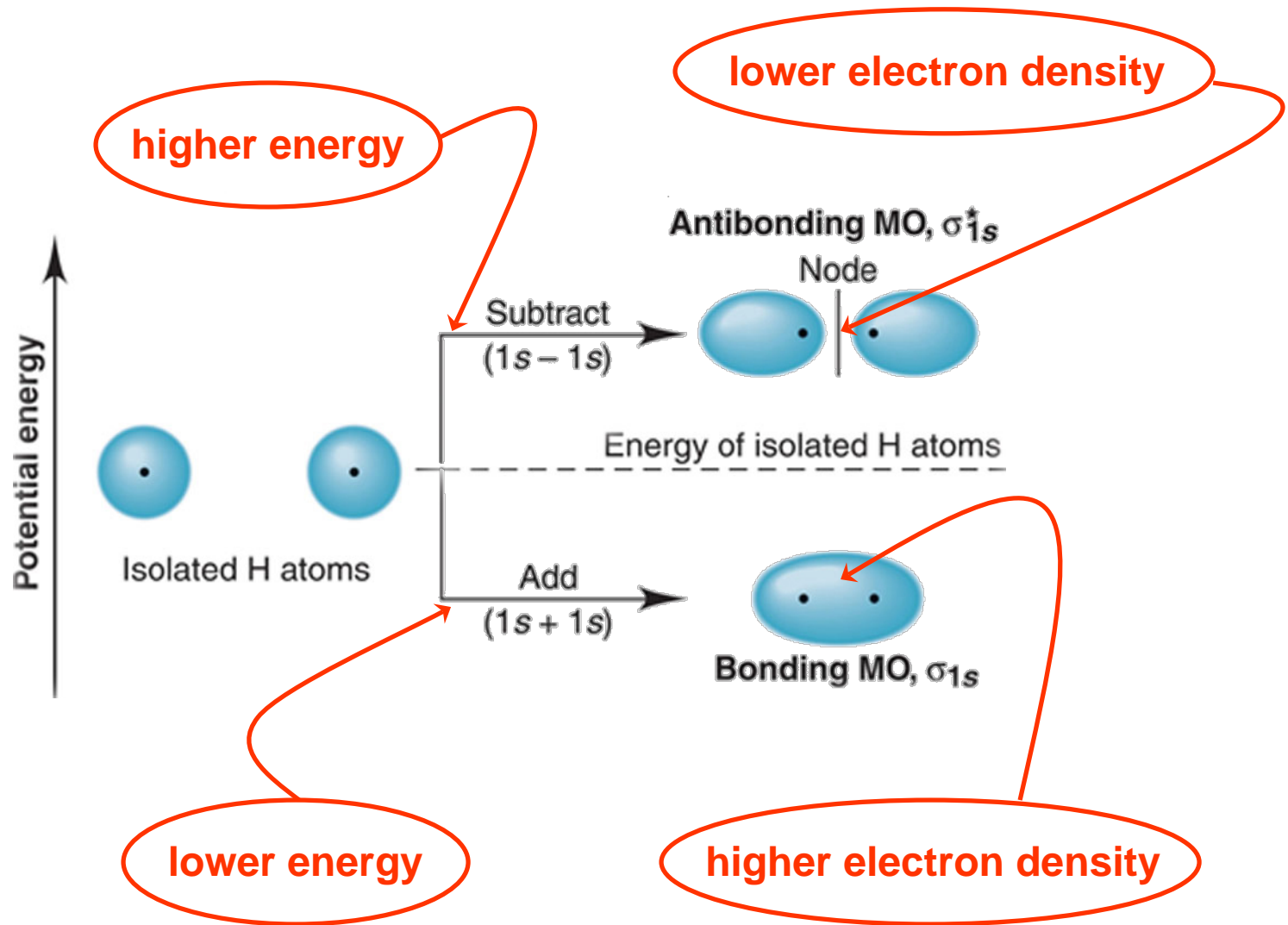


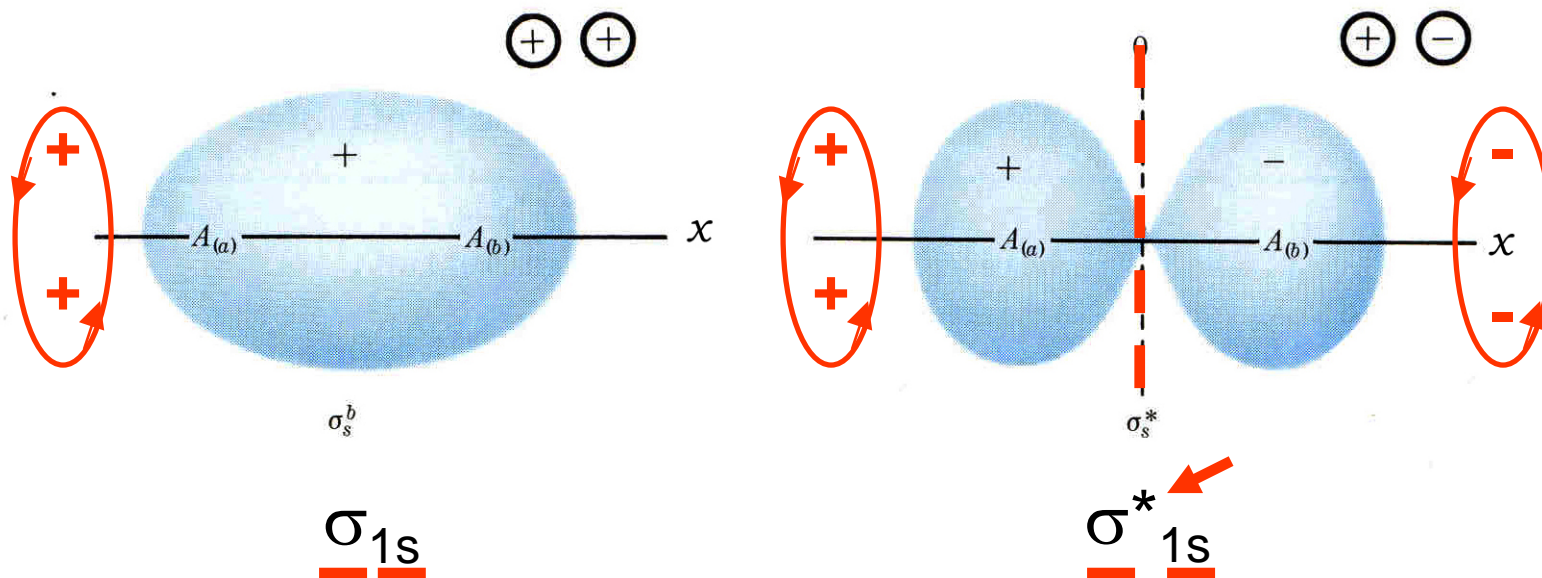
destructive interference



constructive interference

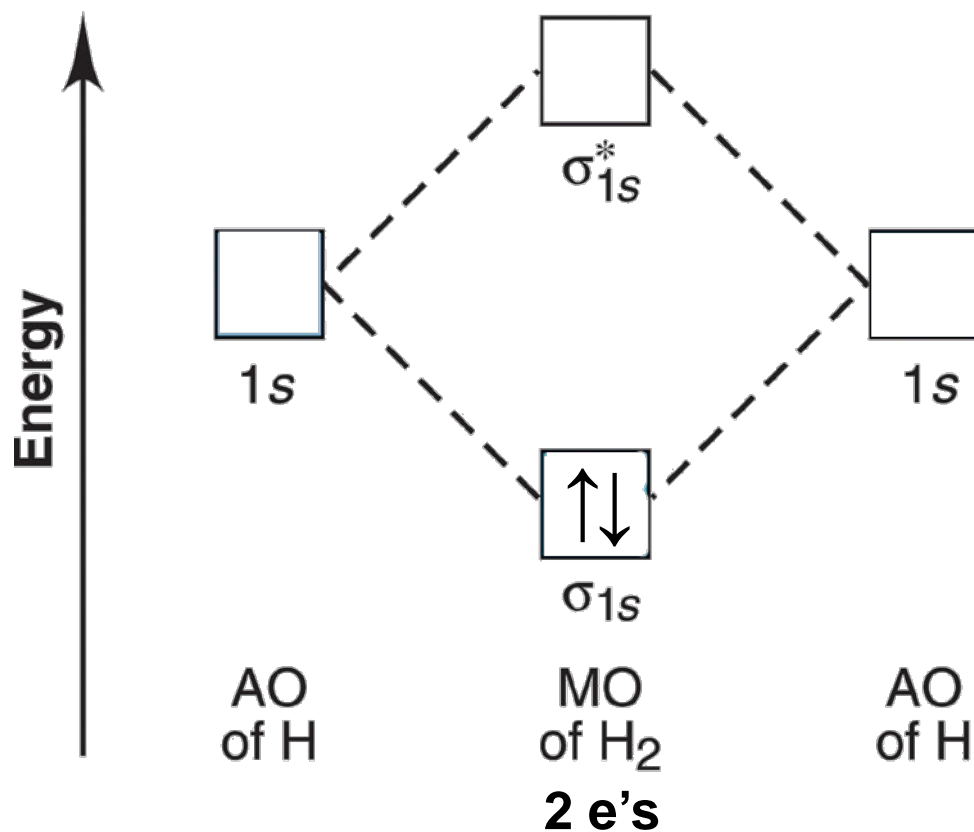
1s molecular orbitals in hydrogen molecule





- σ : cylindrically symmetric around internuclear axis (x)
- $*$: antibonding (destructive interference)
- 1s: from 1s a.o.'s

molecular orbital energy diagram (figure 14.28)

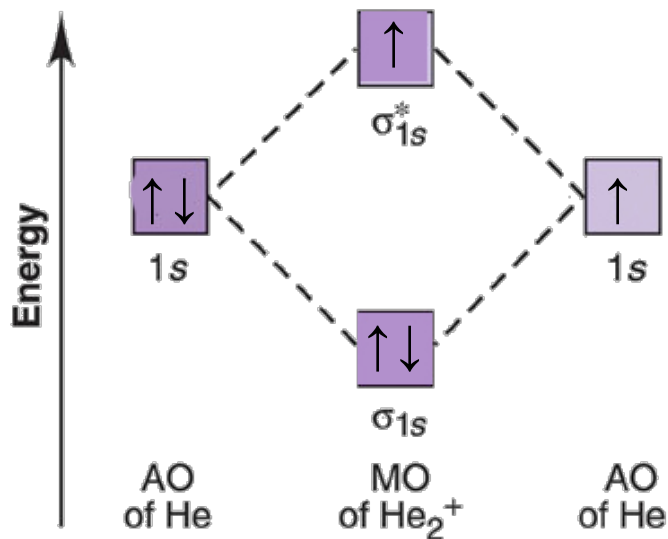


configuration: σ_{1s}^2

H_2 bond order = $\frac{1}{2} (2-0) = 1$ (single bond)



