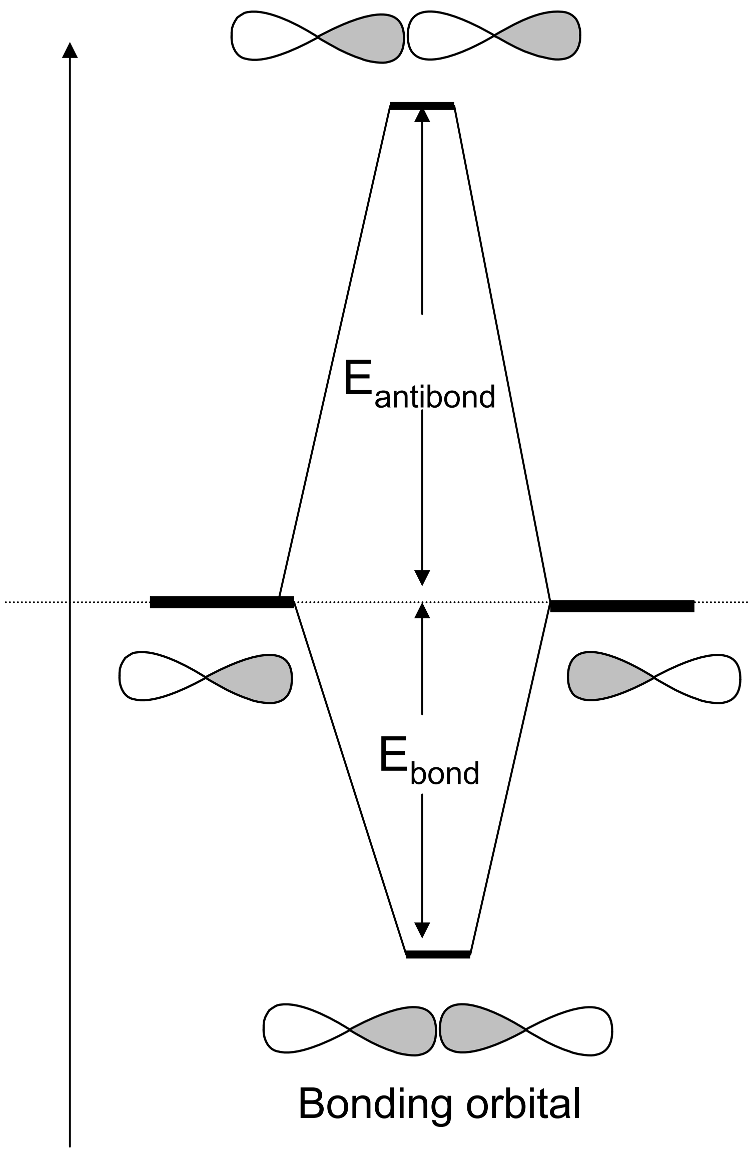
Perturbation of the first and second orders

