

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!!!

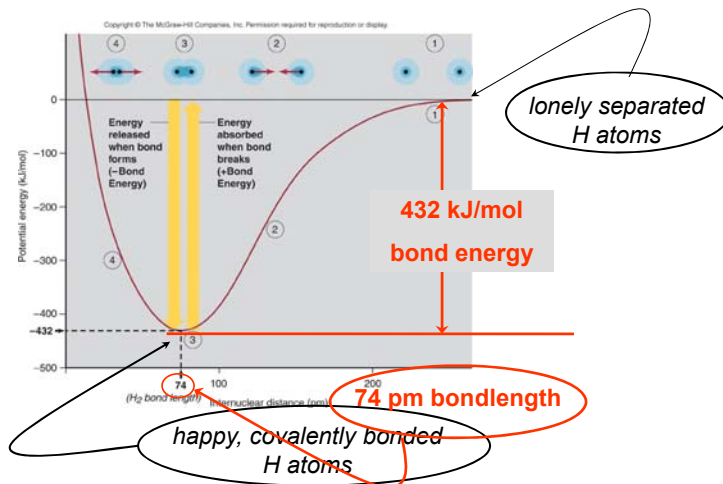
- WE WILL BE COVERING SECOND PART OF CHAPTER 14 (pp 676-688) **FIRST**
- You will go **CRAZY** unless you concentrate on the material presented in lecture and homework

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Lectures 13-14

why do atoms form bonds to become molecules?



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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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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 (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:

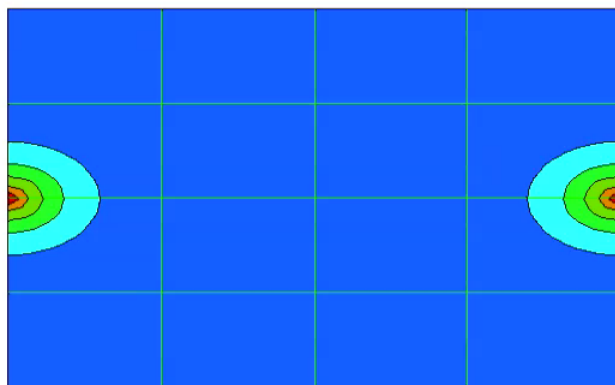
- add (**constructive** interference)
- subtract (**destructive** interference)

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constructive interference of ao's

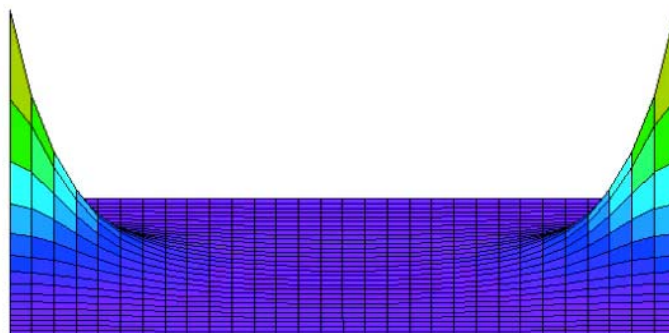


mobond

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

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constructive interference of ao's



mobond

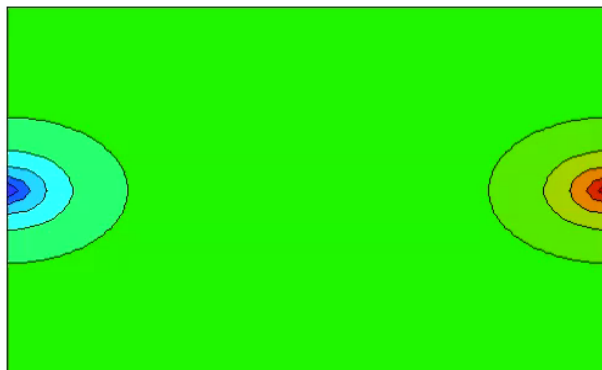
<http://www.wellesley.edu/Chemistry/chem120/mo1.html>

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destructive interference of ao's

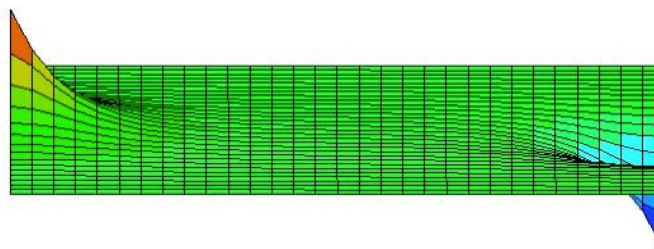


moantibond

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)