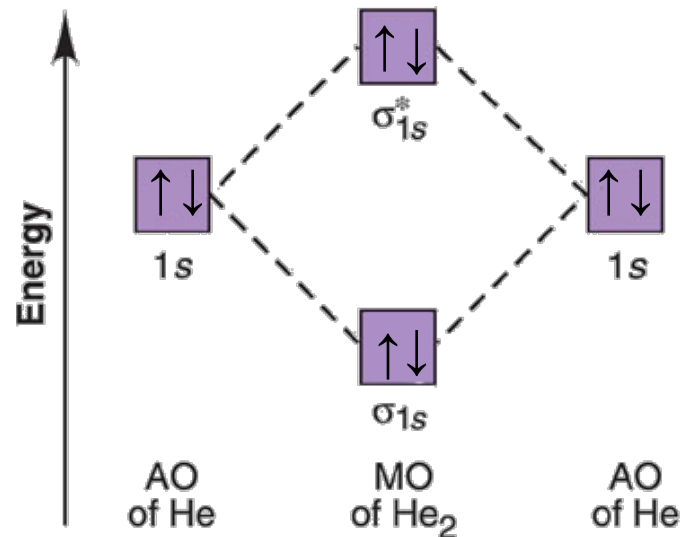
mo diagrams for He_2^+ and He_2 (fig. 14.30, 14.29)



He_2^+ (3e's)

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

bond order $= (2-1)/2 = 0.5$



He_2 (4e's)

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

bond order $= (2-2)/2 = 0$

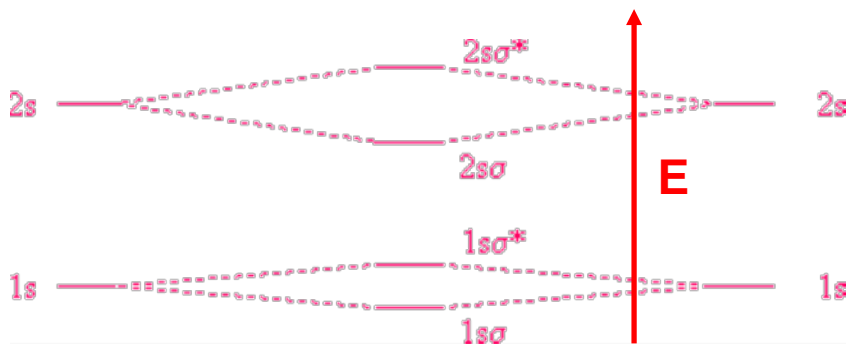
no covalent He_2 molecule observed

when will two a.o.'s interact to form an m.o. ??

- two a.o.'s must have **similar** energy
(for homonuclear diatomics $1s \leftrightarrow 1s$, $2s \leftrightarrow 2s$, $2p \leftrightarrow 2p$, etc, also $2s \leftrightarrow 2p$ to some extent)
- the two a.o.'s must have non-zero overlap *(be able to have net constructive and destructive interference; see in a moment)*
- the degree of stabilization of the bonding m.o. and the degree of destabilization of antibonding m.o. depend on the extent of the interaction (overlap) between a.o.'s

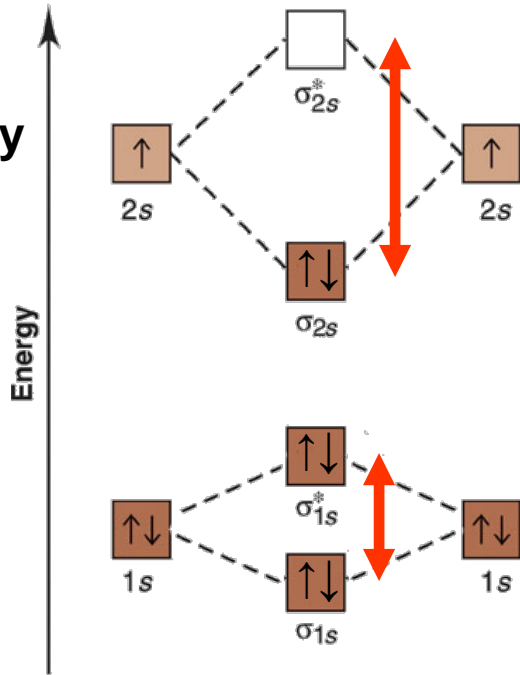
homonuclear diatomic molecules of the second period

- the 1s atomic orbitals on the two atoms interact to give σ_{1s} and σ^*_{1s} molecular orbitals
- the 2s atomic orbitals on the two atoms interact to give σ_{2s} and σ^*_{2s} molecular orbitals
- although the σ_{2s} has a lower energy than an 2s atomic orbital, the energy of the σ_{2s} is higher than the σ^*_{1s}



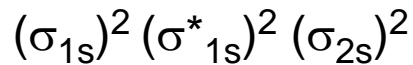
resulting energy level diagrams for Li_2 and Be_2 (fig 14.34, +extra)

σ_{2s} and σ_{2s}^* differ in energy

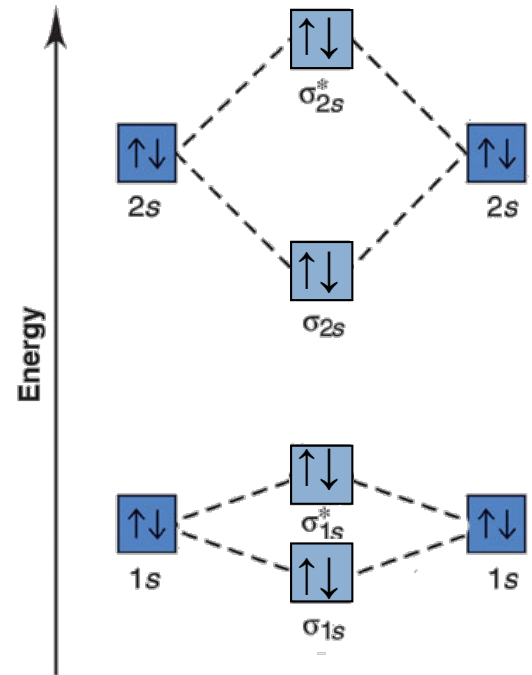


AO of Li MO of Li_2 AO of Li

Li_2 6e's

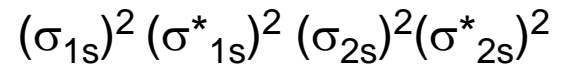


$$\text{b.o.} = (4-2)/2=1$$



AO of Be MO of Be_2 AO of Be

Be_2 8e's



$$\text{b.o.} = (4-4)/2=0$$

2nd row atoms
 σ_{1s} and σ_{1s}^*
have nearly same
energy



no covalent Be_2 molecule observed

**Molecular Orbitals
constructed
from
Atomic p-Orbitals**

pp. 680-684

Learning Objectives Worksheet 9, Sections I-II



Chemistry 1B-AL Fall 2016, Study Guide and Worksheet IX

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet IX

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet IX

Learning Objectives and Worksheet IX

Chemistry 1B-AL Fall 2016

Lectures 15-16 Molecular Orbital Theory of Covalent Bonding

WE WILL BE COVERING CHAPTER 14 IN A DIFFERENT ORDER THAN THE TEXT: first we will cover the quantum mechanics of covalent bond formation (pp 676-682, lectures 15-16) in diatomics and then polyatomic bonding and structure (pp. 683-676 & 680-692, lectures 17-18)

Supplemental video: MIT opencourse on diatomic molecules molecular orbital theory:
http://videlectures.net/mit5111/09_01ayer_1ac14/

Now that we understand, from a Lewis structure perspective, how molecules may be formed from atoms that are covalently bonded by electron pairs, we are ready to return to quantum mechanics to ask "what are the wavefunctions that describe the electrons in an electron-pair bond?" Again, exact numerical solutions of the Schrödinger equation give molecular properties that exactly match experimental values; and again, as in many-electron atoms, an "orbital approximation" will provide an excellent picture of the quantum mechanics of covalent bond formation. To describe the electronic structure of molecules we will place electrons in "molecular orbitals" in a way similar to the Aufbau Principle for placing electrons in "atomic orbitals".

I. Introduction to the quantum mechanics of the covalent bond

1. What are two properties of the hydrogen molecule, H_2 , that correspond to the concept that in H_2 , an electron pair bond occurs between the two H atoms?

2. In forming a molecular orbital, two atomic orbitals (i.e. the waves describing the orbitals) can interact in what two ways:

i.

ii.

3. Destructive interference of two atomic orbitals (a.o.'s) leads to a _____ molecular orbital that has a _____ energy that the constituent a.o.'s and a greater electron density _____ than the sum of the a.o. electron densities.

4. Destructive interference of two atomic orbitals (a.o.'s) leads to an _____ molecular orbital that has a _____ energy that the constituent a.o.'s and a lower electron density _____ than the sum of the a.o. electron densities.

Molecular orbitals for first and second row homonuclear diatomics

1. Bond order is defined as

$$b.o. = \frac{1}{2} [\text{no. of } \sigma_{2s} \text{ m.o.'s} - \text{no. of } \sigma_{2s}^* \text{ m.o.'s}]$$
 giving a bond order of _____ for the 'single' electron-pair bond in the molecule H_2 .
2. Understand orbital energy diagram for m.o.'s constructed from two 1s a.o.'s. What would be the electronic configuration for the ground state of H_2^+ ? _____
 What is the bond order of H_2^+ ? _____.

3. What two factors that dictate whether two atomic orbitals will interact to form molecular orbitals?

i.

ii.

4. If two atomic orbitals have a very small spatial overlap, there will be a _____ energy difference between the bonding and antibonding molecular orbitals formed from combinations of these a.o.'s.

5. Understand the orbital energy level diagrams for m.o.'s constructed from 1s and 2s a.o.'s. In Li_2 and Be_2 , note that the energy difference between the σ_{2s} and σ_{2s}^* m.o.'s greater than the energy difference between the σ_{1s} and σ_{1s}^* m.o.'s. Why is this?

