Class 3.1
Basic Molecular Orbital Theory Diatomics

Monday, Sept. 13
CHEM 462
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Reading, etc.

- Continuation of Chapter 3. Sections 3-7 – 3.10 in this set of notes.
- Download the "resume of MO theory" from the class Web site for use in conjunction with today's class.
- Next: Appendix I. Read <u>all</u> of the Appendix; this is material on symmetry..

Intro to MO Theory

- Usual approach: **L**inear **C**ombination of **A**tomic **O**rbitals:

$$\text{Atomic Orbitals}: \{\varphi_i; i = 1, \ldots N\}$$

$$\text{Molecular Orbitals}: \{\psi_\mu; \mu = 1, \ldots N\}$$

$$\psi_\mu = \sum_{i=1}^{N} c_{i\mu}\varphi_i = c_{1\mu}\varphi_1 + c_{2\mu}\varphi_2 + \ldots + c_{N\mu}\varphi_N$$

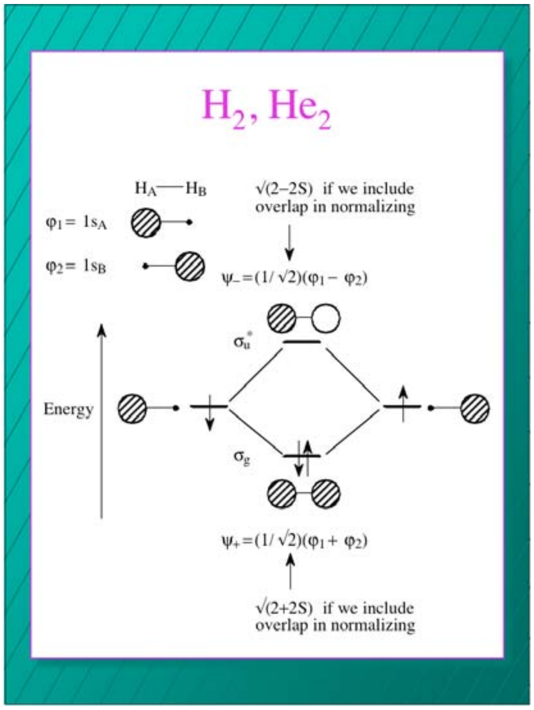
- Coefficients give the contributions that each of the individual AOs make to the MO

MO Theory - General Features

Starting with *N* AOs, we can make *N* molecular orbitals. No more and no less.

MOs are mutually *orthogonal* and *normalized*: overlap between any two MOs is zero and overlap of a MO with itself = 1.

Pauli exclusion principle: an MO can accommodate 2 electrons. One is spin-up ($m_s = +1/2$), one is spin-down ($m_s = -1/2$).