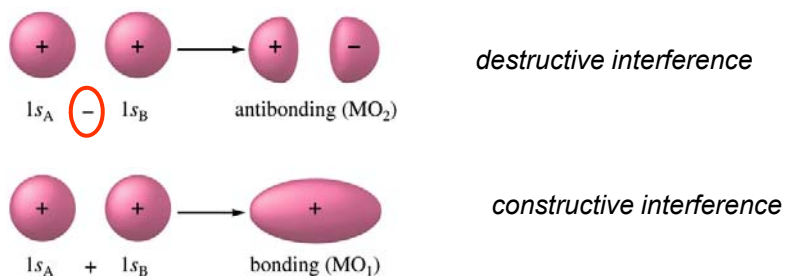
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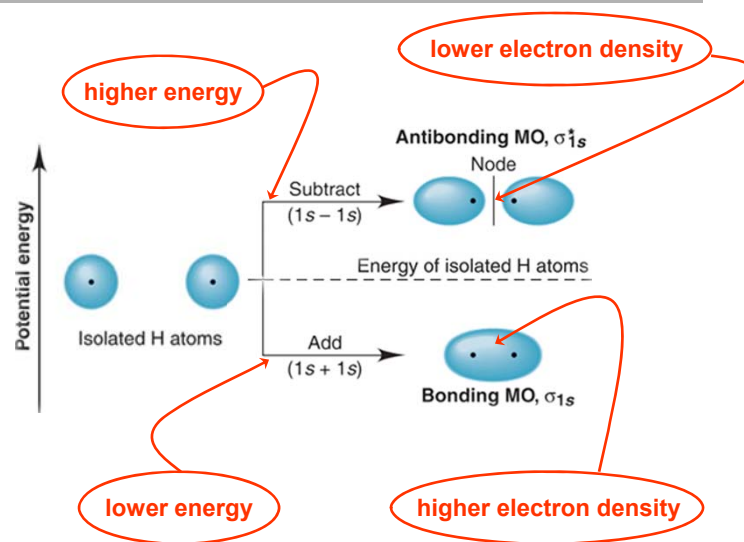
constructive and destructive interference of 1s orbital "waves"

Figure 14.25



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1s molecular orbitals in hydrogen molecule

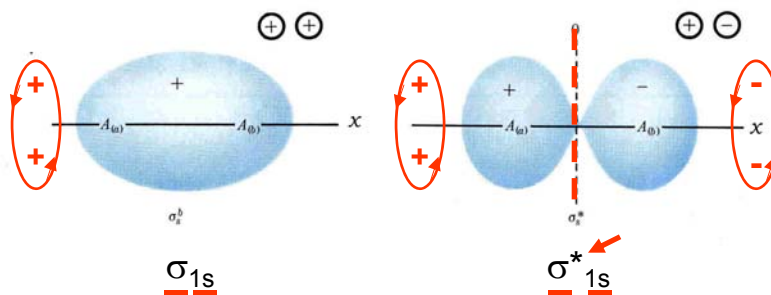


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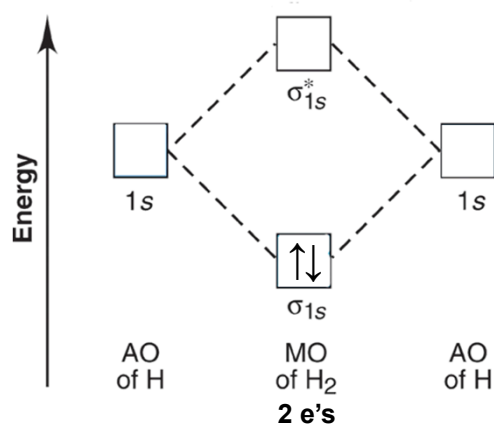
from handouts for chapter 13 (Dickerson, Gray, Haight)



- 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

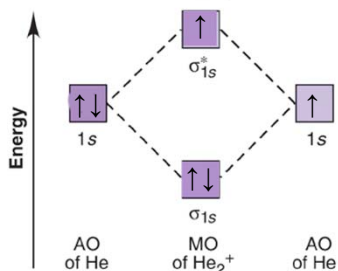
H₂ bond order = $\frac{1}{2}(2-0)=1$ (single bond)

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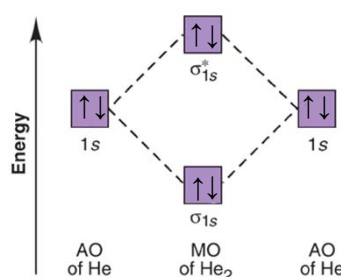
mo diagrams for He₂⁺ and He₂ (fig. 14.30, 14.29)



He₂⁺ (3e's)

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

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



He₂ (4e's)

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

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

no covalent He₂ 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 $1s \leftrightarrow 1s$, $2s \leftrightarrow 2s$,
 $2p \leftrightarrow 2p$, 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

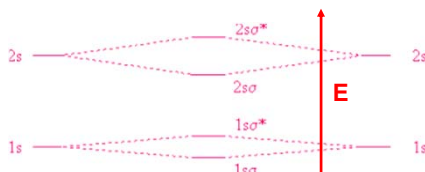
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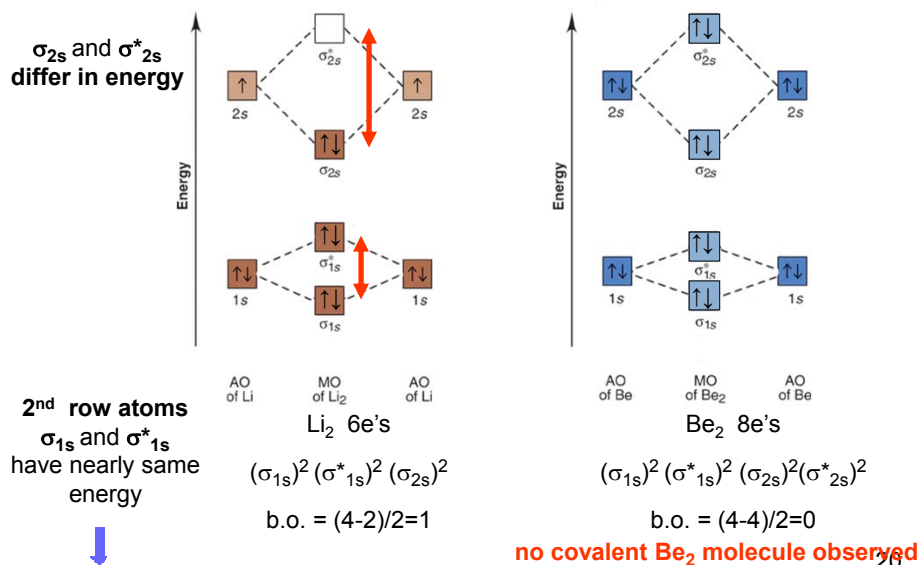
homonuclear diatomic molecules of the second period