6. Understand the orbitals resulting from interactions among the 2p a.o.'s on the two atoms in a diatomic molecule. Let us assume (as does the text) that the internuclear axis is in the x-direction. In a homonuclear diatomic ($A-A'$) which are true and which are false (circle correct choice):

- i. The six 2p a.o.'s (3 on A, 3 on A') interact to form six m.o.'s. T F
- ii. Among the six 2p a.o.'s, the 2p_x on A will only interact with the 2p_x on A' to form σ_{2p} and σ_{2p}^* m.o.'s. T F
- iii. The 2p_y a.o. on A and the 2p_y a.o. on A' will not interact to form m.o.'s since these atomic orbitals have very different energies. T F
- iv. In the 'simple' picture (little 2s-2p mixing as in O_2 and F_2), the π_{2p} m.o. will have a lower energy than the σ_{2p} m.o., since the side-on interaction of 2p_y ↔ 2p_y a.o.'s is greater than the end-on interaction of 2p_x ↔ 2p_x a.o.'s on A and A'. T F
- v. Of the six m.o.'s formed by the 2p a.o.'s, the σ_{2p}^* will, in general, have the highest energy due to the greatest destructive interference between 2p_x ↔ 2p_x a.o.'s on A and A'. T F
- vi. In homonuclear diatomics a 2s a.o. on A and a 2p_x a.o. on A' will never interact in forming m.o.'s since there is no possibility of net constructive or destructive interference between these a.o.'s. T F
- vii. In homonuclear diatomics a 2s a.o. on A and a 2p_y a.o. on A' will never interact in forming m.o.'s since there is no possibility of net constructive or destructive interference between these a.o.'s. T F

7. Understand basis of orbital designations:

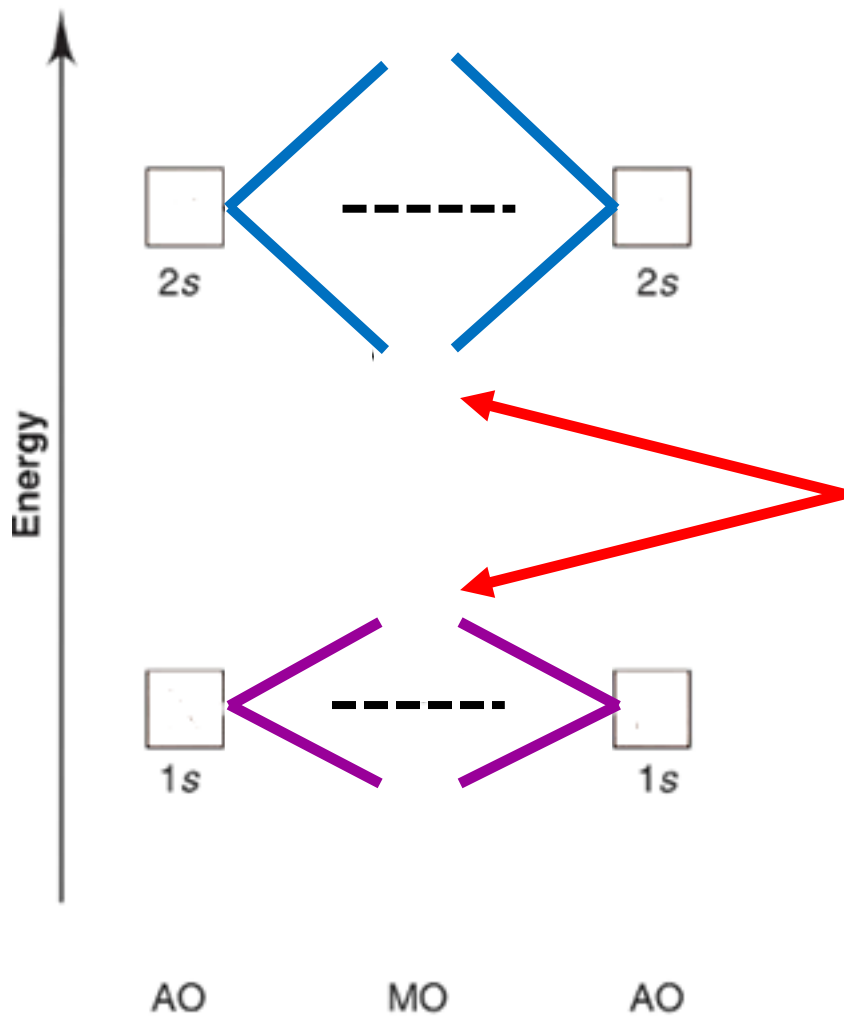
- i. A π_{2p} m.o. has the π designation because the orbital changes _____ for equivalent positions on one side of the molecule and the other relative to a plane that includes the internuclear axis.
- ii. The σ_{2s}^* m.o. has the _____ sign for all points on a circle that is centered on the internuclear axis and is contained in a plane perpendicular to this axis.
- iii. The σ_{2s}^* m.o. has a _____ plane halfway between the two atoms of a homonuclear diatomic molecule since it is an _____ orbital.

3

when will two a.o.'s interact to form an m.o. ??

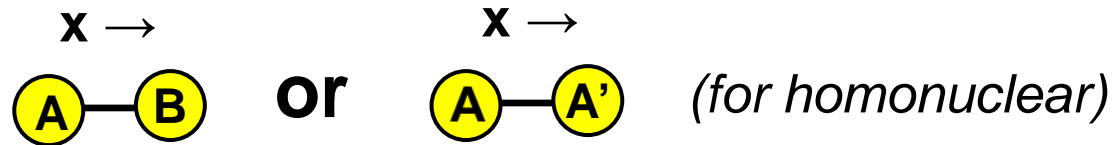
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- the degree of stabilization of the bonding m.o. and the degree of destabilization of antibonding m.o. depend on the extent of the interaction (overlap) between a.o.'s

m.o.'s from 1s and 2s a.o.'s



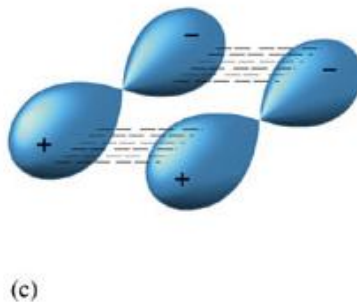
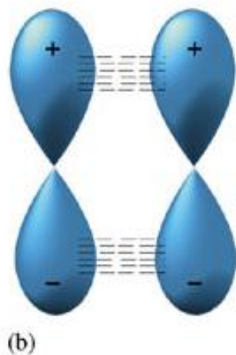
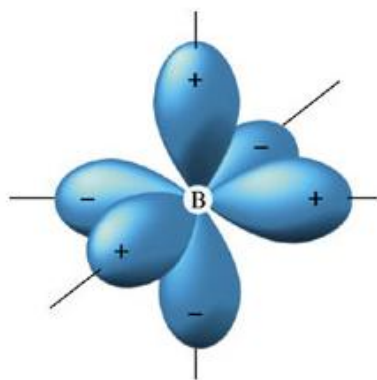
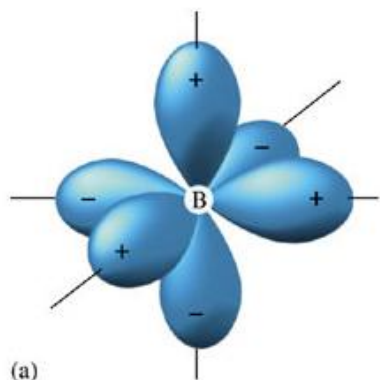
how $p_x \leftrightarrow p_x$, $p_y \leftrightarrow p_y$ and and $p_z \leftrightarrow p_z$ interact

- text uses x-direction for interatomic direction



- start with 6 different atomic orbitals:
 $\{2p_x, 2p_y, 2p_z\}_{\text{atom A}}$ $\{2p_x, 2p_y, 2p_z\}_{\text{atom A}'}$
- all six 2p atomic orbitals have the same energy
(*in homonuclear diatomic*)

Zumdahl figure 14.35 (interaction among 2p a.o.s on different atoms)



side-on interactions



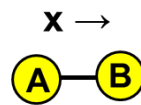
(d)

end-on interaction^{d.}

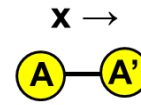
molecular orbitals from atomic p-orbitals (simple story)

- from interactions of the six p-orbitals (3 each from two atoms), six mo's will be formed
- these 2p mo's will have higher energies than the σ_{2s} and σ_{2s}^* (*2p ao's have higher energy than 2s*)
- *only the interactions ($p_x \leftrightarrow p_x$, $p_y \leftrightarrow p_y$, and $p_z \leftrightarrow p_z$) occur (in the simple story)*
- *“end-on” p-orbitals ($p_x \leftrightarrow p_x$) have greater interactions than “side-by-side p-orbitals ($p_y \leftrightarrow p_y$, and $p_z \leftrightarrow p_z$)*

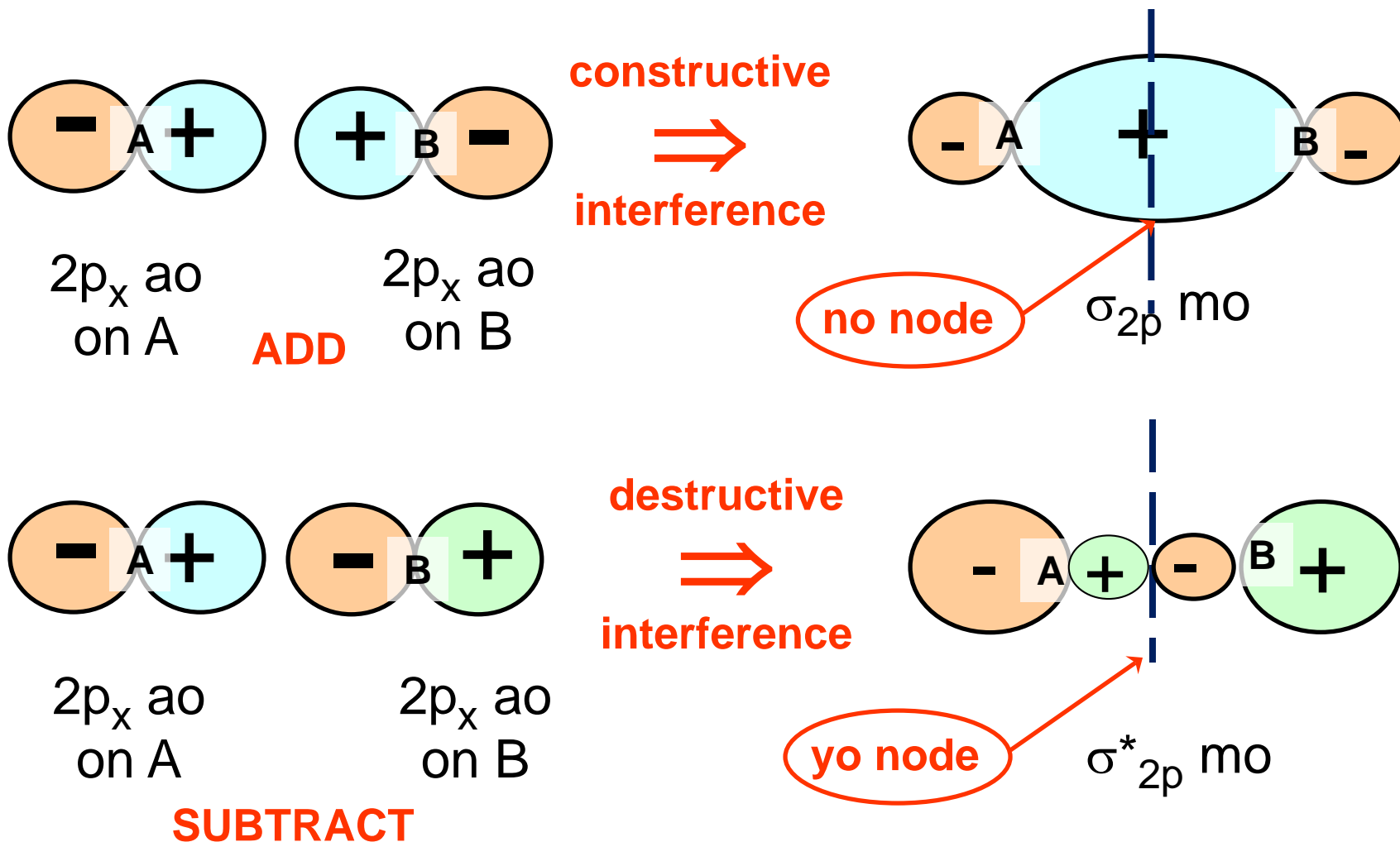
how $p_x \leftrightarrow p_x$ interact ("end-on")