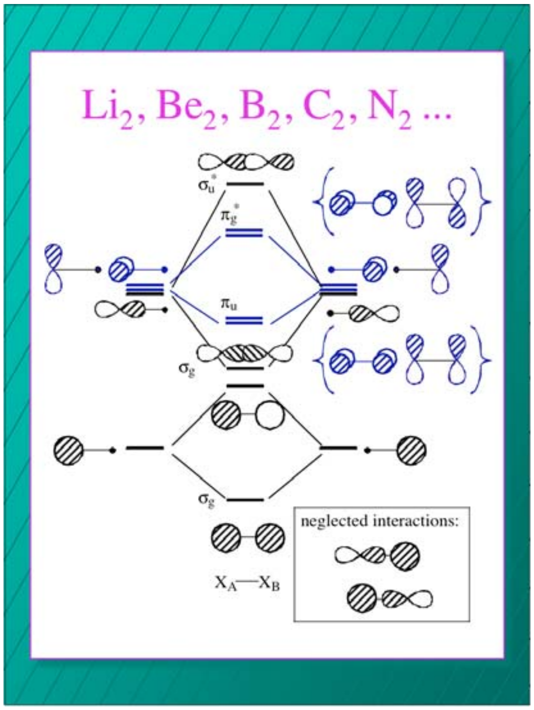
H_2, He_2

$\sqrt{(2-2S)}$ if we include overlap in normalizing

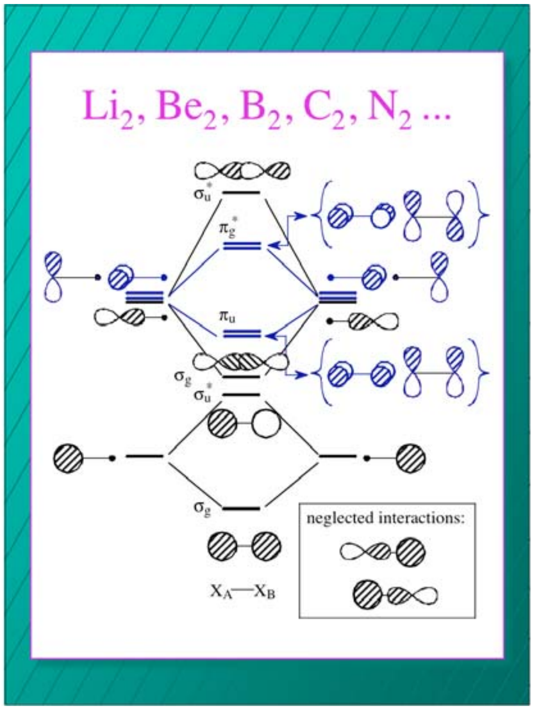
$\psi_- = (1/\sqrt{2})(\varphi_1 - \varphi_2)$

$\psi_+ = (1/\sqrt{2})(\varphi_1 + \varphi_2)$

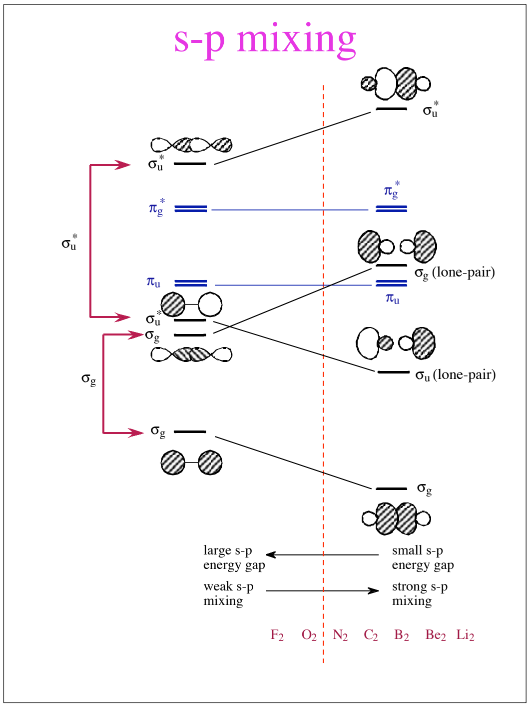
$\sqrt{(2+2S)}$ if we include overlap in normalizing



Li_2, Be_2, B_2, C_2, N_2 ...



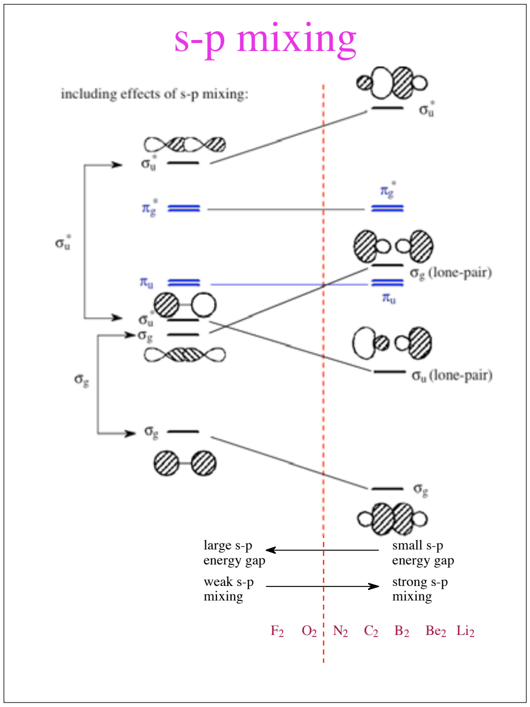
Li_2, Be_2, B_2, C_2, N_2 ...