- 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 Li₂ and Be₂ (fig 14.34, +extra)



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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

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 Worksheet IX
Chemistry 1B-AL, Fall 2016

Section IX-AL Molecular Orbital Theory of Covalent Bonding

YOU WILL BE COVERING CHAPTER IX IN A DIFFERENT ORDER THAN THE TEXT. But we will cover the quantum mechanics of covalent bond formation (pp. 474-484, sections IX-20) in diatomic and then polyatomic bonding and structure (pp. 483-479 & 482-483, sections IX-21)

Supplemental video: MOI applications on diatomic molecules molecular orbital theory: http://tubechemistry.net/1081112701_video_0614/

Now that we understand, from a basic 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, what spectral evidence 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?

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

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

5. Molecular orbitals for first and second row homonuclear diatomics

1. Bond order is defined as _____

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

giving a bond order of _____ for the "single" electron pair bond in the molecule H_2 .

2. Understand orbital energy diagrams for H_2 '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?

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 H_2 's constructed from $2s$ and $2p$ A.O.'s. In H_2 and He_2 , note that the energy difference between the σ_{2s} and σ_{2s}^* , $m=0$ is greater than the energy difference between the σ_{2p} and σ_{2p}^* , $m=0$. Why is this?

6. Understand basis of orbital designations

1. A σ_{2p} $m=0$ has the σ 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.

2. The σ_{2p}^* , $m=0$ 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.

3. The σ_{2p}^* , $m=1$ has _____ plane halfway between the two atoms of a homonuclear diatomic molecule since it is an _____ orbital.

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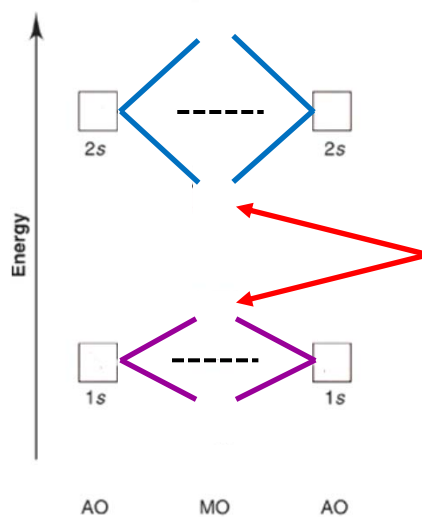
Lectures 13-14

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

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



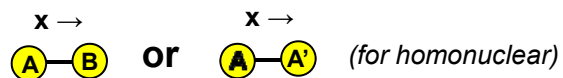
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how $p_x \leftrightarrow p_x$, $p_y \leftrightarrow p_y$ and $p_z \leftrightarrow p_z$ interact

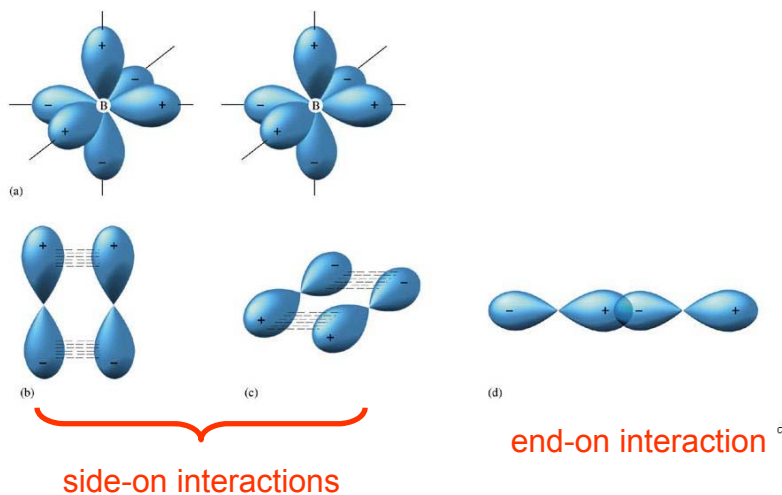
- text uses x-direction for interatomic direction



- 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)

