

Chemistry 2000 Slide Set 2: LCAO-MO theory for homonuclear diatomic molecules

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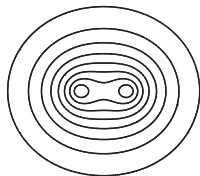
MO theory for homonuclear diatomic molecules

- We want to develop MO theory for diatomic molecules involving atoms beyond H and He.
- Initially, we will focus on **homonuclear** diatomic molecules, i.e. those in which both atoms are of the same element.

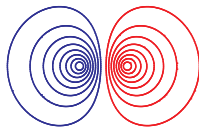
Convention: The bond axis is the z axis.

Review: LCAO-MO theory of first-row diatomics

- In the last lecture, we combined 1s AOs to obtain sigma bonding and antibonding molecular orbitals for the **first row** of the periodic table:



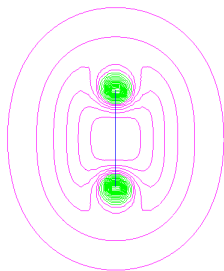
σ_{1s}



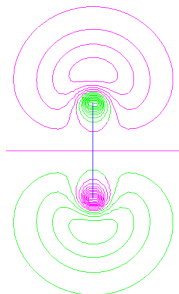
σ_{1s}^*

LCAO-MOs of higher orbitals

- We can combine higher AOs in a similar way.
- σ and σ^* orbitals obtained from the 2s AOs:



σ_{2s}

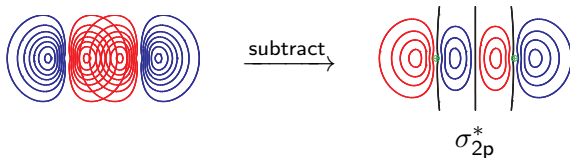
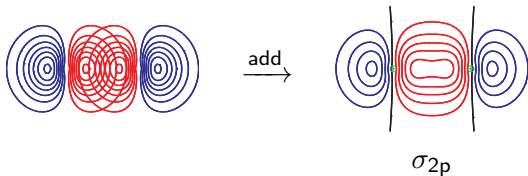


σ_{2s}^*

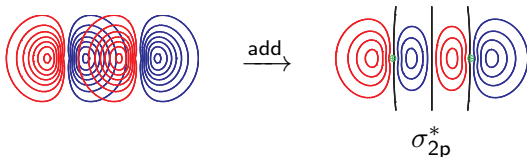
- Note that these look very similar to the corresponding MOs obtained by LCAO of first-row 1s AOs. The change in sign of the AO is far from the bonding region and has relatively little effect on bonding.

2p orbitals can be combined in two different ways:

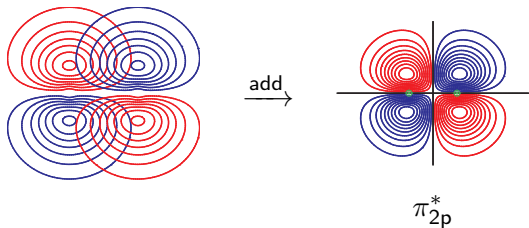
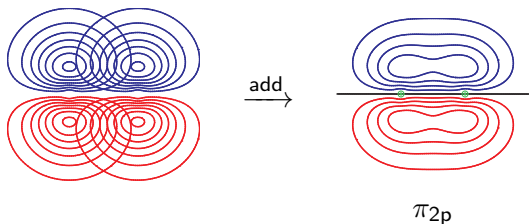
- 1 The $2p_z$ orbitals are oriented toward each other so adding them gives sigma (cylindrically symmetric) orbitals:



Note: Subtracting the $2p_z$ orbitals is equivalent to adding them out of phase:

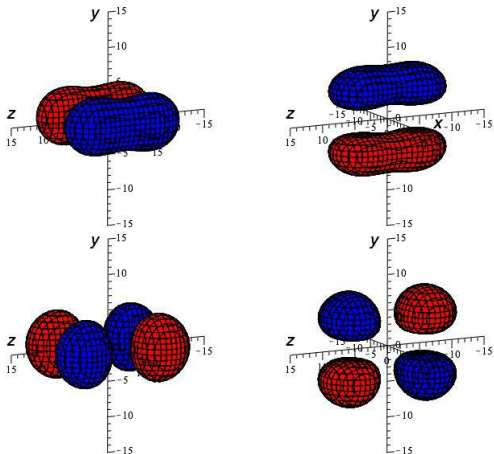


- 3 The $2p_x$ and $2p_y$ orbitals are perpendicular to the bond axis. Adding them gives π orbitals:



Pi orbitals have a nodal plane **through** the bond axis.

