Chemistry 1B-AL, Fall 2016
Lectures 13-14

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

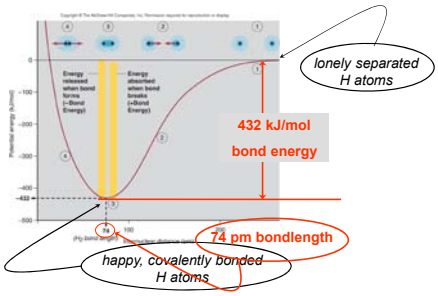
1

LISTEN UP!!!

- 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

2

why do atoms form bonds to become molecules?



3

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 !!!

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***m**olecular **o**rbital (**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 (Ψ^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

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interaction of atomic orbitals to form molecular orbitals

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

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

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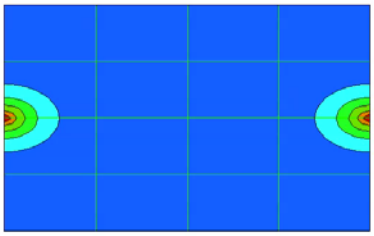
constructive interference of ao's



mobond

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

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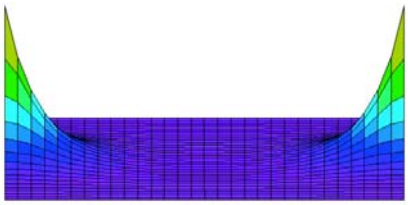
constructive interference of ao's



mobond

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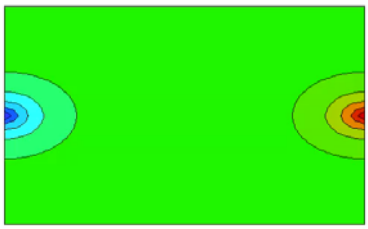
destructive interference of ao's



moantibond

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

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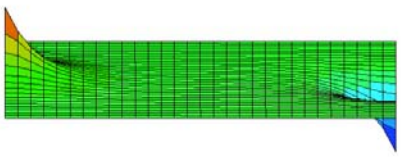
destructive interference of ao's



moantibond

orig
http://www.wellesley.edu/Chemistry/chem120/mo1.html

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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*

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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)*

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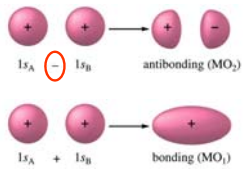
constructive and destructive interference of 1s orbital "waves"

Figure 14.25



destructive interference

constructive interference

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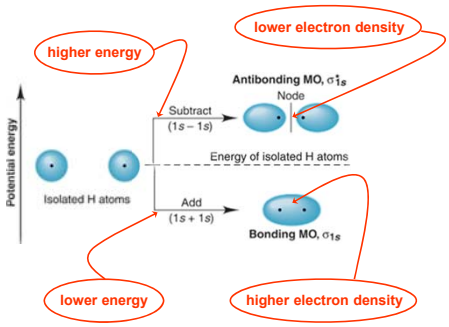
1s molecular orbitals in hydrogen molecule



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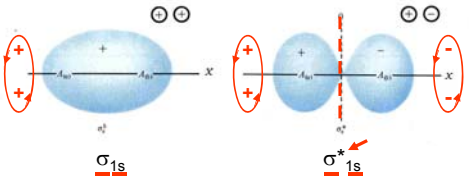
from handouts for chapter 13 (Dickerson, Gray, Haight)



σ_{1s} σ^*_{1s}

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

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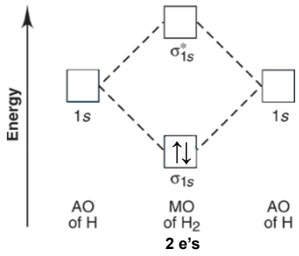
molecular orbital energy diagram (figure 14.28)



configuration: σ_{1s}^2

H_2 bond order = ½ (2-0)=1 *(single bond)*

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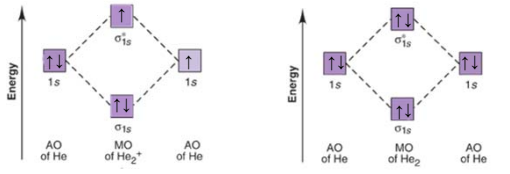
mo diagrams for He_2^+ and He_2 (fig. 14.30, 14.29)



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

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

- two a.o.'s must have **similar** energy *(for homonuclear diatomics 1s ↔ 1s, 2s ↔ 2s, 2p ↔ 2p, etc, also 2s ↔ 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

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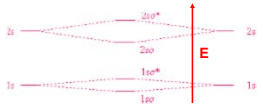
homonuclear diatomic molecules of the second period

