

Review for Exam 2

Tips:

VBT

- 1) pick useful coordinate systems
↳ set some known coefficients to zero, or known values (based on geometry). ↗ orthogonality
- 2) hybridization (% contribution of each orbital) will tell you something about chemical properties.
↳ % s, % p, % d → bond strength, bond length, bond energy, etc.
- 3) math is hard, but at least set up system of equations
↳ normality condition
↳ orthogonality condition
↳ % orbital contribution condition

MO theory

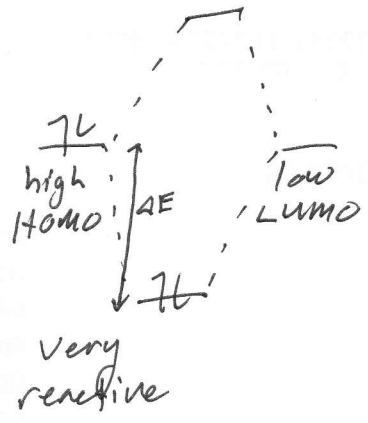
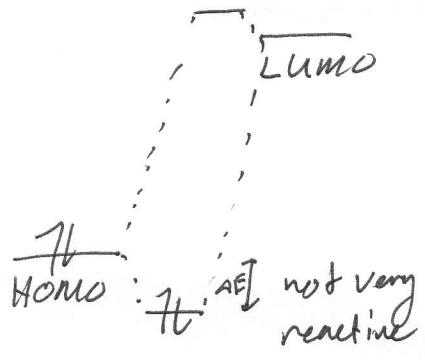
- 4) Know some common MO diagrams (diatomics (homonuclear, heteronuclear), AlH_2 , AlH_3 , AlH_4 , etc.) and how to derive them.
↳ extend to other systems by applying isolobal analogy, re-plot a.o. energies, reevaluate overlap and energy matching, ionization (# of e^-).
- 5) also know how to come up w/ shapes of orbitals.
↳ shape → bonding/anti-bonding/non-bonding
→ reactive sites

[Cont]

6) PE spectrum \rightarrow ideal spectrum, perfect resolution.
 \hookrightarrow only filled orbitals give peaks.
 \hookrightarrow unpaired e^- ?

7) Reactions: just MO mixing (same rules \rightarrow symmetry, overlap, energy match)

Generally: HOMO of molecule ① + LUMO of molecule ② (or singly occupied MOs, SOMOs).

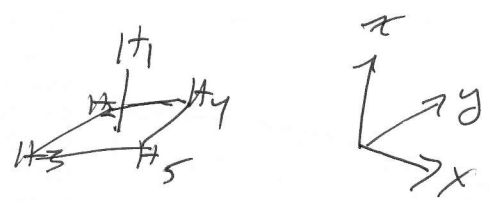
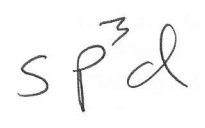


* also compare symmetry and overlap.

8) If you're not provided of a character table, you should be able to solve the problem w/o one. Same thing for missing orbital potential energies. Understand trends.

Valence Bond Theory Example

Consider a square pyramidal hybridization scheme:



1) What is the wavefunctions of the hybrid orbitals?

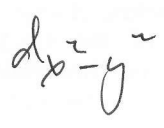
Two types expected: ϕ_{H_1} $\phi_{H_2}, \phi_{H_3}, \phi_{H_4}, \phi_{H_5}$
 (underlined) should all be similar.

2) What does the differences in hybridization tell us about the chemical properties of different bonds?

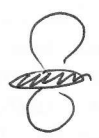
3) Which d orbital do hybridize?

- pick ones w/ the easiest symmetries, or ones which are orthogonal to particular bonds.

Either:



\downarrow
 orthogonal to ϕ_{H_1} , also points along bond (no trig.).



\downarrow
 points along ϕ_{H_1} (no trig.)

why would I not pick d_{z^2} ?

- P_z orthogonal to $\phi_{H_2}, \phi_{H_3}, \phi_{H_4}, \phi_{H_5}$

$\therefore \phi_{H_1} = P_z$ (100% P_z), no room left for d_{z^2} .

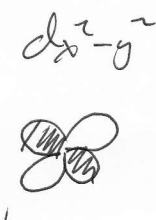
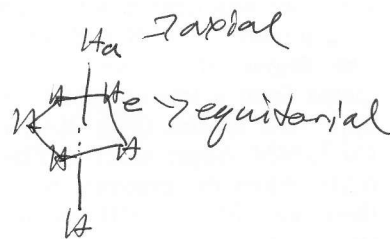
↳ what does this imply about the chemical properties of the H_1 position?

$\therefore d_{x^2-y^2}$ best choice.

what about pentagonal bipyramidal?

which d orbitals?

sp^3d^3



orthogonal to axial bond.

↳ does this have any contribution to $\phi_{equatorial}$?

consider that $\phi_{ax} P_z \perp$ to $\phi_{equatorial}$, so

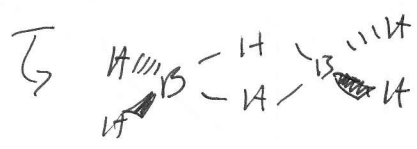
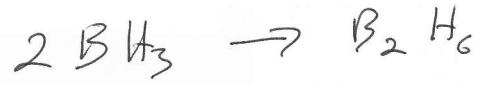
$\phi_{equatorial} = \{ s, p_x, p_y, d_{x^2-y^2}, d_{xy} \}$

↳ \perp to ϕ_{axial} , 80% already accounted for.