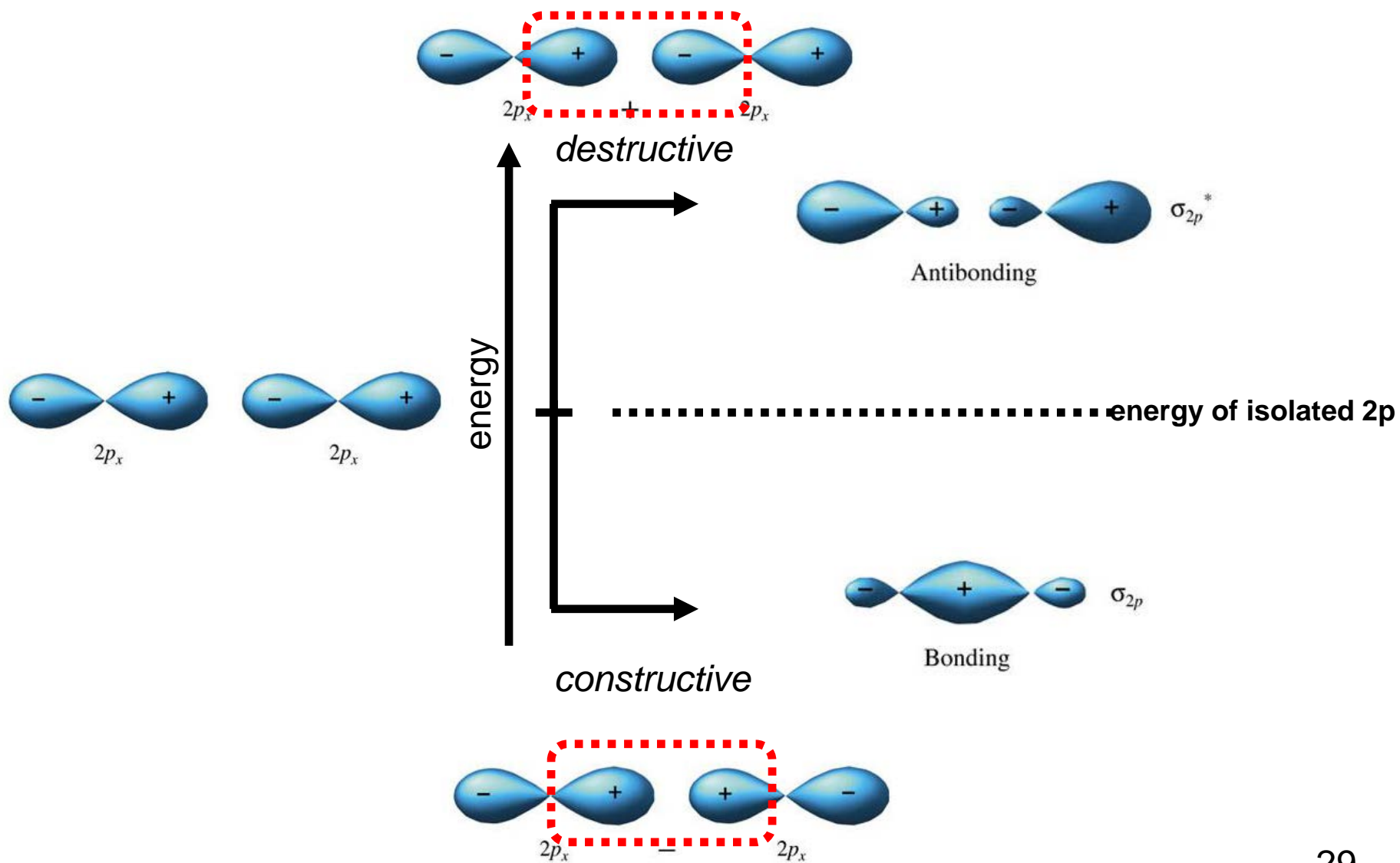
or




(for homonuclear)



from Zumdahl (fig. 14.36)

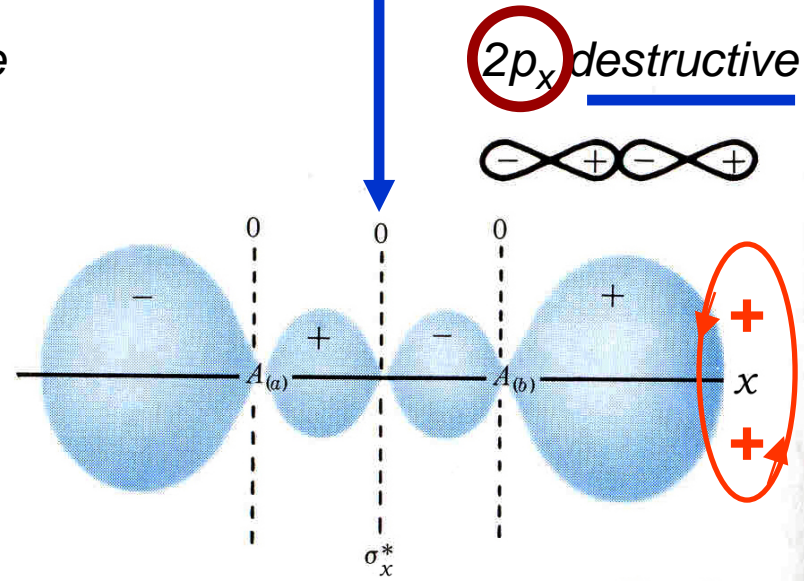
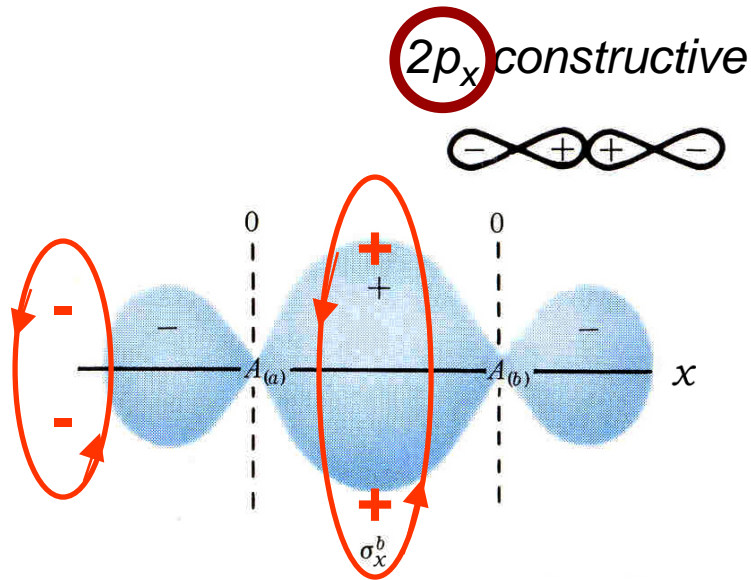


from handouts (DGH) (end-on from $2p_x$ a.o.s)