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



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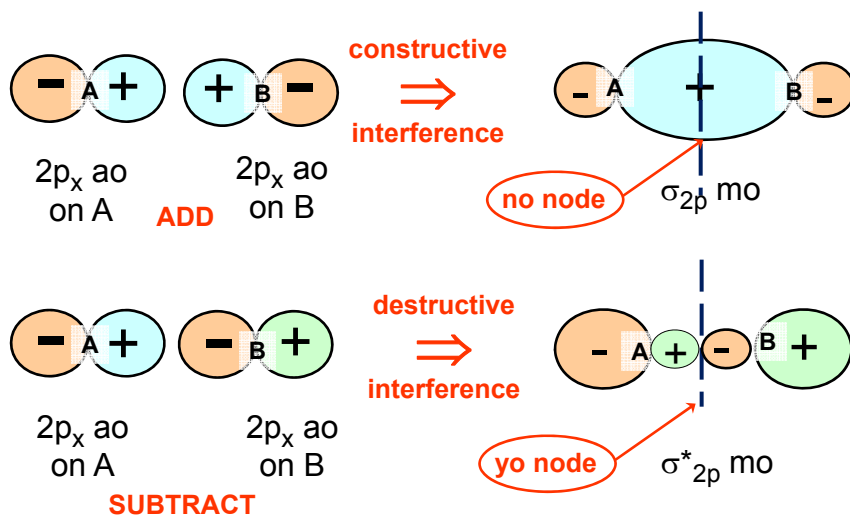
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molecular orbitals from atomic p-orbitals (simple story)

- 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 $p_z \leftrightarrow p_z$)"*

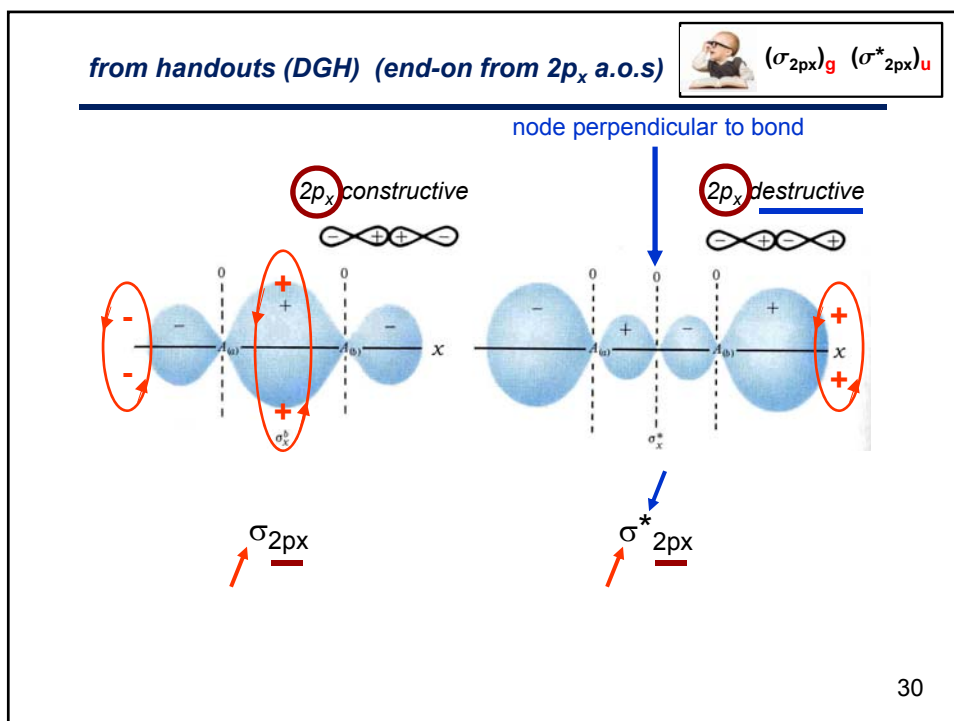
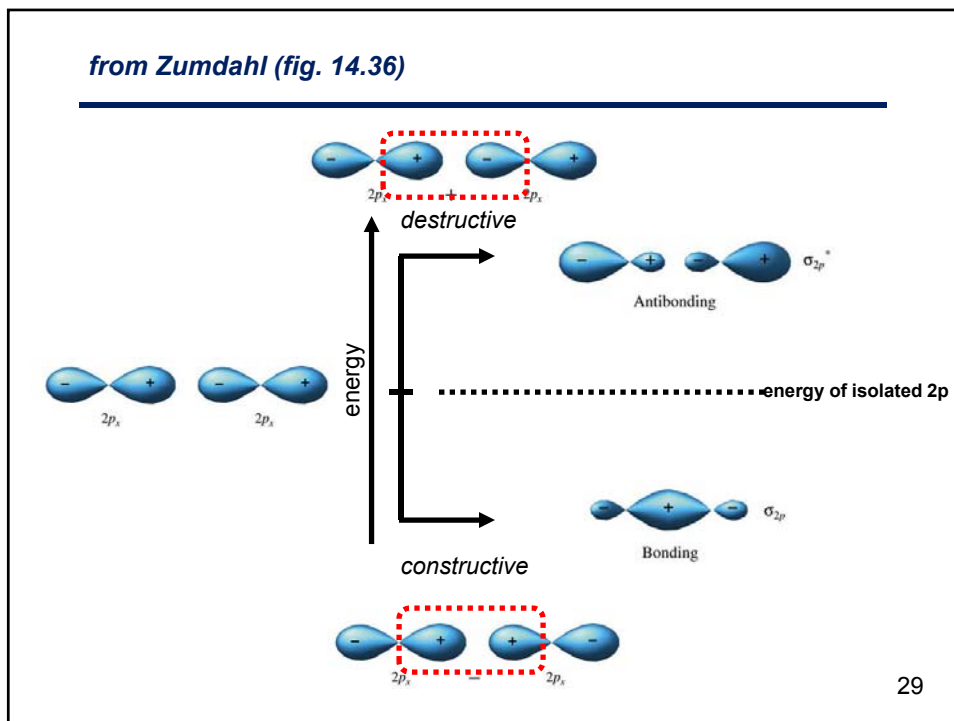
how $p_x \leftrightarrow p_x$ interact ("end-on")