\therefore likely $\phi_{axial} = \{ P_z, d_{z^2} \}$

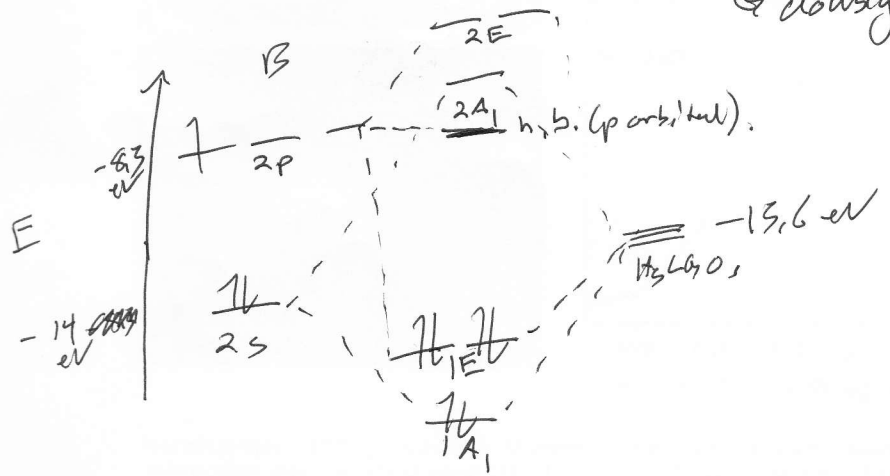
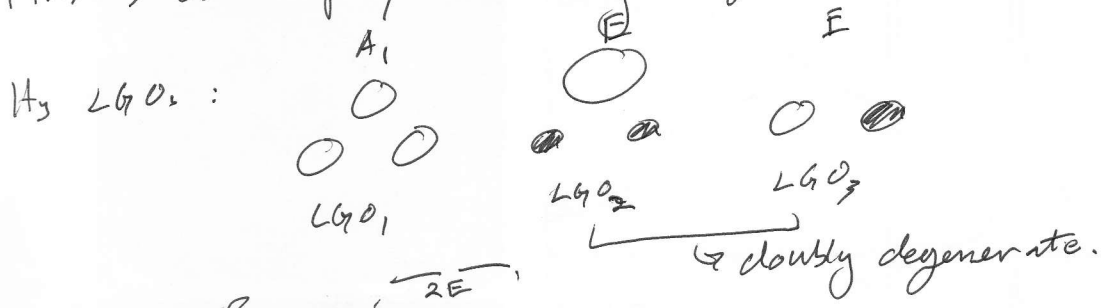
Molecular Orbital Theory Example

Consider the reaction of:



How do we describe this w/ MO theory?

First, come up w/ MO diagram for BH₃



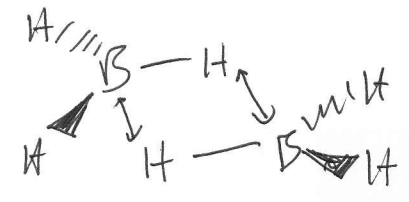
We know that reactions generally proceed through HOMO-LUMO interactions. Match energy and shape.

HOMO

LUMO



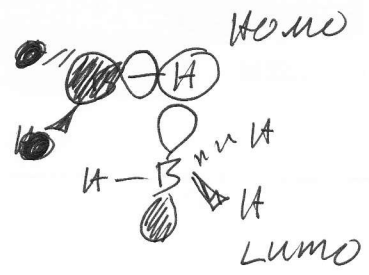
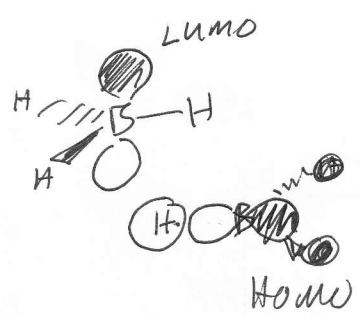
What overlaps / interactions are favorable?



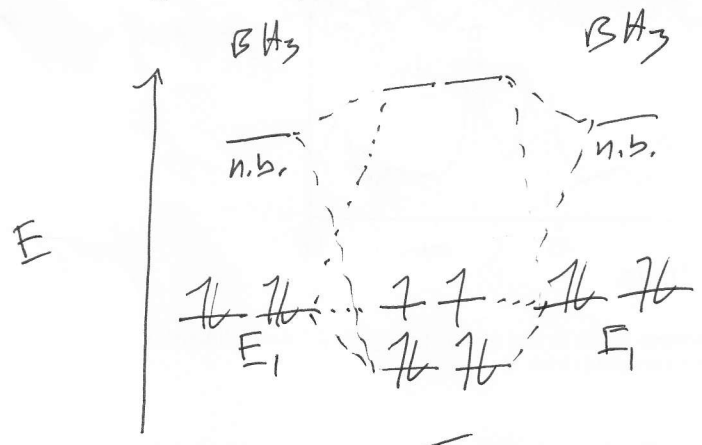
possible mechanism.

Which MO's (HOMO/LUMOs) have best overlap?

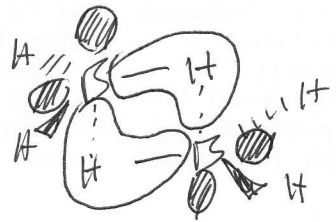
2 interactions



MO diagram of reaction:



↳ shape of MO?



DG 5-9: The Frontier Orbital Concept.