$(\sigma_{2p_x})_g$ $(\sigma_{2p_x}^*)_u$

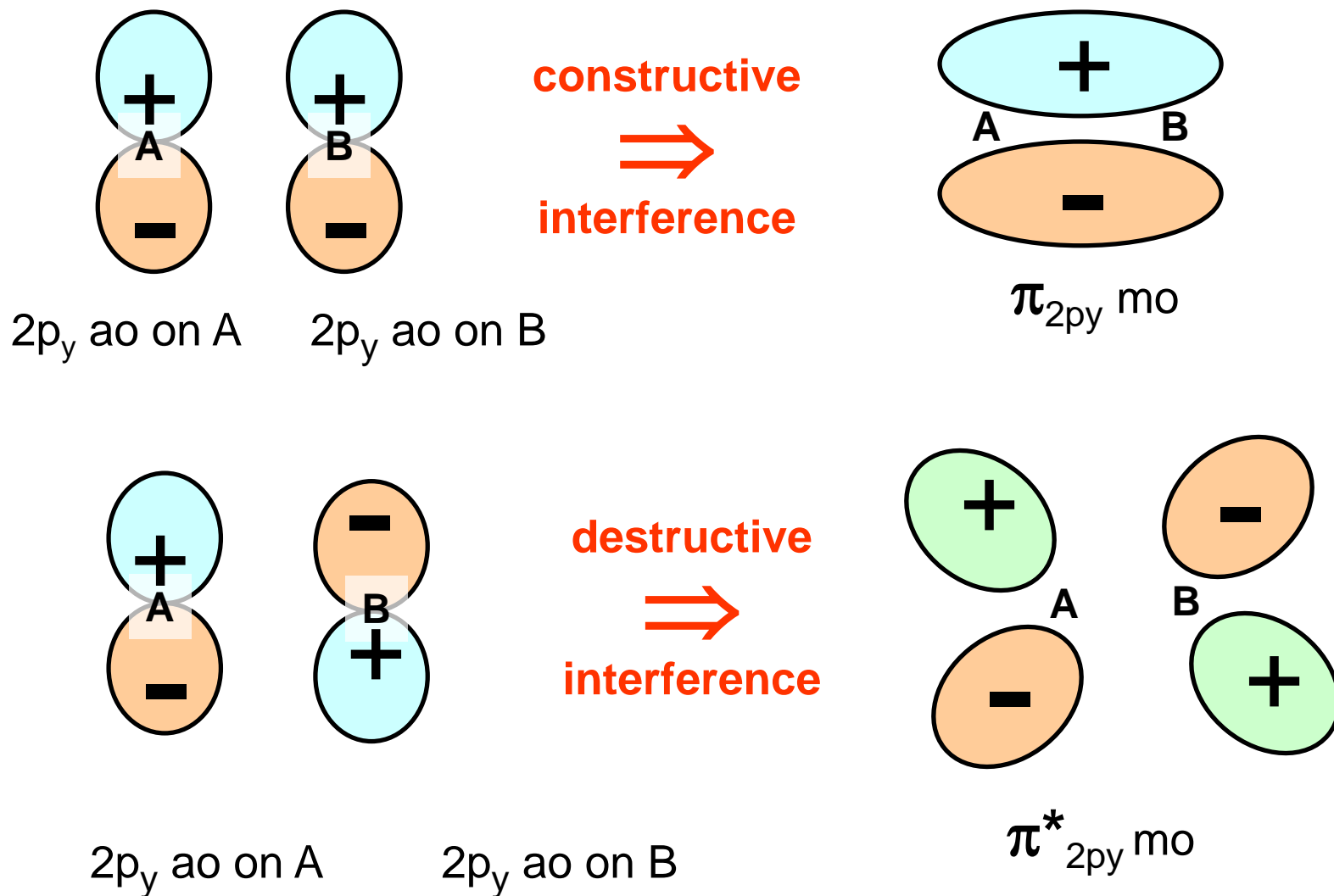
node perpendicular to bond



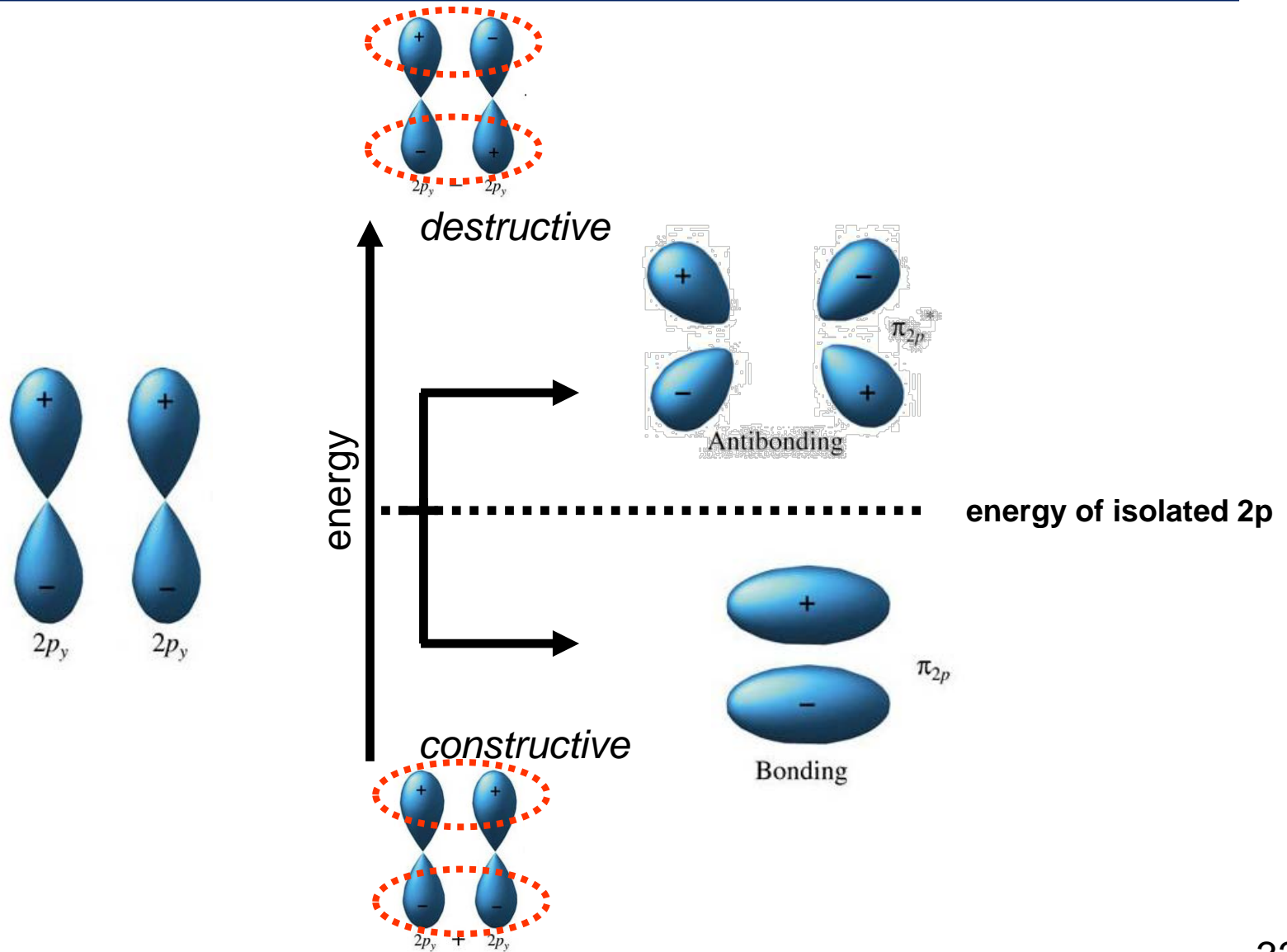
σ_{2p_x}

$\sigma_{2p_x}^*$

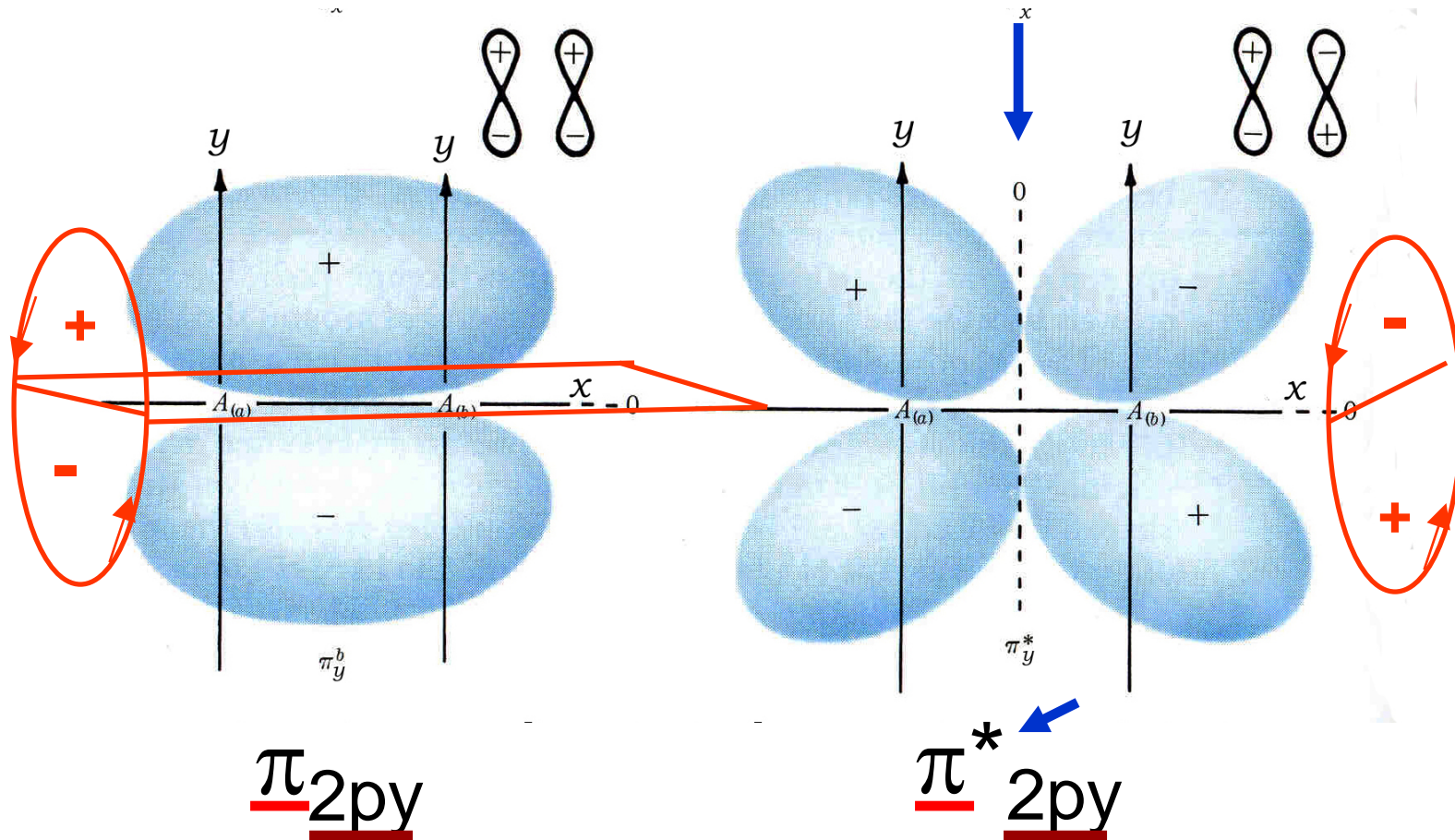
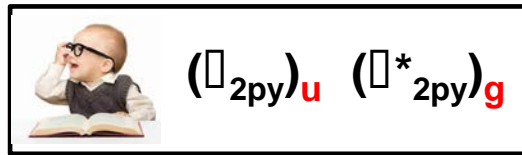
how “side on” , $p_y \leftrightarrow p_y$ and $p_z \leftrightarrow p_z$ interact



from Zumdahl (fig. 14.36) $p_y \pm p_y = \pi$ and π^*

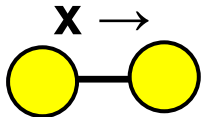


“side-on” p-orbitals from $2p_y$ a.o.’s
(from DGH, see handout)

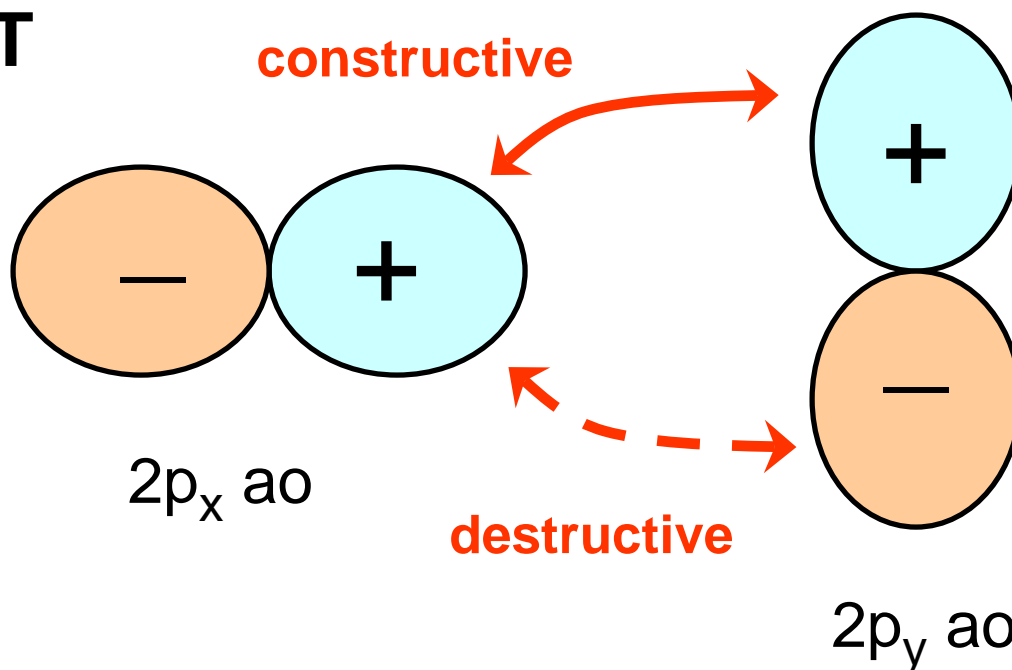


π : one nodal plane (which includes internuclear axis)

why p_x and p_y orbitals **DO NOT** interact

- (reminder) text uses x-direction for interatomic direction 
- $2p_x$ and $2p_y$ atomic orbitals **DO** have the same energy (*meets criterion #1*)