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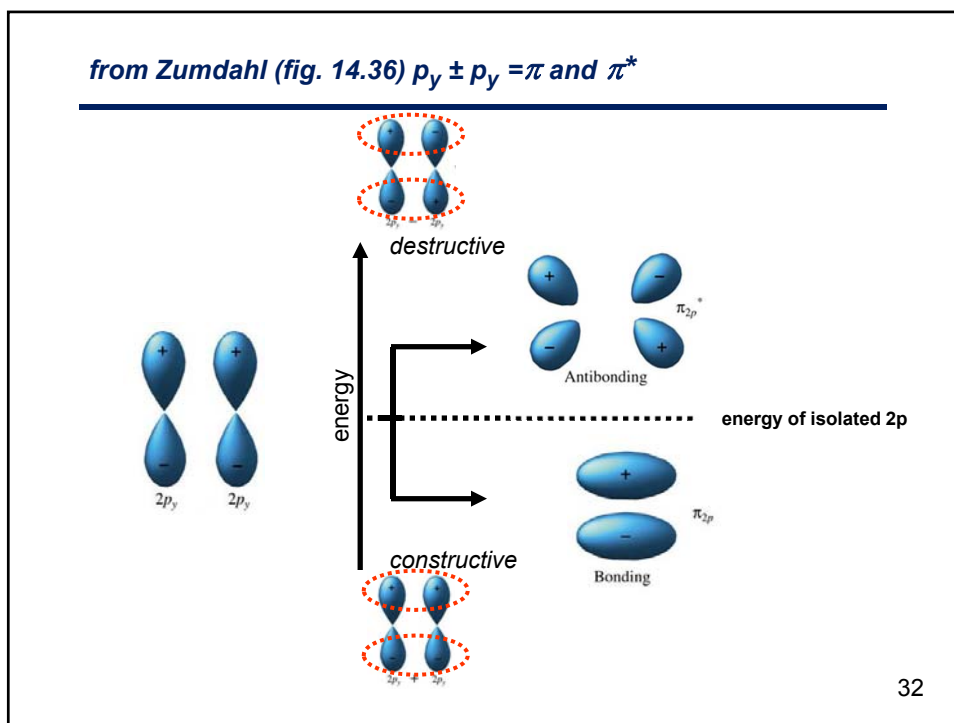
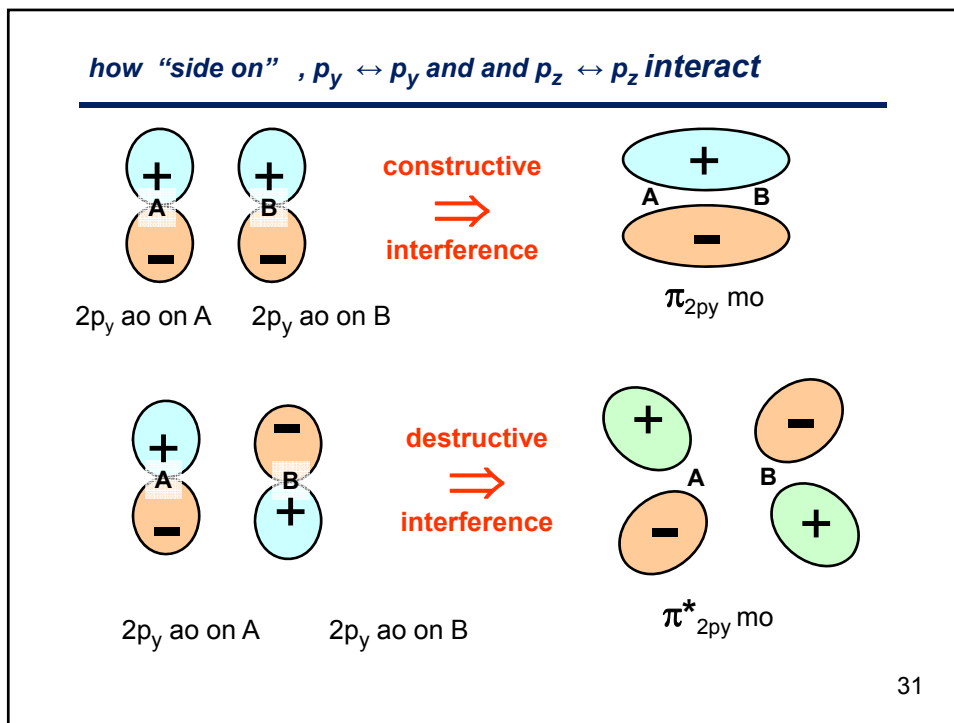
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