Note: There are **two** degenerate π orbitals and **two** degenerate π^* orbitals because we can combine p_x **or** p_y orbitals in this manner:

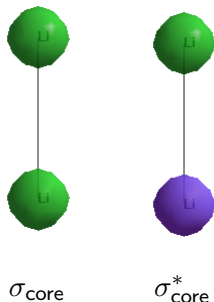


Core orbitals

- Bonding involves the outer (valence) electrons. We can therefore ignore the core electrons.
- If we do an *ab initio* (from first principles) calculation, which includes all the electrons, we can compute MOs that derive from the core electrons. However, these MOs are essentially identical to the corresponding AOs.

Core orbitals (continued)

Example: Here are the core MOs of Li_2 , arising from the two possible linear combinations of the 1s orbitals:

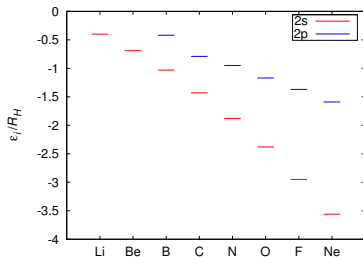


Although formally bonding and antibonding, these two MOs have essentially identical energies. The lack of overlap means that these core orbitals do not participate in bonding.

AO energies and LCAO theory

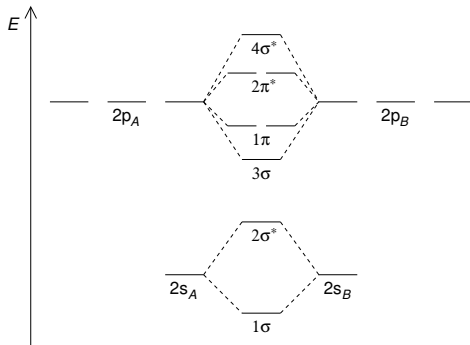
Principle: AOs of similar energies and appropriate symmetries can mix to form MOs.

- 2s and 2p atomic orbital energies:



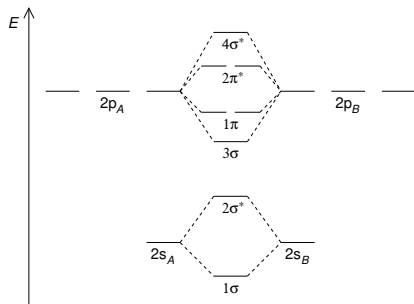
- For higher- Z elements in period 2, there won't be much mixing between the 2s and 2p orbitals, and the MOs will be those described above.

The “normal” MO diagram



- Applies to O_2 , F_2 and Ne_2

The “normal” MO diagram



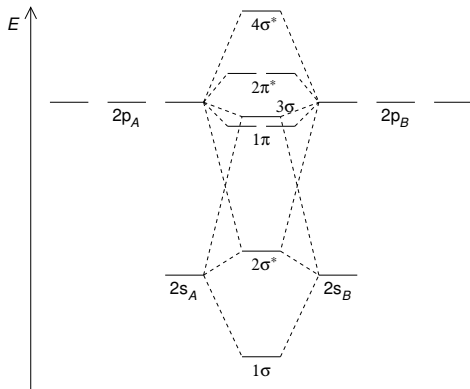
Note that

- 1 We only consider the valence MOs and number these MOs starting from 1 (e.g. lowest **valence** MO is 1σ).
- 2 The σ and π orbitals are numbered independently.

s-p mixing

- The closer the 2s and 2p orbitals are in energy, the more these mix to form MOs.
- s-p mixing lowers the energies of the 1σ and 2σ MOs, and raises the energies of the 3σ and 4σ MOs.
- If this mixing is strong enough, the 3σ can end up higher in energy than the 1π orbitals.

MO diagram with strong s-p mixing



- Applies to $\text{Li}_2\text{-N}_2$

Ground-state electronic configurations of the 2nd period homonuclear diatomics

Bond order

Correlation with Lewis diagram

Paramagnetic or diamagnetic?

Lessons learned from the homonuclear diatomics

- Atomic orbitals of the same symmetry can mix to form MOs. For diatomics, we mean symmetry with respect to the bond axis.

σ symmetry: s, p_z

π symmetry: p_x, p_y

- In order for mixing to be significant, the atomic orbitals must have similar energies.

Rule of thumb: Mixing is (relatively) insignificant if the difference in energy between the AOs is much greater than 1 Ry (1 Rydberg = R_H).