- 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}



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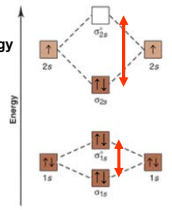
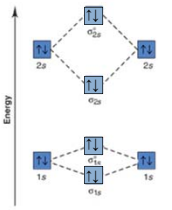
resulting energy level diagrams for Li_2 and Be_2 (fig 14.34, +extra)

σ_{2s} and σ^*_{2s} differ in energy





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

Li_2 6e's

$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2$

b.o. = (4-2)/2=1

Be_2 8e's

$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2(\sigma^*_{2s})^2$

b.o. = (4-4)/2=0

no covalent Be_2 molecule observed

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Molecular Orbitals constructed from Atomic p-Orbitals

pp. 680-684

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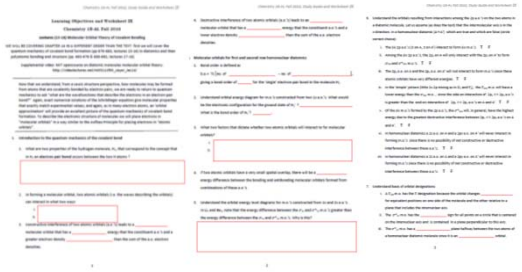
Learning Objectives Worksheet 9, Sections I-II



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

- two a.o.'s must have **similar** energy *(for homonuclear diatomics 1s ↔ 1s, 2s ↔ 2s, 2p ↔ 2p, etc, also 2s ↔ 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

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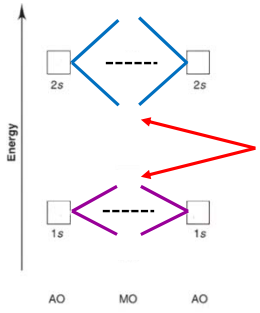
m.o.'s from 1s and 2s a.o.'s



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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

x → A—B or x → A—A' *(for homonuclear)*

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

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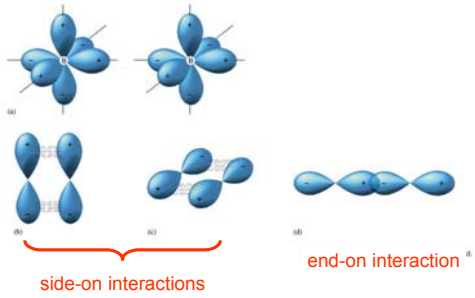
Zumdahl figure 14.35 (interaction among 2p a.o.s on different atoms



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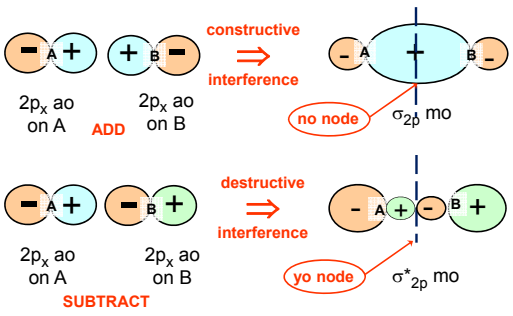
molecular orbitals from atomic p-orbitals (simple story)

- 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") A—B or A—A' *(for homonuclear)*



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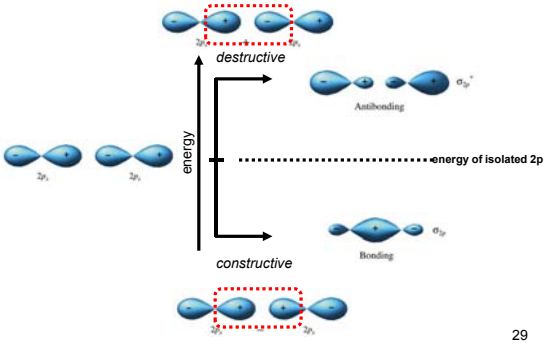
from Zumdahl (fig. 14.36)



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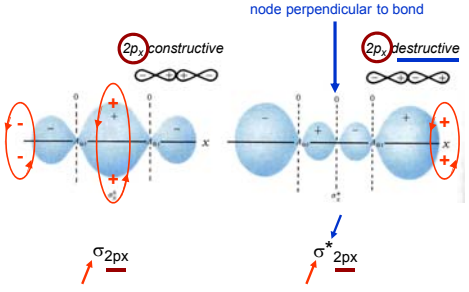
from handouts (DGH) (end-on from $2p_x$ a.o.s) $(\sigma_{2px})_g$ $(\sigma^*_{2px})_u$



