Filled → Empty Orbital Interactions

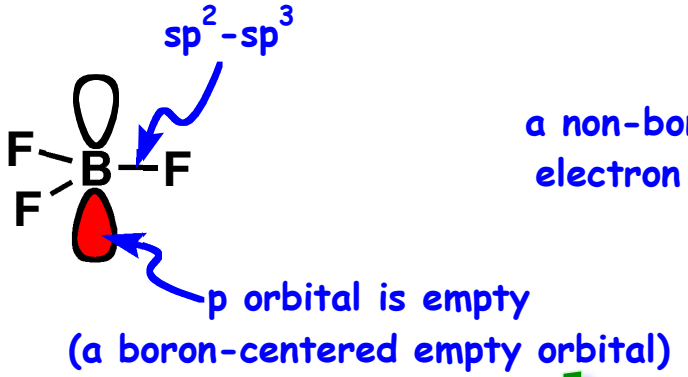
When it comes to molecular structure and reactivity, the only interactions that are important are interactions between filled and empty orbitals. In other words, filled-filled and empty-empty interactions are of no significance. Of all the possible filled-empty orbital combinations, one pairwise combination matters most - it's the interaction between the **highest occupied molecular orbital (HOMO)** and the **lowest unoccupied molecular orbital (LUMO)**. The HOMO & LUMO orbitals are known as the **frontier orbitals**, and the HOMO-LUMO pairwise combination is called the **frontier orbital interaction**. We can systematically enumerate the possible HOMO-LUMO pairwise combinations of the commonly encountered filled (σ, *n*, π) and empty (σ*, *a*, π*) orbitals (note: *a* = an atom-centered empty orbital). The table below shows there are just 9 such combinations. Each combination can either be a sigma-type (coaxial or end-on) or a pi-type (side-by-side), making a total of 18 different frontier orbital interactions that will explain almost everything in chemistry! Whether an interaction is pi-type or sigma-type will depend on constraints imposed by molecular geometry (if there are no constraints, a sigma-type interaction is favored).

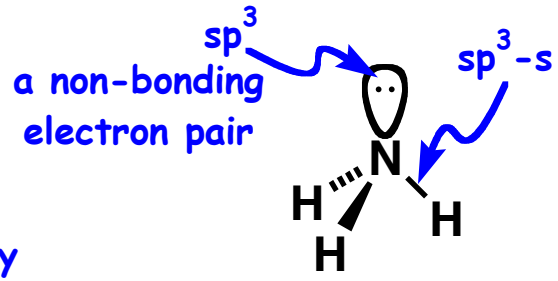
filled \ empty	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*

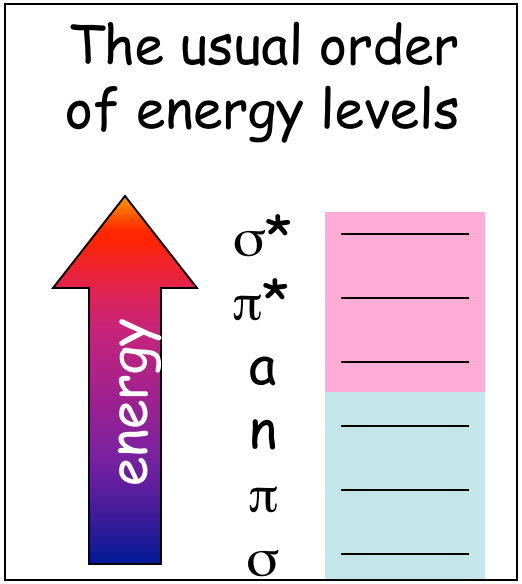
HOMO (filled) + LUMO (empty) = Frontier Orbital Interaction

Frontier Orbitals & Reactivity

Consider the reaction: $BF_3 + NH_3 \rightarrow F_3\bar{B}\text{-}\overset{+}{N}H_3$

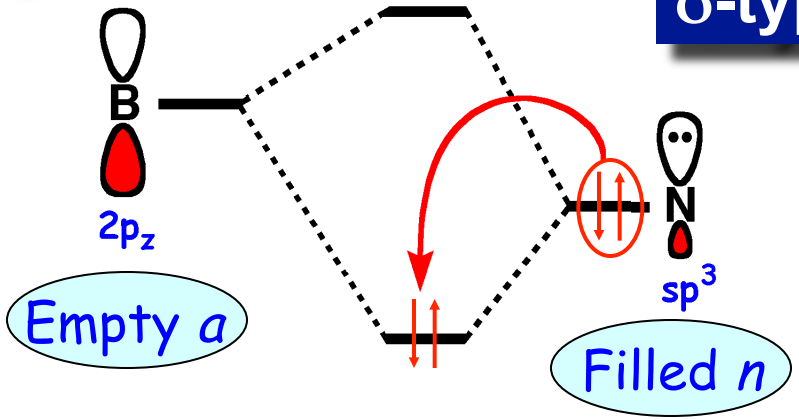






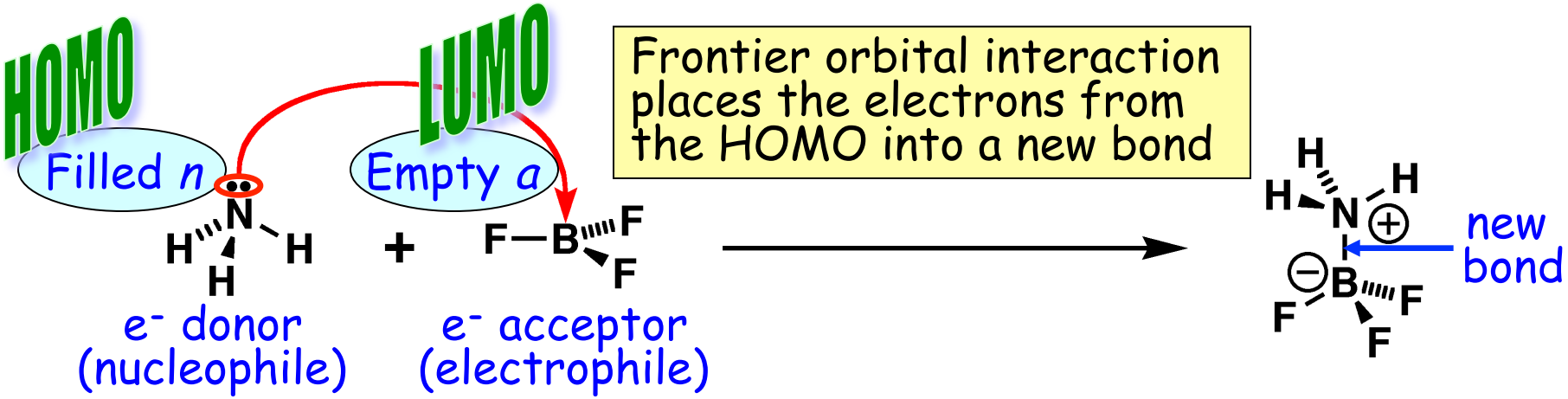
frontier orbitals

An *n* → *a* σ-type interaction



This is the meaning behind our use of curved arrow convention to illustrate electron flow

Curved Arrow Convention & Electron Flow



Looking ahead...some key terms.

HOMO = e⁻ donor, nucleophile, e⁻ source, base
LUMO = e⁻ acceptor, electrophile, e⁻ sink, acid

- curved arrows indicate the movement of electrons only
- arrow starts at the electron source not at an atom
- arrows are to be drawn from electron source (HOMO) to electron sink (LUMO). Never the other way.