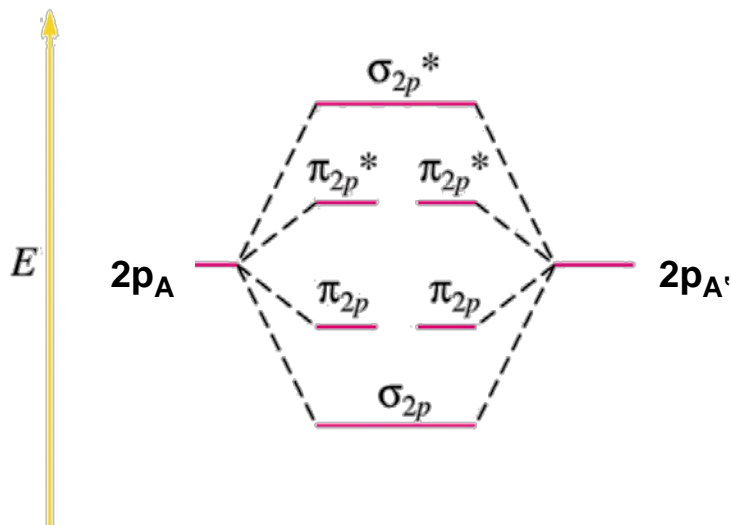
• **BUT**



no net overlap; no net interference; no interaction

energy of mo's from p-orbitals (simple case), figure 14.37

- “end-on” ($p_x \leftrightarrow p_x$) interaction is stronger than side-by-side:
 $E_{\sigma 2p} < E_{\pi 2p}$ and $E_{\sigma^* 2p} > E_{\pi^* 2p}$
- there are two pairs of “side-by-side” p-atomic orbitals ($p_y \leftrightarrow p_y$ and $p_z \leftrightarrow p_z$):
the pairs (π_{2p_y}, π_{2p_z}) have the same energy and ($\pi^*_{2p_y}, \pi^*_{2p_z}$) have the same energy



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- This order applies to O_2 , F_2 , and Ne_2

life is complicated: $2s_A \leftrightarrow 2p_{xB}$ interactions (and $2p_{xA} \leftrightarrow 2s_B$)

- In some atoms, the 2s and 2p orbitals are sufficiently similar in energy that constructive and destructive interactions occur **between 2s and $2p_x$ on differing atoms**
- **$2p$ ao's** will make contributions to the σ_{2s} mo's and **$2s$ ao's** will make contributions to σ_{2p} mo's
- the resulting energy level scheme:
- applies to B_2 , C_2 , and N_2

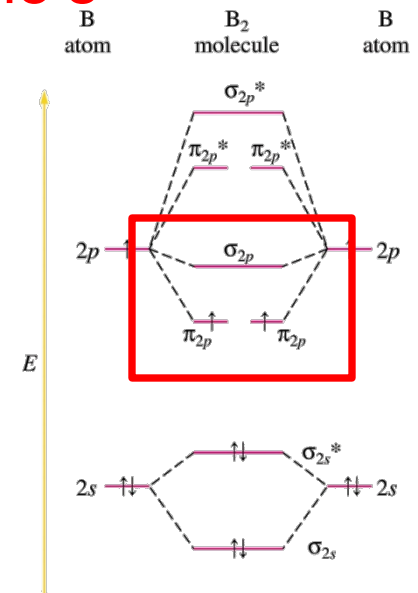
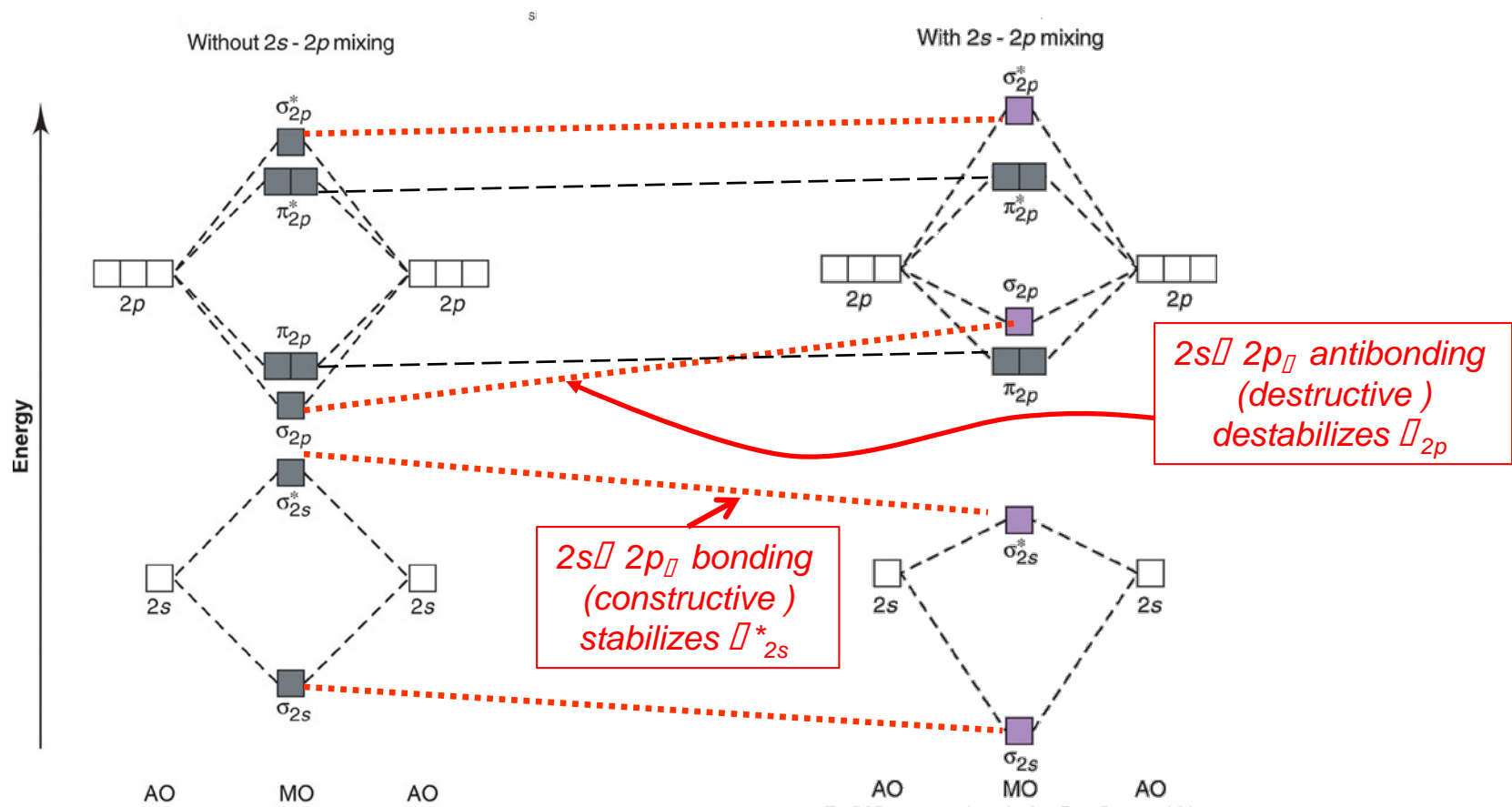


figure 14.40

**summarizing (fig. 14.38 and 14.40) relative mixing effects
(absolute energies of O_2, F_2, Ne_2 would be lower than those of B_2, C_2, N_2)**



simple O_2, F_2, Ne_2

with 2s-2p mixing
 B_2, C_2, N_2

MOLECULAR ORBITALS FOR DIATOMIC MOLECULES HANDOUT



ENERGY LEVELS FOR HOMONUCLEAR DIATOMIC MOLECULES



brianiacs

What do I have to know?

You will be responsible for being able to write or identify ground and excited state configurations for homonuclear diatomic molecules and their ions and be able to:

- I. Determine whether the molecule is paramagnetic or diamagnetic*
- II. Calculate the bond order*
- III. From the bond order determine their relative bond length and bond strength*

**the masses
(everyone)**

4. *What is the effect of 2s-2p mixing on the energy level diagram?*

The 2p_x provides bonding (constructive) interactions in the σ_{2s} and σ_{2s}^ m.o.'s LOWERING their energies.*

The 2s participates in the σ_{2p} and σ_{2p}^ m.o.'s with antibonding (destructive) interactions and thus RAISES the energies of the σ_{2p} and σ_{2p}^* m.o.'s.*

The energies of the π_{2p} and π_{2p}^ m.o.'s are unaffected since there is no 2s mixing with the 2p_y or 2p_z.*

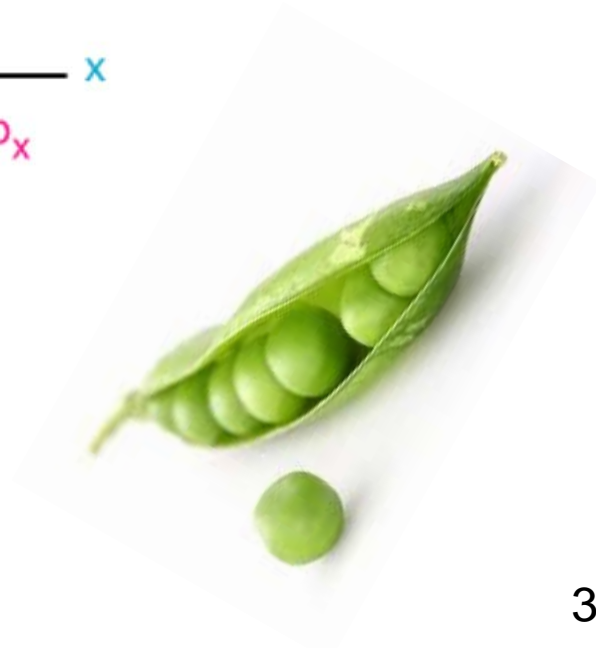
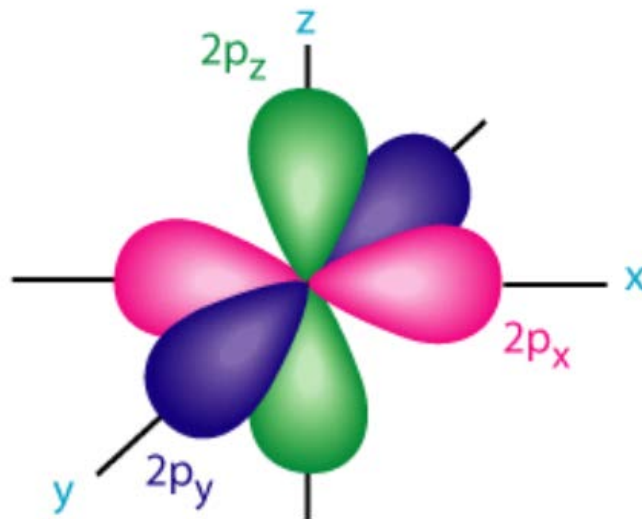
The result TO REMEMBER is that for B₂, C₂, N₂ the π_{2p} has a lower energy than the σ_{2p} .

summarizing (fig. 14.38 and 14.40)



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*finished
with them
p's*



for now

study guides !!!