s-p mixing

large s-p energy gap ← small s-p energy gap

weak s-p mixing → strong s-p mixing



s-p mixing

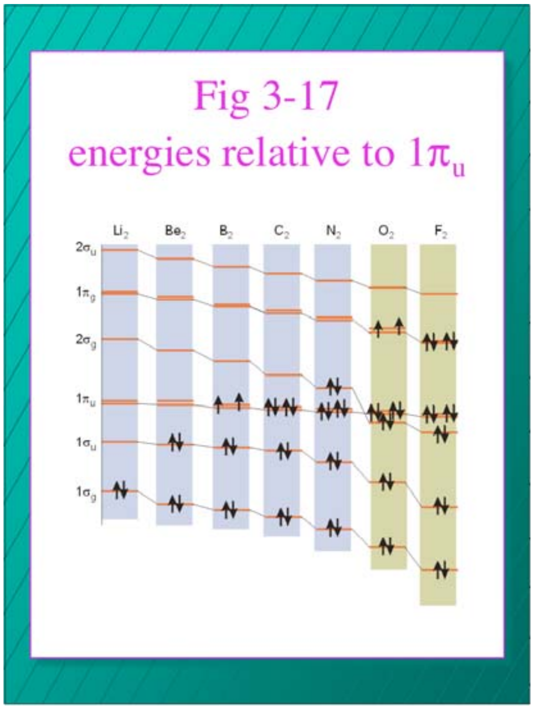
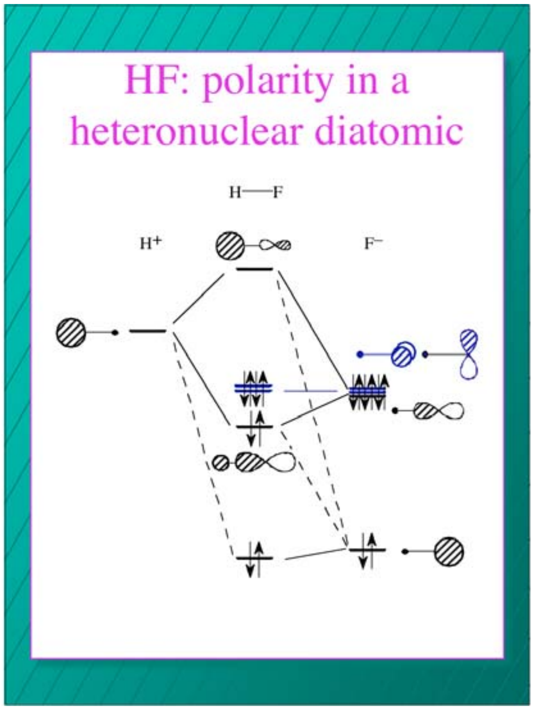
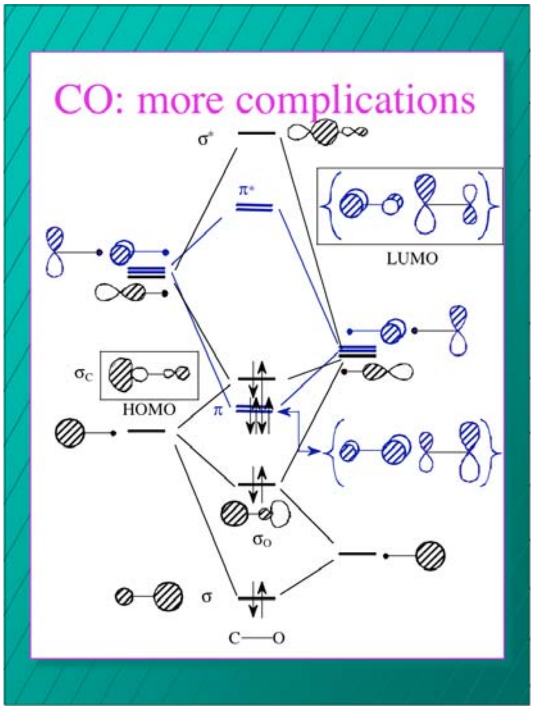


Fig 3-17
energies relative to $1\pi_u$



HF: polarity in a heteronuclear diatomic



CO: more complications