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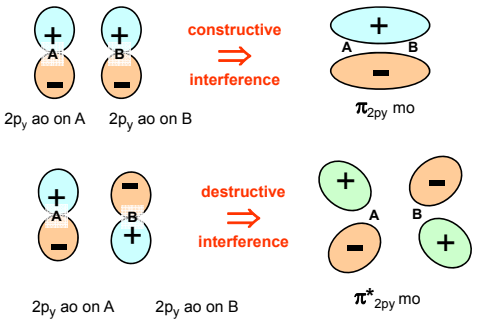
how "side on" , $p_y \leftrightarrow p_y$ and and $p_z \leftrightarrow p_z$ interact



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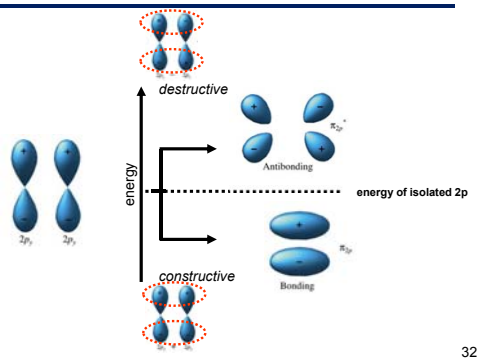
from Zumdahl (fig. 14.36) $p_y \pm p_y = \pi$ and π^*



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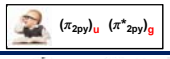
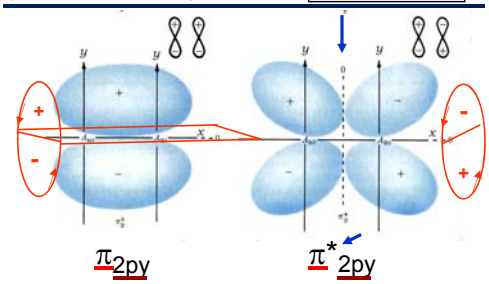
"side-on" p-orbitals from 2p a.o.'s (from DGH, see handout)





π: one nodal plane (which includes internuclear axis)

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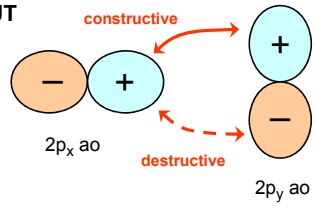
why p_x and p_y orbitals DO NOT interact

- (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

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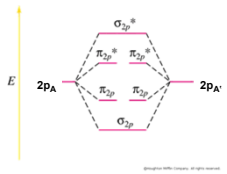
energy of mo's from p-orbitals (simple case), figure 14.37

- "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_{2py}, π_{2pz}) have the same energy and (π^*_{2py}, π^*_{2pz}) have the same energy



- This order applies to O_2 ,F_2, and Ne_2

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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

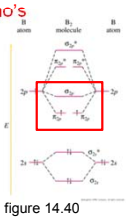

figure 14.40

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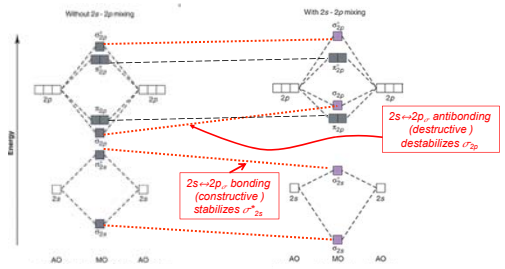
summarizing (fig. 14.38 and 14.40) relative mixing effects
(absolute energies of O_2,F_2,Ne_2 would be lower than those of B_2,C_2,N_2)



simple O_2, F_2, Ne_2

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

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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 $2p_z$ provides bonding (constructive) interactions in the σ_{2p} and σ^*_{2p} 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 $2p_x$ or $2p_y$.
The result TO REMEMBER is that for B_2, C_2, N_2 the π_{2p} has a lower energy than the σ_{2p}

http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/HANDOUTS/DiatomicMoleculeOrbitalEnergyLevels.pdf

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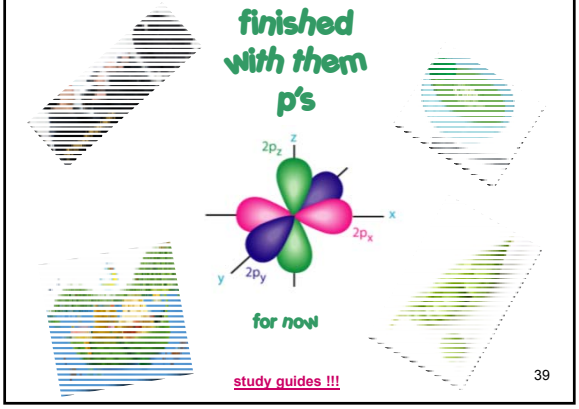

study guides !!!