a) 1^{st} order: degenerate AOs



Antibonding orbital

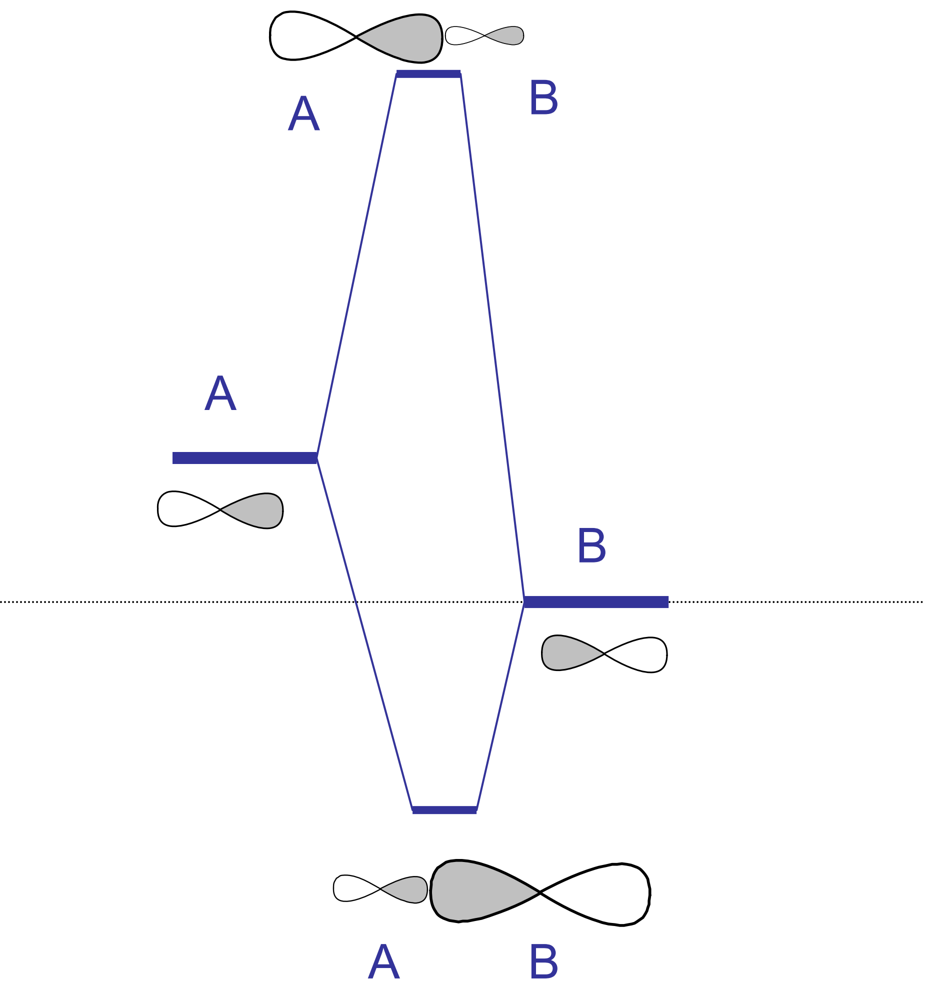
E

$E_{antibond}$

E_{bond}

Bonding orbital

b) 2^{d} order: AOs of different energies



A

B

A

B

A

B

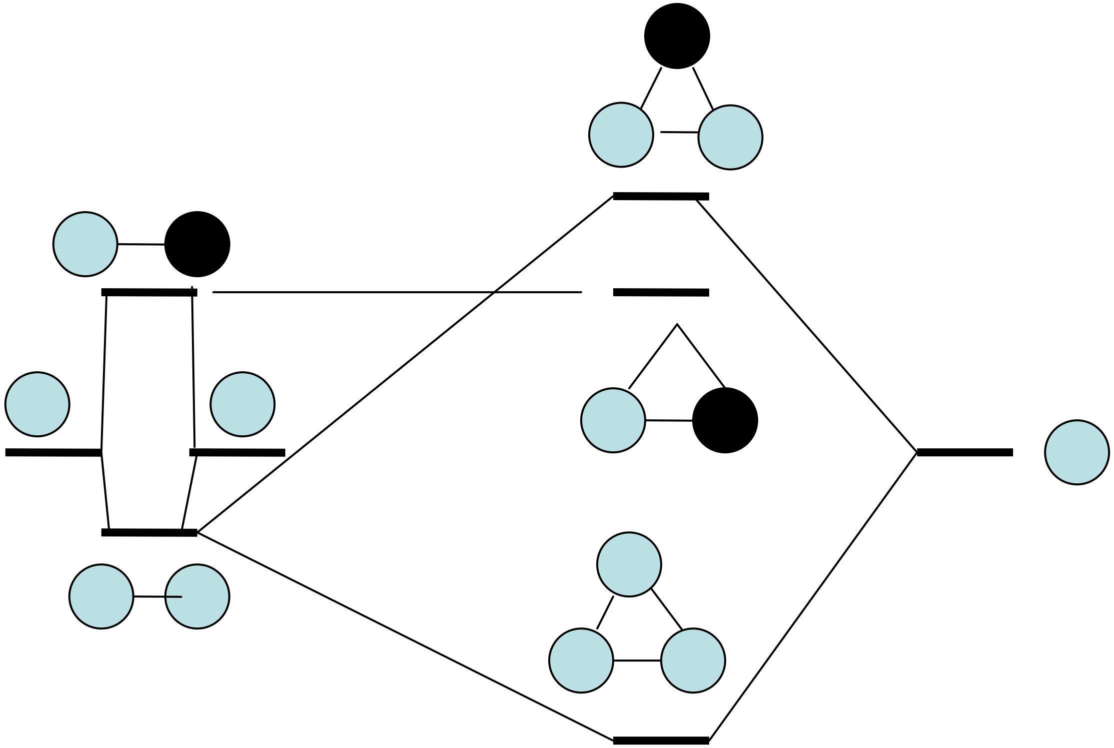
The rules of QMOT

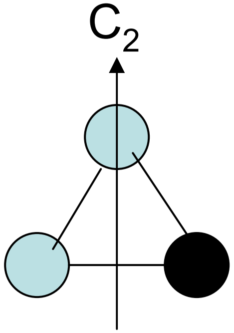
1. Consider **valence** AO only (e.g., for Carbon, (N, O, F) 2s, 2px, 2py and 2pz)

2. Form MOs for entire system as linear combination of AOs. Remember, combination of N AOs gives N MOs (same as for hybrid orbitals)

3. MOs must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule.

For example, H_3^+- ptotonated H_2 molecule of C_2v (D_{3h}?) symmetry





Neither symmetric