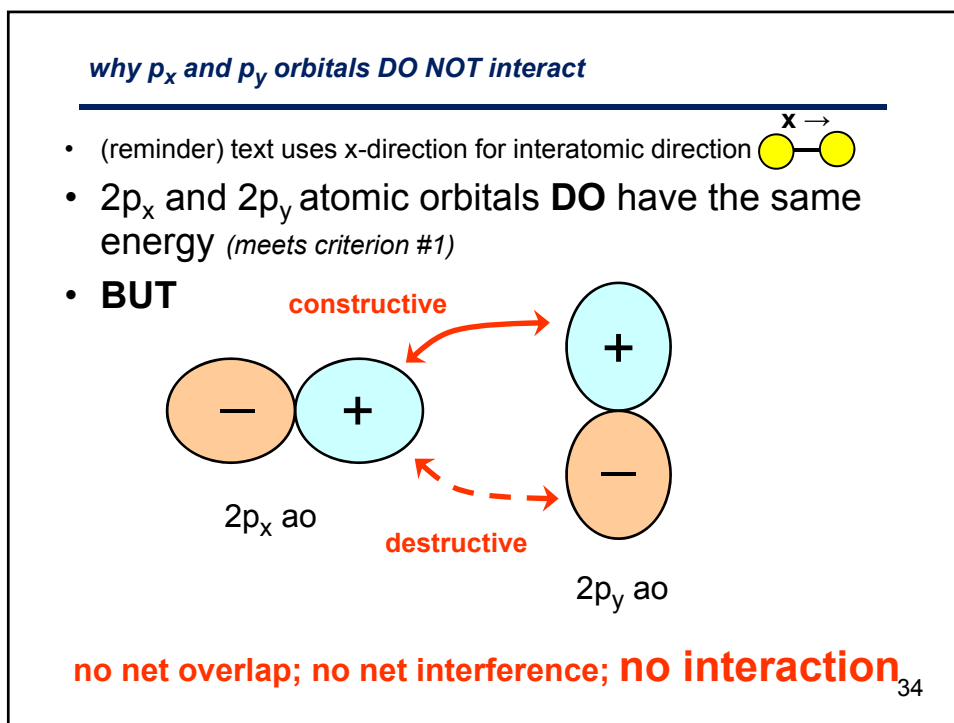
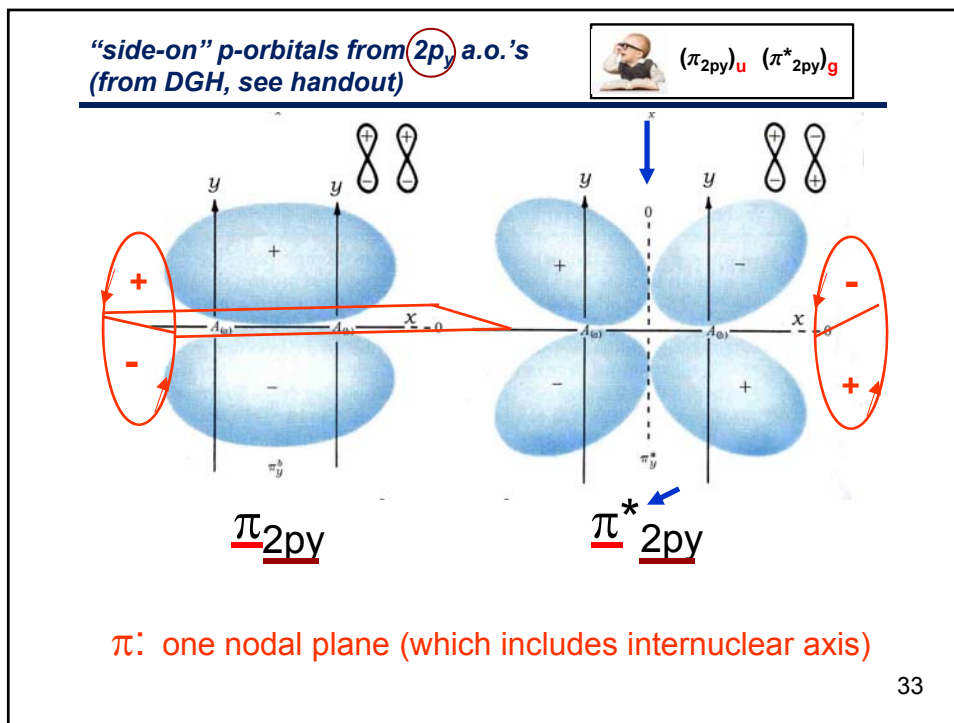
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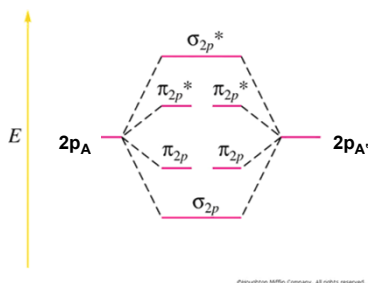