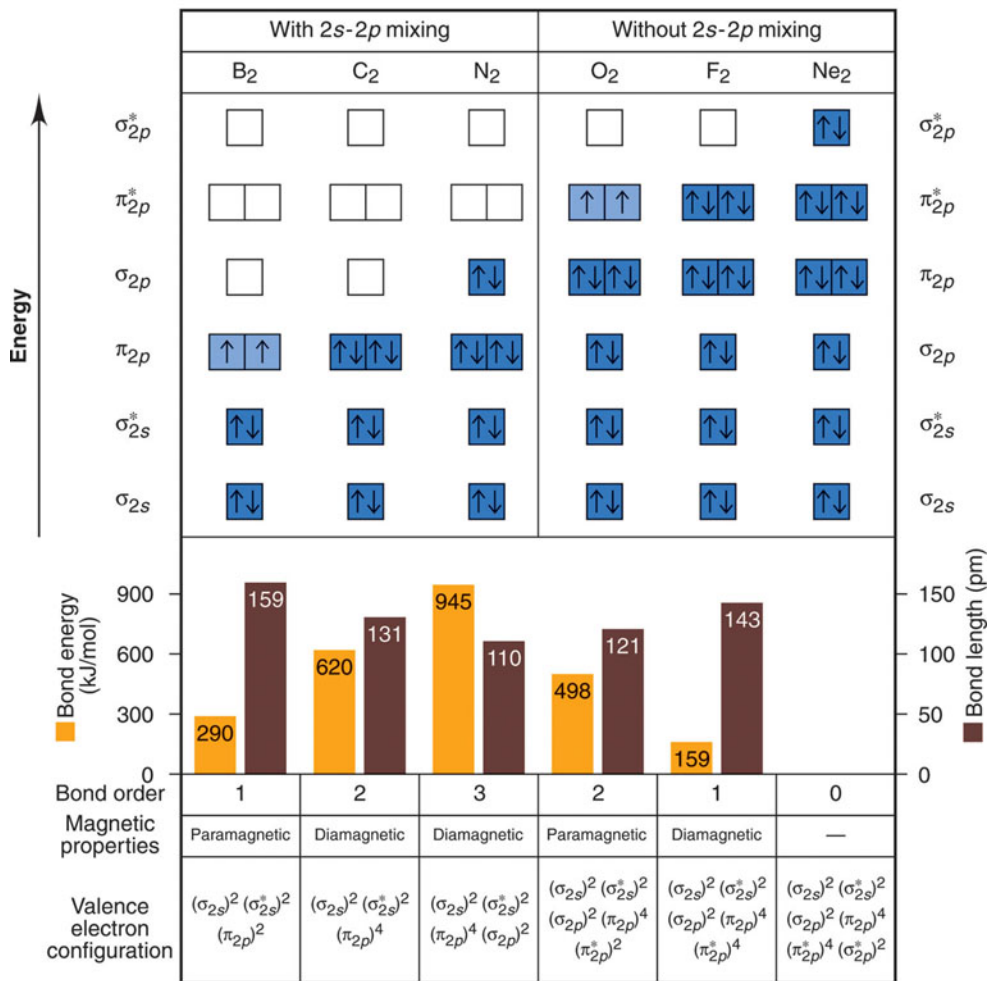
know properties of B_2 , C_2 , N_2 , O_2 , F_2 , and their ions (fig. 14.41)

	B_2	C_2	N_2	O_2	F_2
σ_{2p}^*	—	—	—	σ_{2p}^* —	—
π_{2p}^*	—	—	—	π_{2p}^* \uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}	—	—	$\uparrow\downarrow$	π_{2p} $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
π_{2p}	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	σ_{2p} $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s}^* $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s} $\uparrow\downarrow$	$\uparrow\downarrow$
Magnetism	Para-magnetic	Dia-magnetic	Dia-magnetic	Para-magnetic	Dia-magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143



properties of B_2, C_2, N_2, O_2, F_2 , and their ions (Silberberg fig. 11.21)

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mo's and properties of homonuclear diatomic molecules (fig 14.41)

mole cule	configuration	b.o	Bond energy (kJ/mol)	Bond Length (pm)	P or D
Li ₂	$(\sigma_{2s})^2$	1	105	267	D
Be ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$	0	0	?	?
B ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^2 \uparrow \uparrow$	1	290	159	P
C ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^4$	2	620	131	D
N ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^4 (\sigma_{2p})^2$	3	942	110	D
O ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^2 \uparrow \uparrow$	2	495	121	P
F ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^4$	1	154	143	D
Ne ₂	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^4 (\sigma^*_{2p})^2$	0	0	?	?

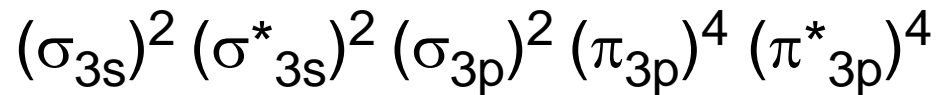


N₂ diamagnetic O₂ paramagnetic

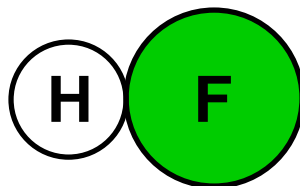
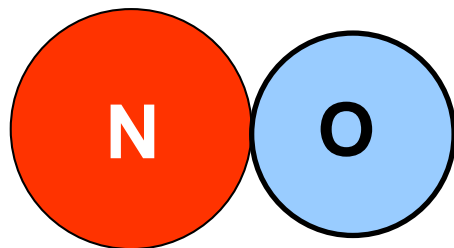


Joanna and Steve

just like second row but using 3s and 3p orbitals



heteronuclear diatomic molecules

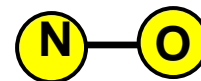


same rules for homonuclear m.o.s apply BUT now:

- 'same' a.o.s on two atoms will not have the same energy (still, a.o.s with similar energies combine to form m.o.s)
- the two a.o.'s will NOT contribute equally to a given mo

heteronuclear diatomic (NO, fig. 14.43)

$\mathbf{x} \rightarrow$

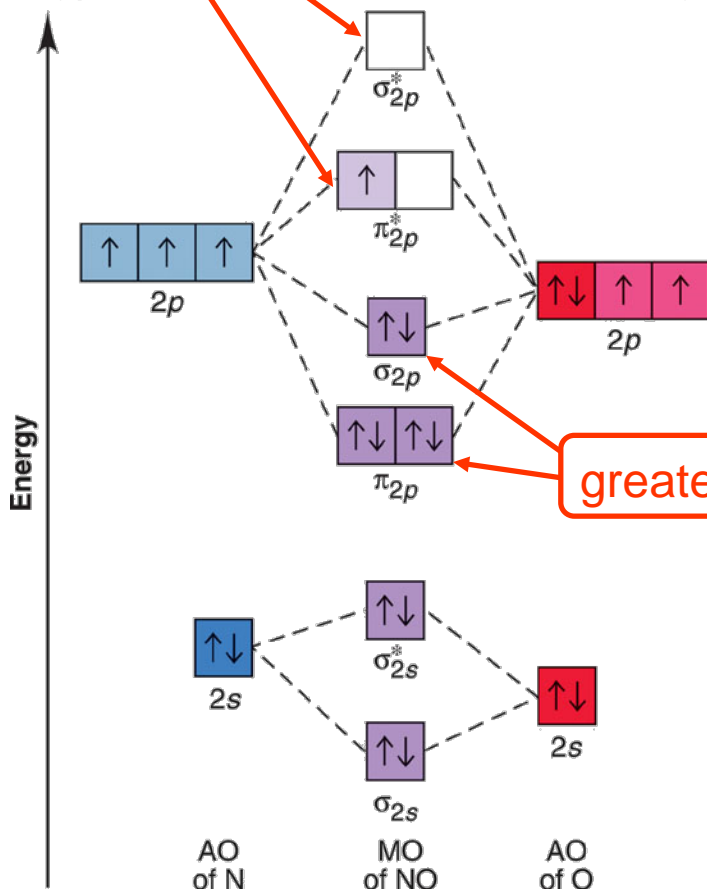


greater 2p on N

observations NOT predicatble from Lewis structures

- N-O bond stronger than double bond; b.o= 2.5
- unpaired electron resides to a greater extent on N

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energy of O a.o.'s LOWER (but ~similar) to N a.o.'s

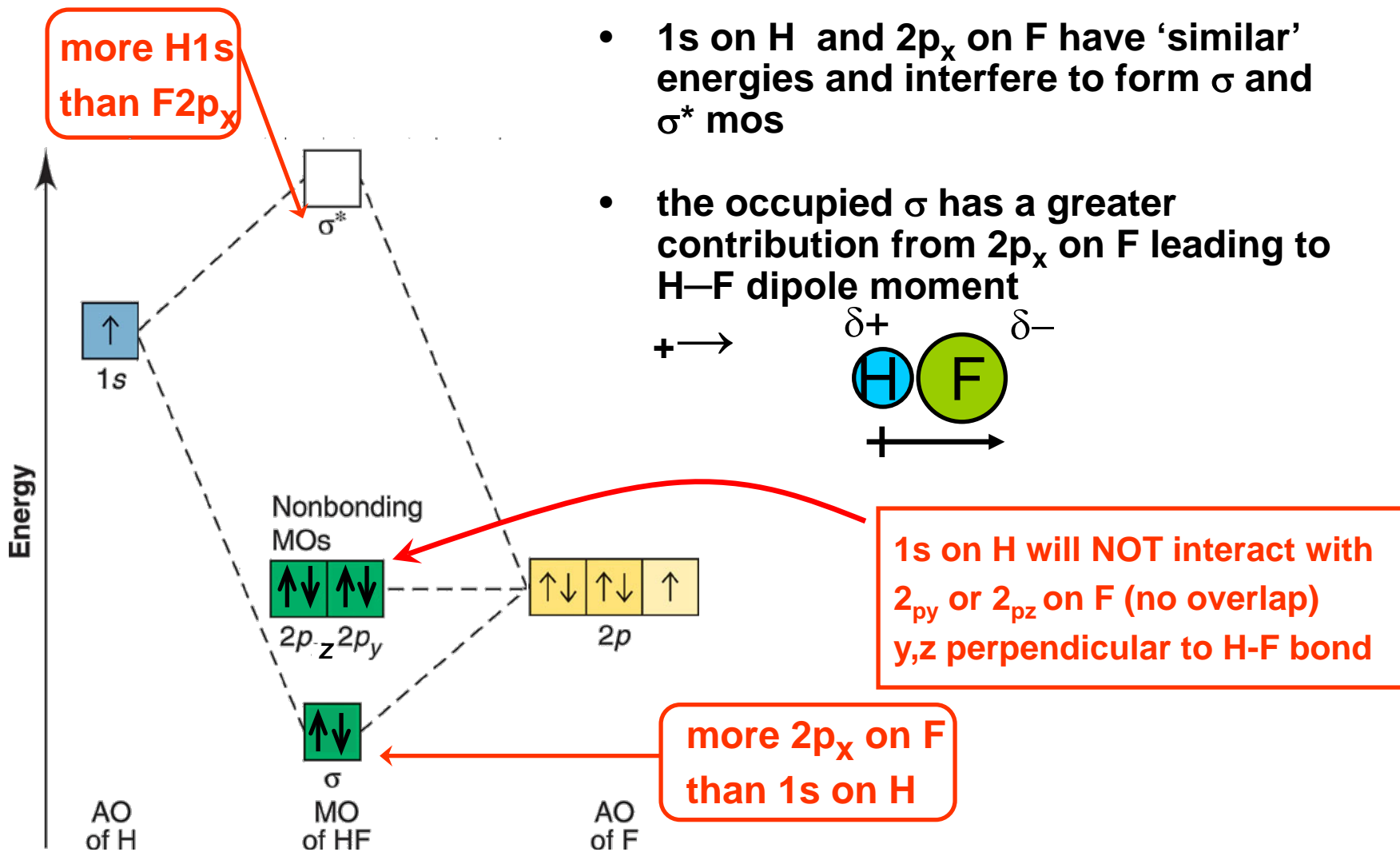
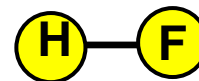
greater 2p on O