no asymmetric

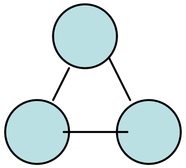
H_3^+ - the simplest polyatomic molecule and the most abundant ion in the Universe

Experimentally- triangular structure, H-H distance is 1Å.

The protonation energy of H_2 is surprisingly large:
$H_2 + H^+ \rightarrow H3^+$ ΔH = -100 kcal/mol

$H + H \rightarrow H_2$ ΔH = -103 kcal/mol

Delocalization of 2 electrons over 3 centers

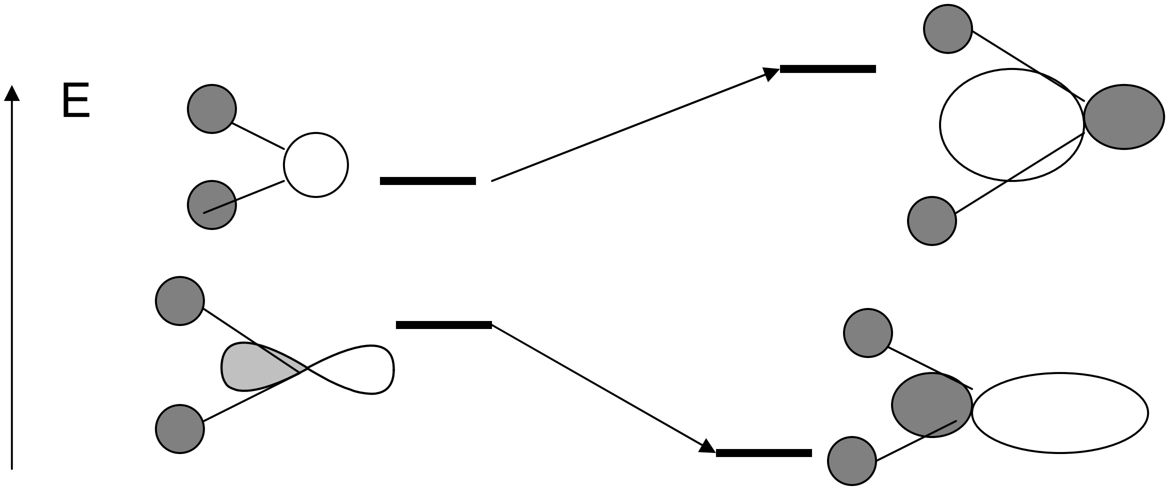


4. Compose MOs for structures of higher symmetry and then produce MOs for related but less symmetric systems by systematic distortion of the MOs of higher symmetry. For example, for the CH_2 system, start with linear HCH ($D_{\infty h}$) then bend the system (C_{2v}).

