[TP] When atomic orbitals (AO's) on different atoms combine, the resulting molecular orbital (MO) is ...

17% 1. less stable than the AO's
17% 2. has the same energy as the AO's
17% 3. more stable than the AO's
17% 4. 1 and 2
17% 5. 1 and 3
17% 6. 2 and 3

BOSTON UNIVERSITY

Lecture 34 CH101 A2 (MWF 11:15 am)

Monday, December 3, 2018

Begin ch 10: Modeling bonding in molecules: http://goo.gl/1h0S9C

- Mixing atomic orbitals (AO's) makes molecular orbitals (MO's)
- 1s MO's: CDF https://goo.gl/eliM2a
- AO-MO correlation diagrams
- Bond order: H_2^+ to He_2 (!)

Next lecture: Only valence AO's affect bonding/antibonding: CDF: https://goo.gl/QLHdRf ; Bond order: Li_2^+ to Be_2 (!) ; 2p MO's: CDF https://goo.gl/2MEiRA ; B_2 to Ne_2 ; When atoms are different, use Symmetry, Overlap, Energy (SOE) to decide which AOs combine ; Covalent versus ionic character ; MO description of hydroxide, OH^-, and HOH (water)

BOSTON UNIVERSITY

Bonding in diatomic molecules
http://goo.gl/1h0S9C

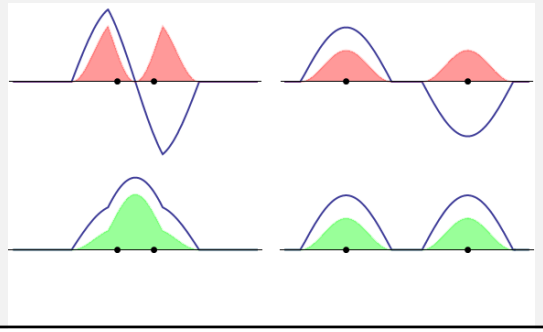
BOSTON UNIVERSITY

Atoms interact by combining waves

AO "+" AO → 2 MO's
"+" means combining

BOSTON UNIVERSITY

1s molecular orbitals:
http://quantum.bu.edu/CDF/101/1sMolecularOrbitals.cdf



BOSTON UNIVERSITY

9

Relative AO phase determines MO character

here the different phases of the p orbital are labelled positive and negative – this can be confusing and so is best avoided

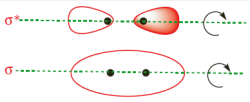
here the different phases of the p orbital are shown by shading one half and not the other

BOSTON UNIVERSITY

10

σ MO's have cylindrical symmetry

Antibonding orbitals are designated with a * e.g. σ*, or π*



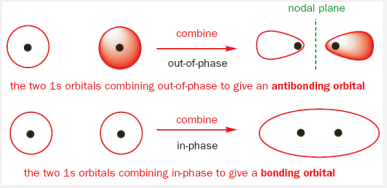
we can rotate about this axis without changing the MOs

both MOs have rotational symmetry about the axis through the two nuclei

BOSTON UNIVERSITY

11

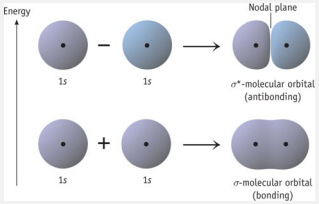
1sσ and 1sσ*



BOSTON UNIVERSITY

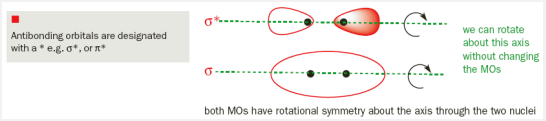
12

1sσ and 1sσ*

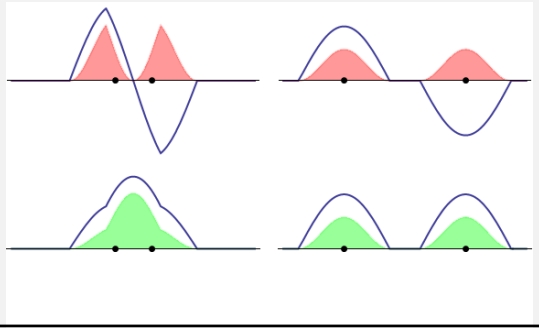


Mahaffy et al., Figure 10.20, p. 400

σ is "bonding" and σ* is "antibonding"