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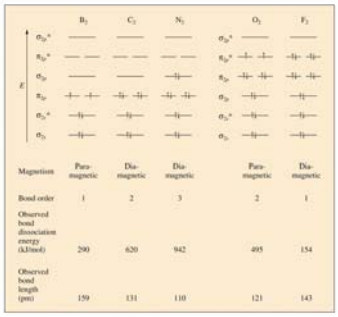
know properties of B_2,C_2, N_2, O_2, F_2, and their ions (fig. 14.41)



HW #6 Due Monday, 7 Nov: WebAssign

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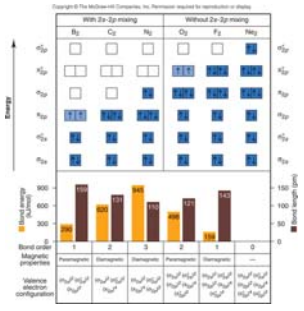
properties of B_2,C_2, N_2, O_2, F_2, and their ions (Silberberg fig. 11.21)



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

molecule	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	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^2$ ↥ ↥	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	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^2$ ↥ ↥	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	?	?

HW #6 Due Monday, 7 Nov: WebAssign

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N_2 diamagnetic O_2 paramagnetic

Joanna and Steve

http://app.jackyoutube.com/video/KcGEev8qulA/Liquid%20Nitrogen%20vs.%20Liquid%20Oxygen:%20Magnetism.html#_ 43

third row

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

Cl_2 (14 VE's)

$(\sigma_{3s})^2 (\sigma^*_{3s})^2 (\sigma_{3p})^2 (\pi_{3p})^4 (\pi^*_{3p})^4$

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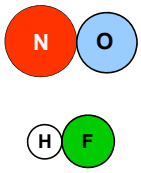
heteronuclear diatomic molecules



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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

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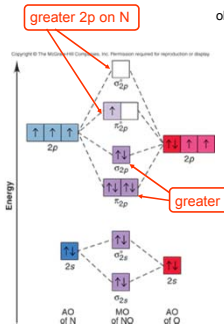
heteronuclear diatomic (NO, fig. 14.43)



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

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

need to be 'told' use light atom energy scheme

11 valence e's

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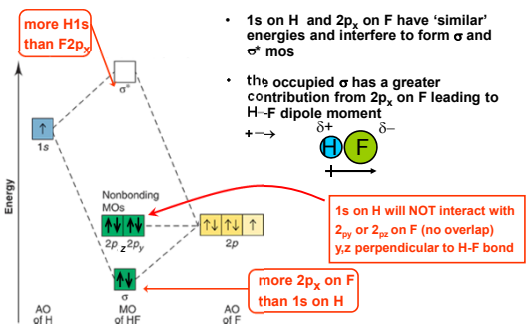
heteronuclear diatomic (HF fig 14.45)



- **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**

1s on H will NOT interact with 2p$_y$ or 2p$_z$ on F (no overlap) y,z perpendicular to H-F bond

more 2p$_x$ on F than 1s on H

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

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Chemistry 1B-AL, Fall 2016
Lectures 13-14

delocalized bonding (p 688): NOT on midterm

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)

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the floating frog

Site Index Page

352 SCIENCE NEWS, VOL. 153 DECEMBER 6, 1997

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.

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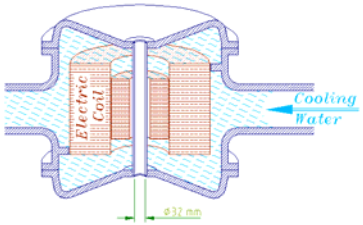
the magnet



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the frog

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

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

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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.

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END OF MATERIAL FOR MIDTERM #2 FALL 2016

On to hybridization !!!

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Lectures 13-14

End of Sessions 13-14

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bond order

bond order =
½ [no. of bonding electrons
- no of antibonding electrons]

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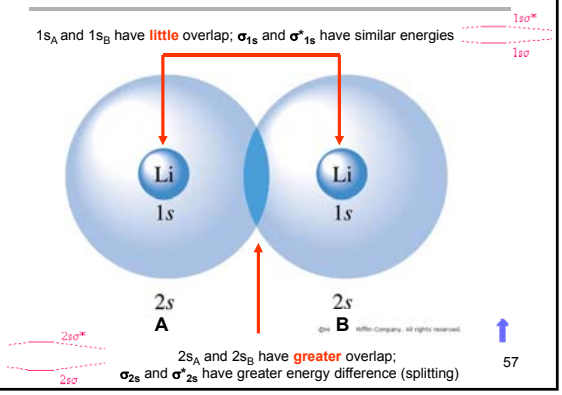
Zumdahl fig. 14.33



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