5. Molecules with similar structures, such as BH_3, CH_3^+, CH_3, CH_3^-, NH_3, OH_3^+, have qualitatively similar MOs, the major difference is the number of electrons that occupy the common MO system. Firstly build MOs, then occupy them with valence electrons

6. The total energy of the system is a sum of the energies of occupied MOs.

7. If the two highest energy MOs of a given symmetry were derived primarily from the different kinds of AOs (s and p), then mix the two MOs to form hybrid orbitals. For example, for the AH2 system (p.3), mix C and E orbitals to form hybrids C’ and E’.



8. a) The smaller the initial energy gap between 2 interacting orbitals, the stronger the mixing.

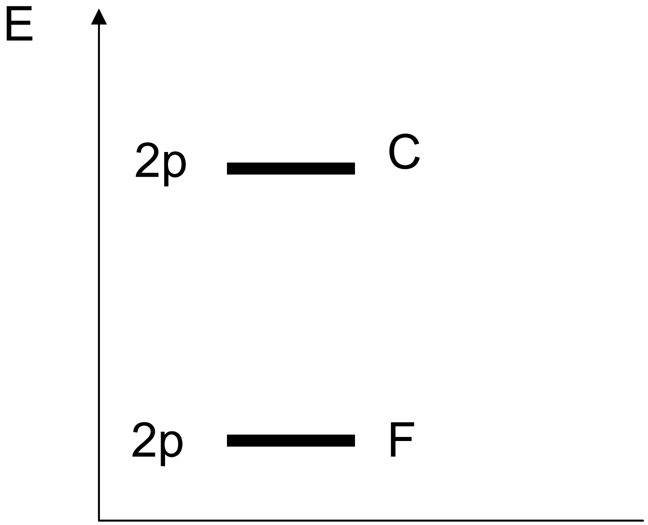
b) The energy of stabilization, E_{stab}, is always smaller than energy of destabilization, E_{destab}. Thus, 4electron-2center, 4e-2c, interaction is always repulsive, 3e-2c is weakly bonding, 2e-2c is bonding.

c) If orbitals of different energies interact (b), the one of lower energy, B, will contribute more in binding orbital; the one of higher energy, A, will contribute more in antibonding orbital.

d) The more electronegative atoms have lower energy (more negative) AOs

	H	B	C	N	O	F	Cl
Electroneg	2.1	2.0	2.5	3.0	3.5	4.0	3.0
IE,eV	13.6	8.3	11.3	14.5	13.6	17.4	13.0

e) The larger the overlap between interacting orbitals, the larger the interaction. σ-bonds are stronger than π-bonds.