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Lectures 13-14

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

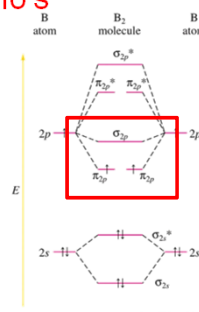


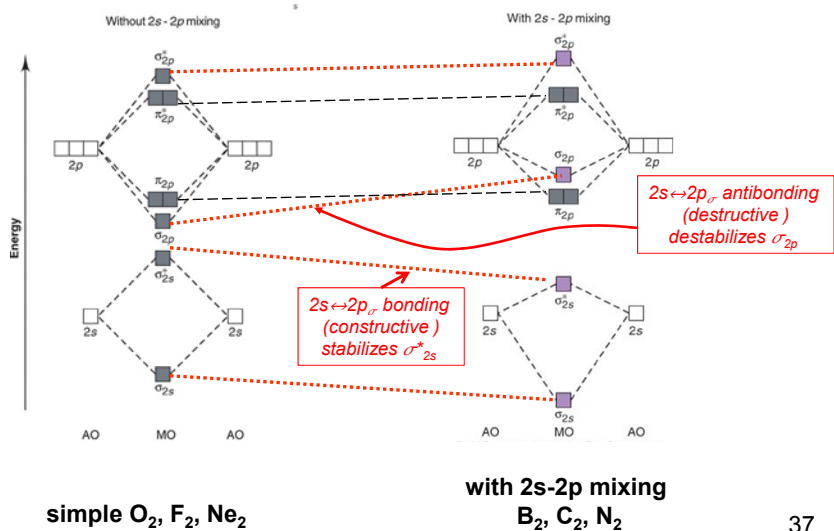
figure 14.40

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Lectures 13-14

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)



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 B_2, C_2, N_2 the π_{2p} has a lower energy than the σ_{2p} .

summarizing (fig. 14.38 and 14.40)



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Lectures 13-14

**finished
with them
p's**

for now

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)

	B_2	C_2	N_2	O_2	F_2
σ_{2p}^*	—	—	—	σ_{2p}^* —	—
π_{2p}^*	—	—	—	π_{2p}^* ↑ ↑	↑ ↑
σ_{2p}	—	—	↑ ↑	σ_{2p} ↑ ↑	↑ ↑
π_{2p}	↑ ↑	↑ ↑	↑ ↑	π_{2p} —	—
σ_{2s}^*	↑ ↑	↑ ↑	↑ ↑	σ_{2s}^* —	—
σ_{2s}	↑ ↑	↑ ↑	↑ ↑	σ_{2s} —	—
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

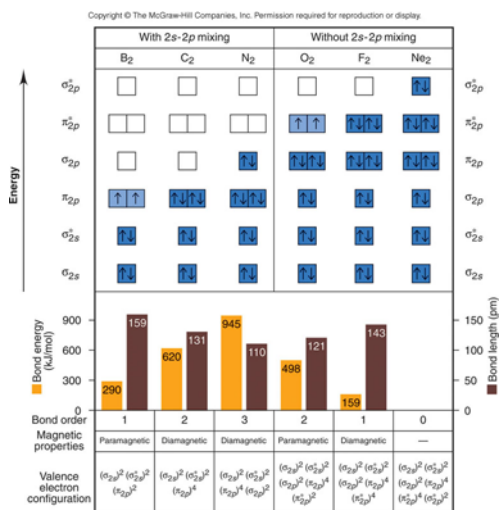
HW #6 Due Monday, 7 Nov: WebAssign

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properties of B₂, C₂, N₂, O₂, F₂, 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	(σ _{2s}) ²	1	105	267	D
Be ₂	(σ _{2s}) ² (σ _{2s} [*]) ²	0	0	?	?
B ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (π _{2p}) ² ↑ ↑	1	290	159	P
C ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (π _{2p}) ⁴	2	620	131	D
N ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (π _{2p}) ⁴ (σ _{2p}) ²	3	942	110	D
O ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (σ _{2p}) ² (π _{2p}) ⁴ (π _{2p} [*]) ² ↑ ↑	2	495	121	P
F ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (σ _{2p}) ² (π _{2p}) ⁴ (π _{2p} [*]) ⁴	1	154	143	D
Ne ₂	(σ _{2s}) ² (σ _{2s} [*]) ² (σ _{2p}) ² (π _{2p}) ⁴ (π _{2p} [*]) ⁴ (σ _{2p} [*]) ²	0	0	?	?



HW #6 Due Monday, 7 Nov: WebAssign



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N₂ diamagnetic O₂ paramagnetic



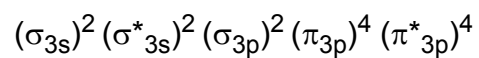
Joanna and Steve

http://app.jackyoutube.com/video/KcGEev8quIA/Liquid%20Nitrogen%20vs.%20Liquid%20Oxygen:%20Magnetism.html#_43

third row

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

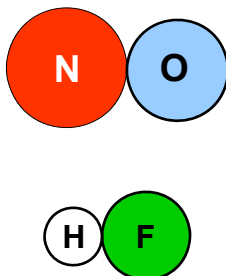
Cl₂ (14 VE's)



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Lectures 13-14

heteronuclear diatomic molecules



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heteronuclear diatomic molecules:

