

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 19: Molecular orbitals and homonuclear diatomics

References

1. Levine, *Physical Chemistry*, 19.1–19.3

Key Concepts

- To solve for the electronic structure and energies of “complex” molecules (i.e. anything more complicated than H_2^+) we employ an approximation, LCAO-MO (linear combination of atomic orbitals to form molecular orbitals).
- Molecular wave functions (orbitals) are formed by mathematically combining atomic wave functions (orbitals).
 - If we add two atomic orbitals in phase ($\psi_A + \psi_B$) we obtain a bonding molecular orbital. Bonding molecular orbitals stabilize a bond between two atoms because they are at a lower energy than the parent atomic orbitals. The electron density of a bonding MO is typically oriented in a way that will stabilize or connect the two atoms.
 - An anti-bonding orbital is formed when subtracting two atomic orbitals (or adding them out of phase), namely $\psi_A - \psi_B$. Anti-bonding MO's destabilize bonds because they are higher in energy than the parent atomic orbitals. The electron density of an anti-bonding MO is directed away from the internuclear region.
- Once molecular wave functions are constructed the Schrödinger Equation can be used to find the internuclear distances, R , that minimizes the energy of the system. This becomes more complicated as the molecule becomes large.
- Molecular orbitals are also characterized by their symmetry.
 - σ MO's are symmetric through a rotation about the bond axis. Usually there is electron density located in the bond plane (plane containing the nuclei and the bond axis).
 - π MO's are not symmetric when rotated around the bond axis. The electron density of π MO's is located out of the bonding plane (above and below).
- The strategy for tackling complex molecules is similar to the approach we took in constructing multi-electron atoms: take combinations of solutions we already have and try and fit them to the more complex situation.
- In forming molecular orbitals from atomic orbitals, the total number of orbitals (wave functions) must remain the same.
 - From 2 $1s$ atomic orbitals you form two MO's: σ and σ^* .
 - From 2 sets of $2p$ atomic orbitals (6 AO's total) you form 6 MO's: a σ and σ^* from the interactions of the p_z orbitals. There are also 2 π and 2 π^* MO's formed from the p_x - p_x and p_y - p_y interactions.
- The same rules apply for electron occupation of molecular orbitals: Pauli exclusion (can't have 4 identical quantum numbers, 2 e^- per orbital), Aufbau (MO's fill in order of increasing energy), and Hund's rule (fill to maximize multiplicity).
- The relative energies of MO's becomes complex as the n of the parent AO's increases, as for example in the relative energy of the π_{2p} versus σ_{2p} .