Class 3.1
Basic Molecular Orbital Theory Diatomics

Monday, Sept. 13
CHEM 462
T. Hughbanks

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 all of the Appendix; this is material on symmetry.

Intro to MO Theory

- Usual approach: Linear Combination of Atomic Orbitals:

  Atomic Orbitals: \( \{ \varphi_i, i = 1, K, N \} \)
  Molecular Orbitals: \( \{ \psi_\mu, \mu = 1, K, N \} \)

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

- 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 \( (m_s = -1/2) \).
**H₂, He₂**

\[ \psi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \]

Energy

\[ \psi = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \]

v(2−2S) if we include overlap in normalizing

**Li₂, Be₂, B₂, C₂, N₂ ...**

\[ \psi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \]

Energy

\[ \psi = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \]

neglected interactions:

\[ X_A \rightarrow X_B \]

s-p mixing

large s-p energy gap

small s-p energy gap

strong s-p mixing

weak s-p mixing
s-p mixing

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

HF: polarity in a heteronuclear diatomic

CO: more complications