need to be 'told' use light atom energy scheme

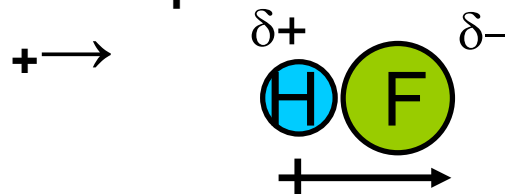
11 valence e's

heteronuclear diatomic (HF fig 14.45)

X →



- 1s on H and $2p_x$ on F have 'similar' energies and interfere to form σ and σ^* mos
- the occupied σ has a greater contribution from $2p_x$ on F leading to H–F dipole moment



6 valence e's ($1s^2 2s^2$ essentially all on F)

P 688 “Delocalized bonding” will be covered after we study hybridization (lectures 17-18) and will NOT be on midterm #2 and

P 692 “Spectroscopy” later (lectures 19-20)

Floating Frogs

Magnets help living organisms defy gravity

By CORINNA WU

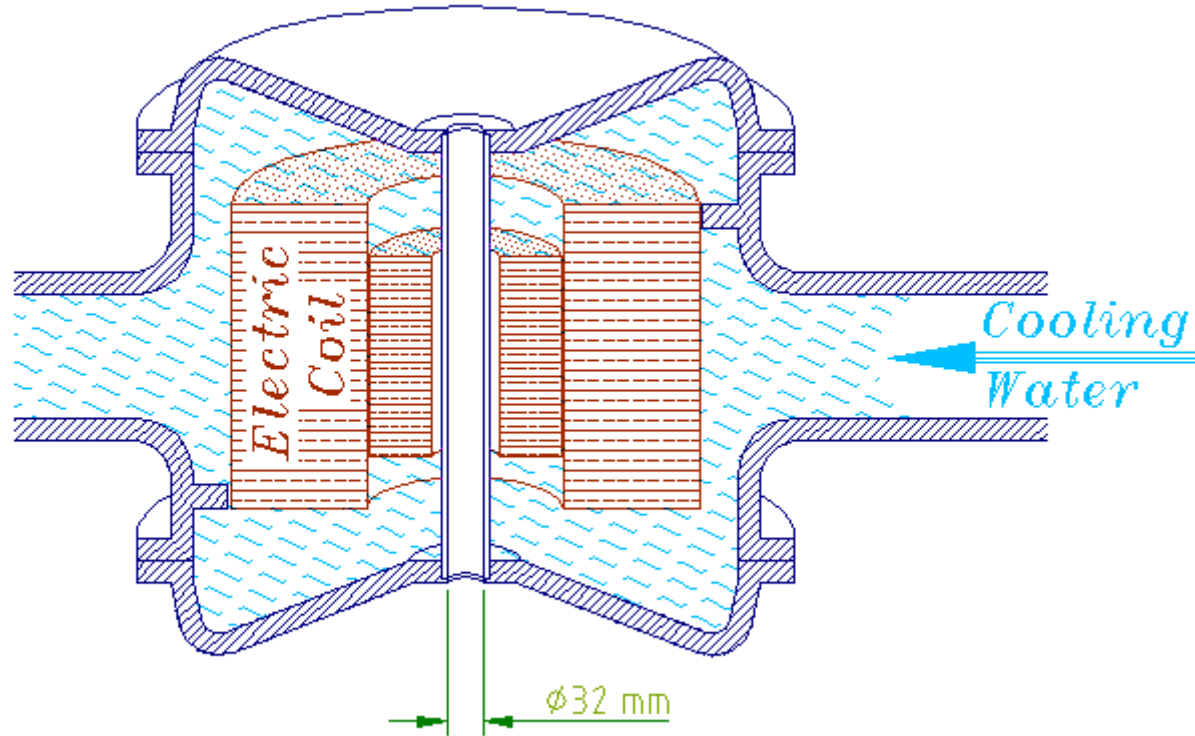
Floating Frogs

by Corinna Wu

(This was demonstrated on both Dan Rather's CBS News and CNN in April of 1997)

Asked to think of an animal that can fly, most people don't picture a frog. Nonetheless, in April 1997, a team of British and Dutch researchers announced success in levitating a live frog by using a powerful magnet. According to one of the human observers, the frog emerged from the flight unharmed and "happily joined" his fellow frogs in a biology department.

the magnet



The Frog That Learned to Fly (Molecular Magnetism and Levitation)



originally from: <http://www.hfml.ru.nl/pics/Movies/frog.mpg>

the frog's OK !!!

researchers announced success in levitating a live frog by using a powerful magnet. According to one of the human observers, the frog emerged from the flight unharmed and "happily joined" his fellow frogs in a biology department.



END OF MATERIAL FOR MIDTERM #2 FALL 2016

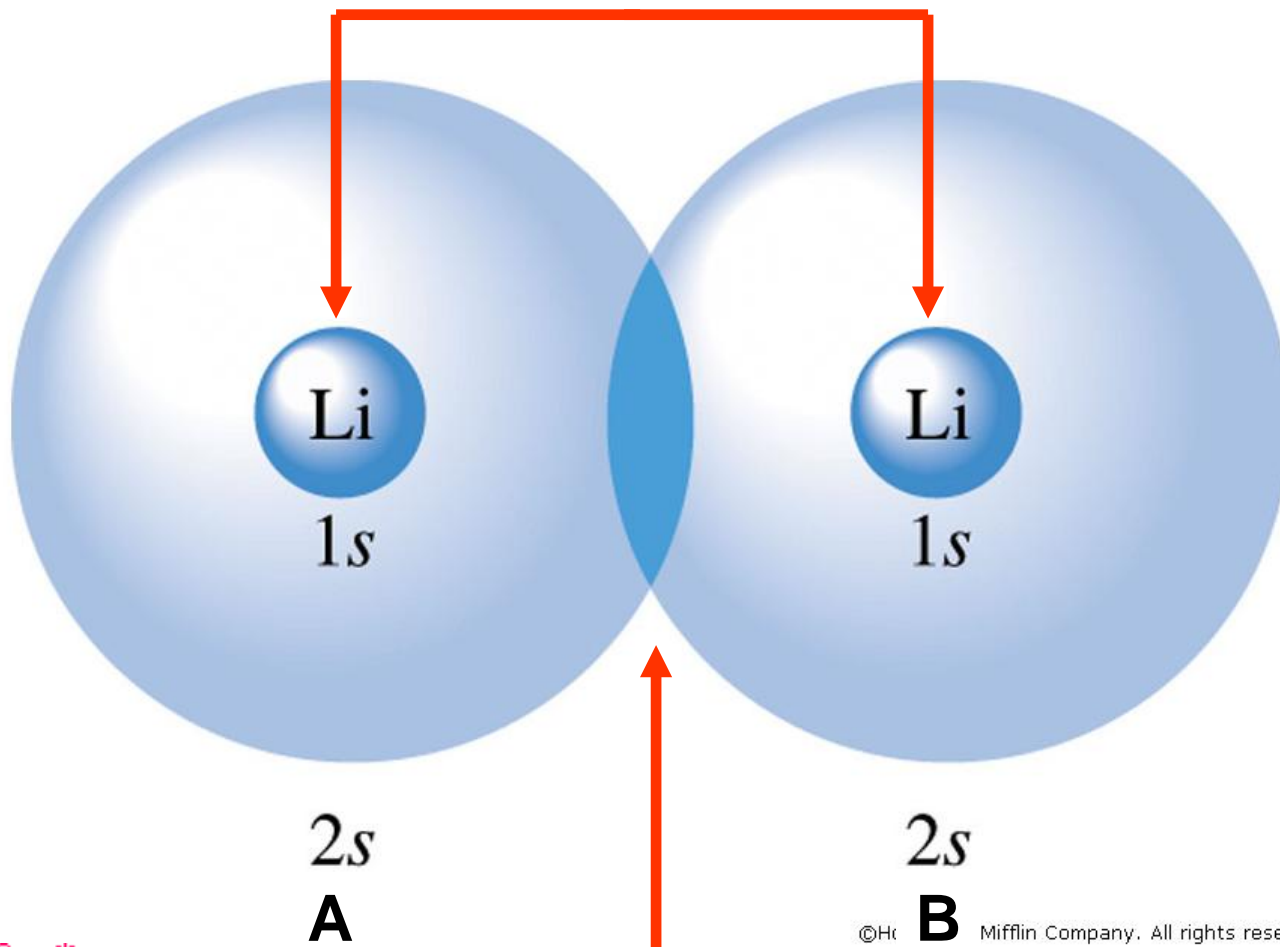
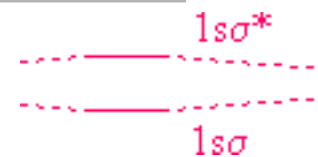
On to hybridization !!!

End of Sessions 13-14

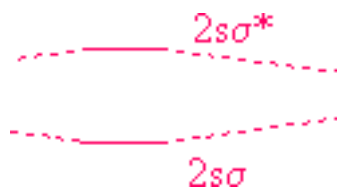
$$\text{bond order} = \frac{1}{2} [\text{no. of bonding electrons} - \text{no of antibonding electrons}]$$



$1s_A$ and $1s_B$ have **little** overlap; σ_{1s} and σ^*_{1s} have similar energies



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$2s_A$ and $2s_B$ have **greater** overlap; σ_{2s} and σ^*_{2s} have greater energy difference (splitting)

