

Acids/Bases w/ MO Theory

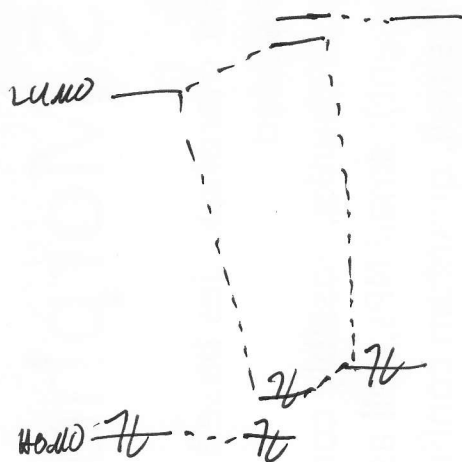
All Chemical reactions \rightarrow movement of electrons.
(except nuclear)

\rightarrow Lewis Acid / Lewis Base interaction
 \rightarrow HOMO / LUMO interactions.

In practicality, too much work to calculate MO diagram for every molecule/atom from scratch, utilize periodic/experimental trends as shortcuts (informed by MO theory).

Largely dictated by energy matching:

- 1) Large mismatch (large HOMO-LUMO gap) 2) small mismatch (small HOMO-LUMO gap)

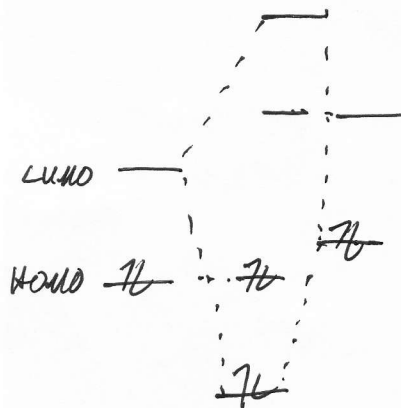


Strong ionic bond

(LUMO very high, HOMO very low)