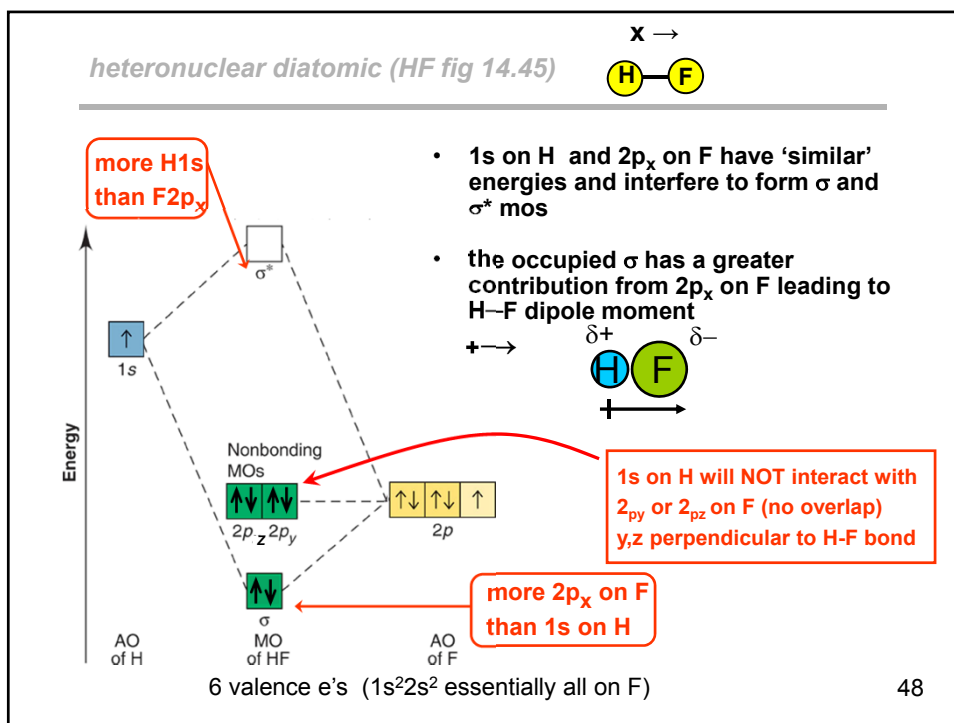
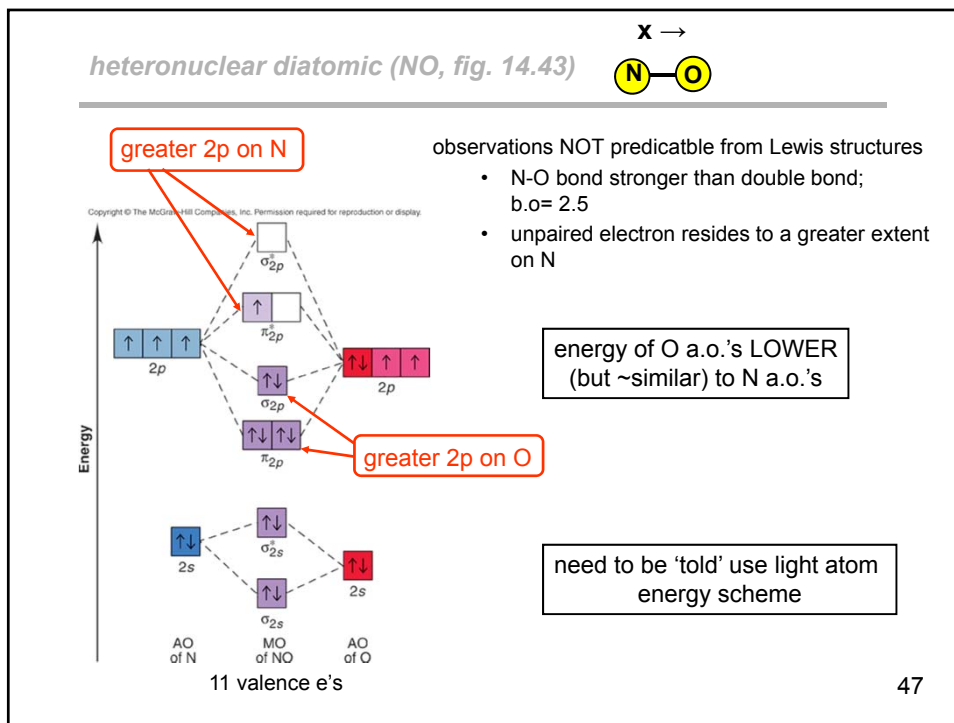
same rules for homonuclear m.o.s apply BUT now:

- '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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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](#)

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SCIENCE NEWS, VOL. 152

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)

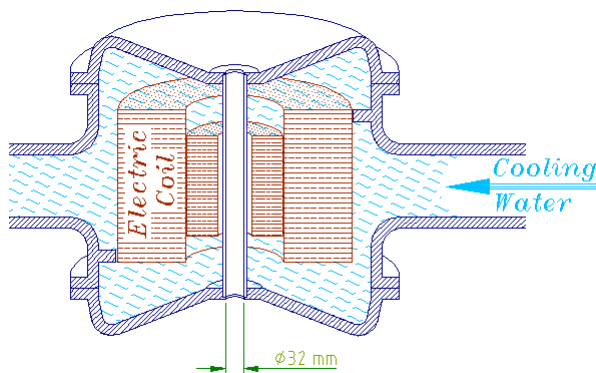
Asked to think of an animal that can fly, most people don't picture a frog. Nonetheless, in April 1997, a team of British and Dutch researchers announced success in levitating a live frog by using a powerful magnet. According to one of the human observers, the frog emerged from the flight unharmed and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

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the magnet



51

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
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On to hybridization !!!

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bond order

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



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Zumdahl fig. 14.33

