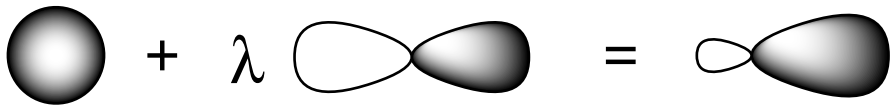
Polarization Functions- Extended Basis Sets

Minimum Basis Sets : Just valence orbitals: STO-3G, 3-21G, 6-31G
For H just 1s
For Li-Ne just 2s, $2p_x$, $2p_y$, $2p_z$
For Na-Ar just 3s, $3p_x$, $3p_y$, $3p_z$ (note no d's for P, S, Cl)

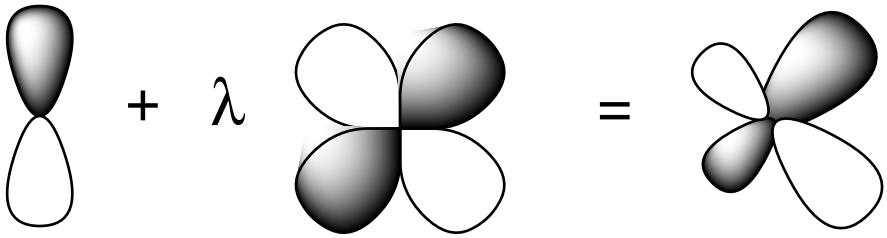
Polarization Functions: For H add p functions
For Li-Ca add d functions (also MNDO/d)
For transition metals add f functions

Polarization functions give more room for the electrons to get away from each other to minimize electron-electron repulsion.

For H add p functions



For Li-Ca add d functions



H_2 at 6-311G** :

$$\Psi_{MO} = 0.186\ 1S_A(\text{inner}) + 0.288\ 1S_A(\text{middle}) + 0.133\ 1S_A(\text{outer}) + 0.023\ 2P_{ZA} + 0.186\ 1S_B(\text{inner}) + 0.288\ 1S_B(\text{middle}) + 0.133\ 1S_B(\text{outer}) - 0.023\ 2P_{ZB}$$

3-21G(*) Good general purpose level for medium to large systems
For Li-F no polarization functions added
For Na-Ca add d functions

3-21G*, 6-31G*
For Li-F add d functions
For Na-Ca add d functions

3-21G**, 6-31G**
For H add p functions
For Li-F add d functions
For Na-Ca add d functions

6-311G** Needed to get the most benefit out of MP2 calculations
Only useful for small molecules