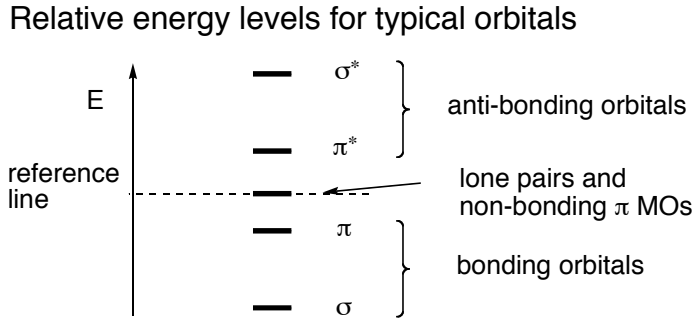
Recap of Chapter 14

1. Atomic orbitals (AOs) in molecules form molecular orbitals (MOs)

2. *n* AOs form *n* MOs; however the contribution of each AO varies between the MOs.

3. There are 5 general types of MOs.



σ orbitals are formed from sp^n hybrids
π orbitals are formed from pure p orbitals (mutually parallel)
Non-bonding orbitals can be either sp^n or π orbitals

4. Only orbitals of the same symmetry can interact: π and σ have different symmetry so they do not interact with each other.

5. All electrons are placed in pairs from the lowest energy level up

6. The **h**ighest **o**ccupied **m**olecular **o**rbital is called HOMO

7. The **l**owest **u**noccupied **m**olecular **o**rbital is called LUMO

8. Almost all chemistry occurs between the HOMO and LUMO orbitals

9. HOMO and LUMO are called frontier molecular orbitals (FMOs) and they define reactivity of the molecule:

   • HOMO controls the donor properties (nucleophilicity, basicity)

- LUMO controls the acceptor properties (electrophilic and acidity)

10. In general, when molecules react, electrons are redistributed in such a way that net electron density follows from an electron rich molecule (nucleophile or donor) to a more electron poor molecule (electrophile or acceptor).
11. Understanding the localization of the HOMO and LUMO (FMOs) allows for understanding the chemical reactivity
12. A new chemical bond will be formed between atoms of non-zero coefficient of MO, and usually there is a preference for the atom with the largest value of the coefficient.
13. π MOs are particular subset of molecular orbitals. The above rules apply to them and they are easy to examine.

Two examples of significance using MOs from Chapter 14

1. UV spectroscopy:

   •Promotion of an electron from a filled to unfield MO is called electronic excitation and occur upon absorption of a quantum of energy (light) in the region 200-400 nm (UV) and 400-800 nm (vis)

• Lowest energy (longest wavelength) electronic absorption for a molecule involves the HOMO-LUMO electronic transition

2. Diels-Alder reaction

is an example of a concerted (single-step) cycloaddition reaction involving the HOMO of diene and the LUMO of the dienophile, and a cyclic array of 6 p electrons.

• This type of reaction is called pericyclic and its stereochemical outcome is controlled by the symmetry of the involved FMOs.