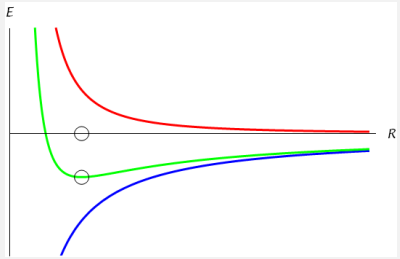


1s molecular orbitals:
http://quantum.bu.edu/CDF/101/1sMolecularOrbitals.cdf



AO-MO correlation diagrams

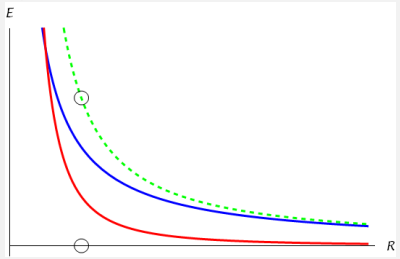
Bonding *PE*, *KE* and total *E*



Attractive (< 0) PE is opposed by repulsive (> 0) KE.
Molecular size is at minimum of total E.

BOSTON UNIVERSITY

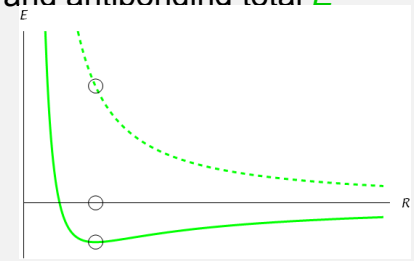
Antibonding *PE*, *KE* and total *E*



Repulsive (> 0) PE enhanced by repulsive (> 0) KE.
No minimum of total E--- atoms fly apart!

BOSTON UNIVERSITY

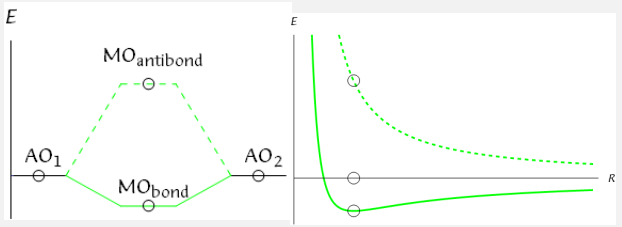
Bonding and antibonding total *E*



What matters are the total bonding and antibonding E at the bonding minimum versus the AO energies---the energy at infinite separation.

BOSTON UNIVERSITY

Correlation diagrams …



… summarize
bonding and antibonding effects

BOSTON UNIVERSITY

[TP] When atomic orbitals (AO's) on different atoms combine, the resulting molecular orbital (MO) is …

17% 1. less stable than the AO's
17% 2. has the same energy as the AO's
17% 3. more stable than the AO's
17% 4. 1 and 2
17% 5. 1 and 3
17% 6. 2 and 3

Bond order: H_2^+ to He_2 (!)

Filling of MO's → H_2 MO configuration

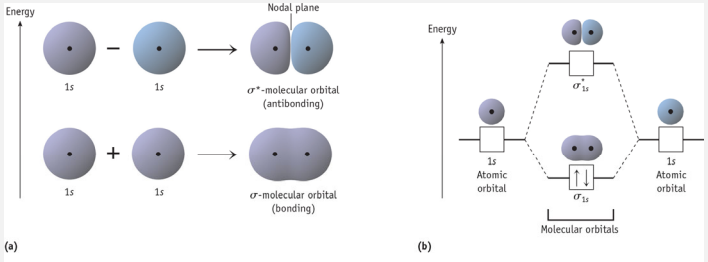
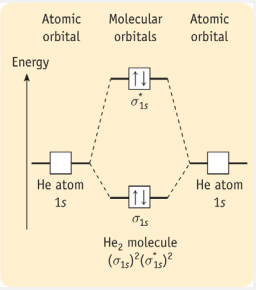


FIGURE 10.20 Molecular orbitals. (a) Bonding and antibonding σ molecular orbitals are derived by mathematical manipulation on two 1*s* atomic orbitals on adjacent atoms. Notice the presence of a node (a plane on which there is zero probability of finding an electron in the antibonding orbital). (b) A molecular orbital diagram for a ground-state H_2 molecule. The two electrons are placed in the σ_{1s} orbital, the lowest-energy molecular orbital.

Mahaffy et al., Figure 10.20, p. 400

Filling of MO's → He_2 MO configuration



Mahaffy et al., Figure 10.21

Bond order

(bonding electrons – antibonding electrons)/2

Division by two is because, by convention, a single "bond" shares a pair of electrons

$H_2^+ = H{\cdot}H^+ \rightarrow$ bond order $= 1/2$

$H_2 = H{:}H \rightarrow$ bond order $= 1$

$He_2 \rightarrow$ bond order $= 0$

$He_2^+ \rightarrow$ bond order $= ...?$

BOSTON UNIVERSITY

25