\rightarrow not very reactive

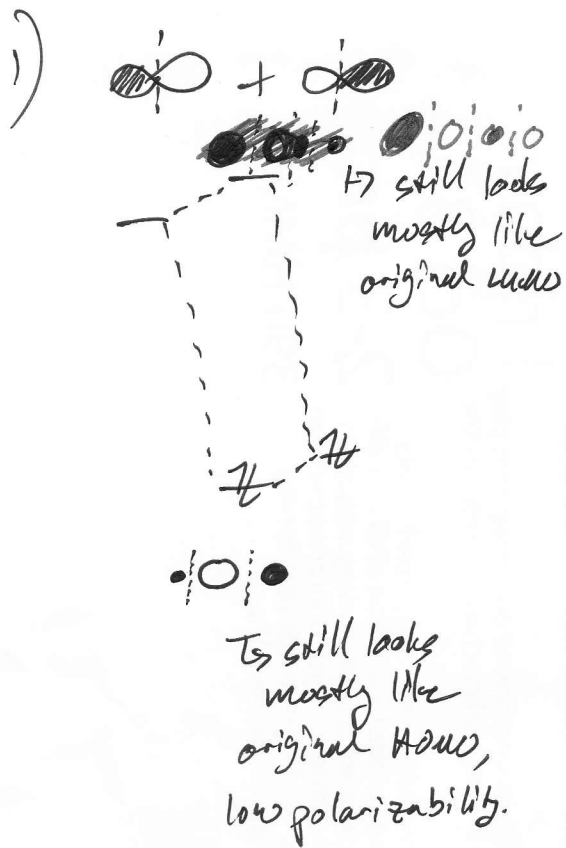
electrostatic attraction



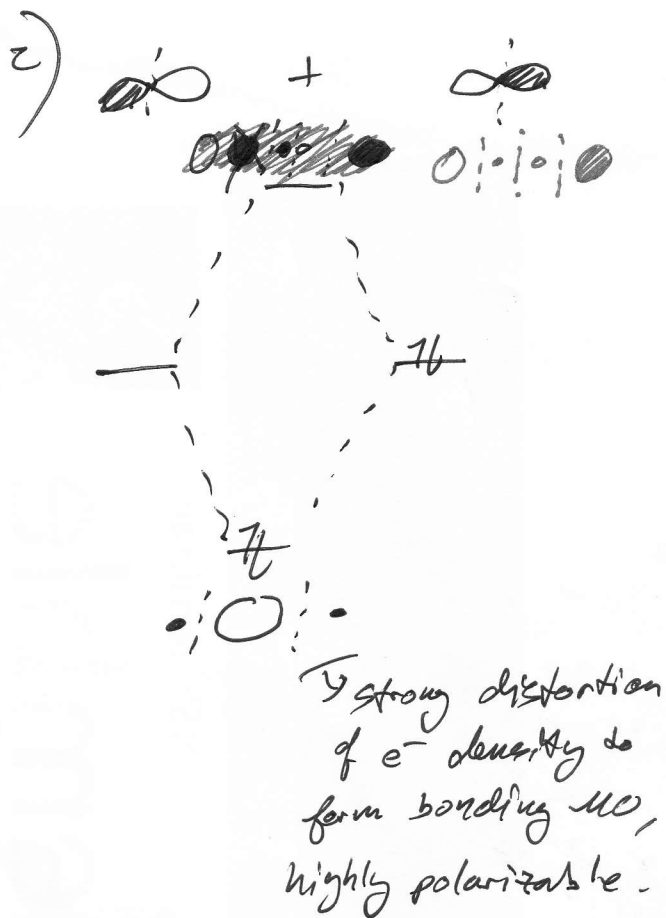
Strong ~~ionic~~ covalent bond

also, possibly non-bonding
d.p. - reaction won't break
bond.

Polarizability?



Hard Acid : Hard Base



Soft Acid : Soft Base

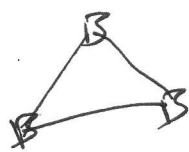
Cluster Chemistry / Projection Operator MOs.

Previously, used P.O. to determine LMOs.

↳ assumed LMO energies were degenerate \rightarrow Ligands far apart (separated by central atom) so int. b.

↳ for cluster chemistry (and eventually solid state), atoms now close enough \rightarrow int. b. occurs, can now order the irreducible representations in terms of energy.

Consider 3-center 2-electron bond!



each contributes an sp^3 , orient towards center of cluster. (radial vs. tangential).

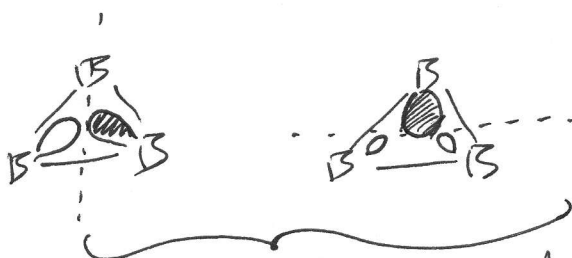
For D_{3h} pt. group, $A_1 + E$

\rightarrow 3 MOs

A_1 :

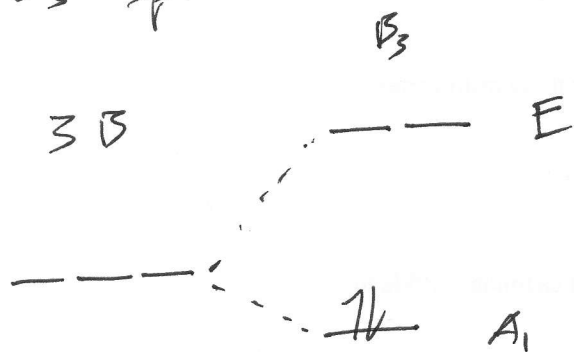


E :



degenerate symmetry,
degenerate energy.

Since the B sp^3 orbitals are close (within 1 bond distance from each other), overlap makes energies of MO's split.



} 3 orbitals, only
} 2 e⁻ needed for bonding.

We will go over more complicated (B_6) case in following lectures.