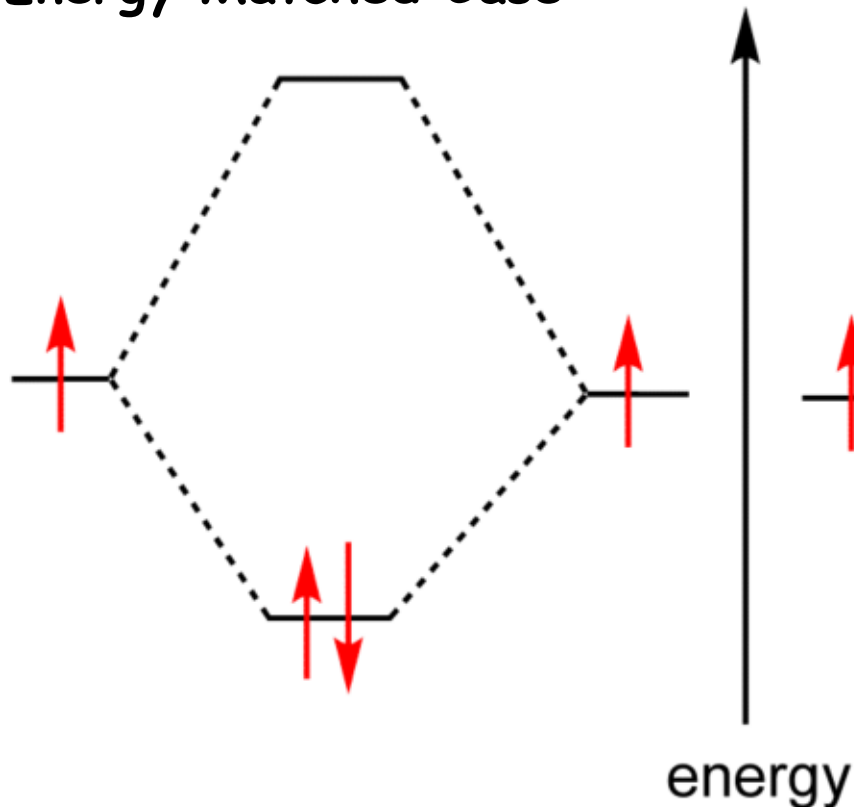


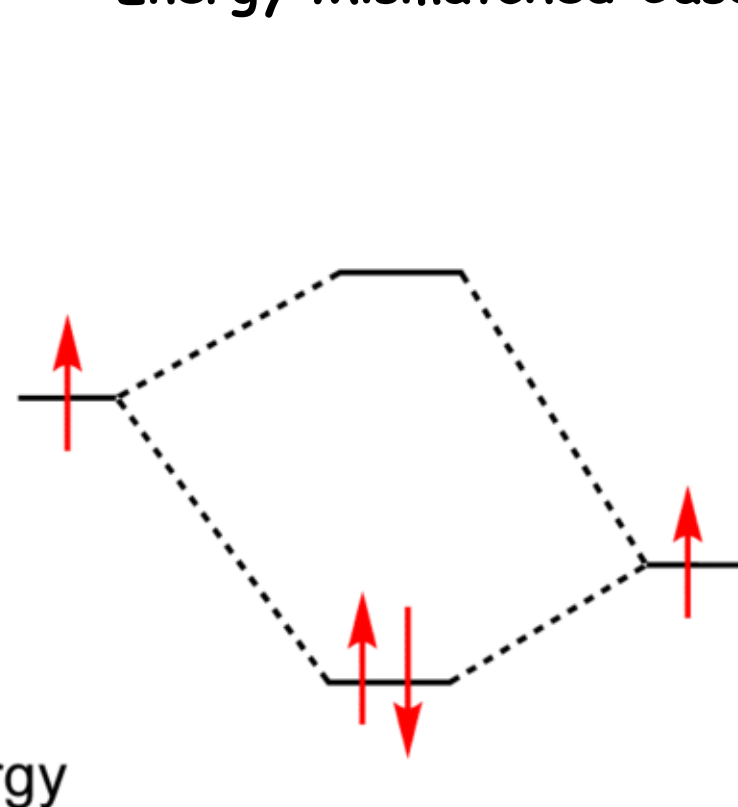
# Energy Mismatched AOs Make Different Contributions to MOs

Energy Matched Case



AOs contribute equally to the MOs

Energy Mismatched Case



AOs make disproportionate contributions to the MOs



# Polarized Bonds: Unequal AO Contributions

## Orbital Interaction Theory

### GUIDELINES GOVERNING ORBITAL INTERACTIONS

(G<sub>1</sub>) The overlap of two atomic orbitals depends on:

- symmetry of the orbitals
- distance between orbitals
- spatial extent of the orbitals
- the energy difference between orbitals ( $E_1 - E_2$ )

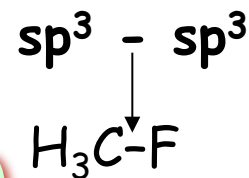
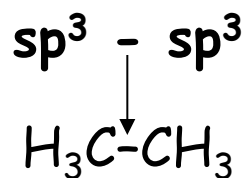
(G<sub>2</sub>) The stabilization of the bonding MO ( $\Psi_1$ ) and destabilization of the antibonding MO ( $\Psi_2$ ) increase as the overlap increases.

(G<sub>3</sub>) As the energy difference between  $\psi_1$  and  $\psi_2$  increases (assuming  $E_1 < E_2$ ), the magnitude of the stabilization decreases, the contribution of  $\psi_1$  to the bonding MO  $\Psi_1$  increases, and the contribution of  $\psi_2$  to the antibonding MO  $\Psi_2$  increases.

(G<sub>4</sub>) The antibonding MO  $\Psi_2$  is slightly more destabilized than the bonding MO  $\Psi_1$  is stabilized.

Compare the C-F Bond in  $\text{CH}_3\text{-F}$  to the C-C bond in  $\text{H}_3\text{C-CH}_3$

# C-C vs. C-F Sigma Bond



**LOWER LUMO**