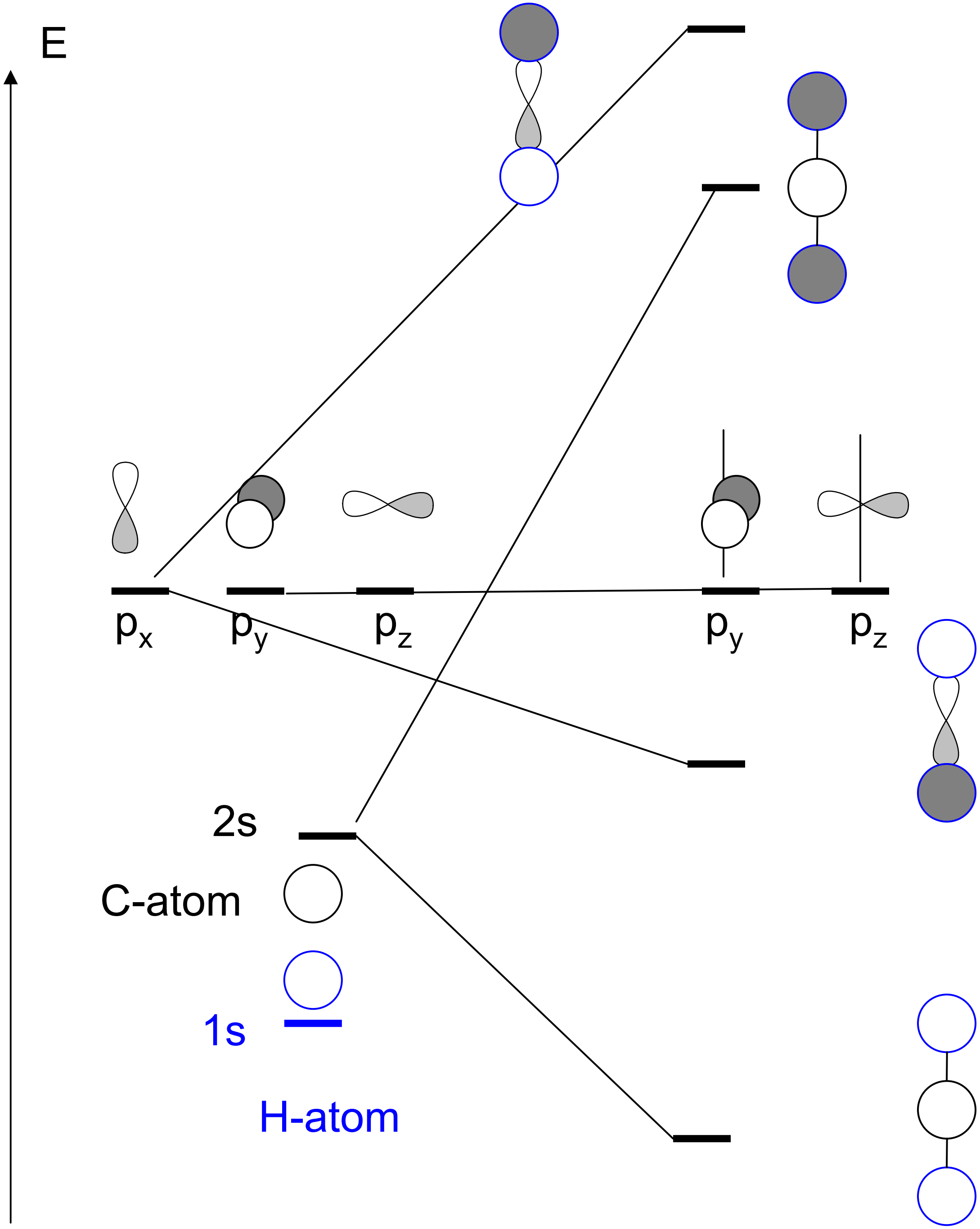
Using QMOT for prediction of geometries and ground electronic states of small systems: AH_2, AH_3, and AH_4, where A is a second period element.

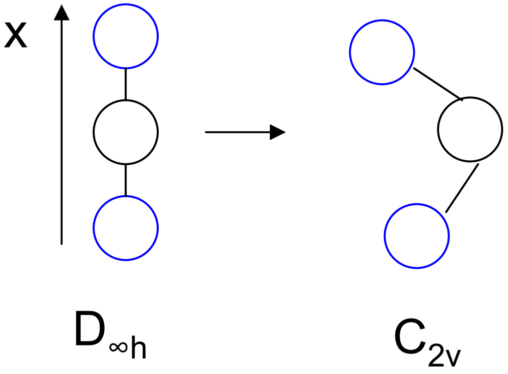
AH_2: A= B, C. N, O

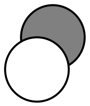
1. Is AH_2 system linear ($D_{\infty h}$) or bent (C_{2v})?
2. Is it closed-shell singlet or triplet? If it is radical (one unpaired electron) is it bent or linear?

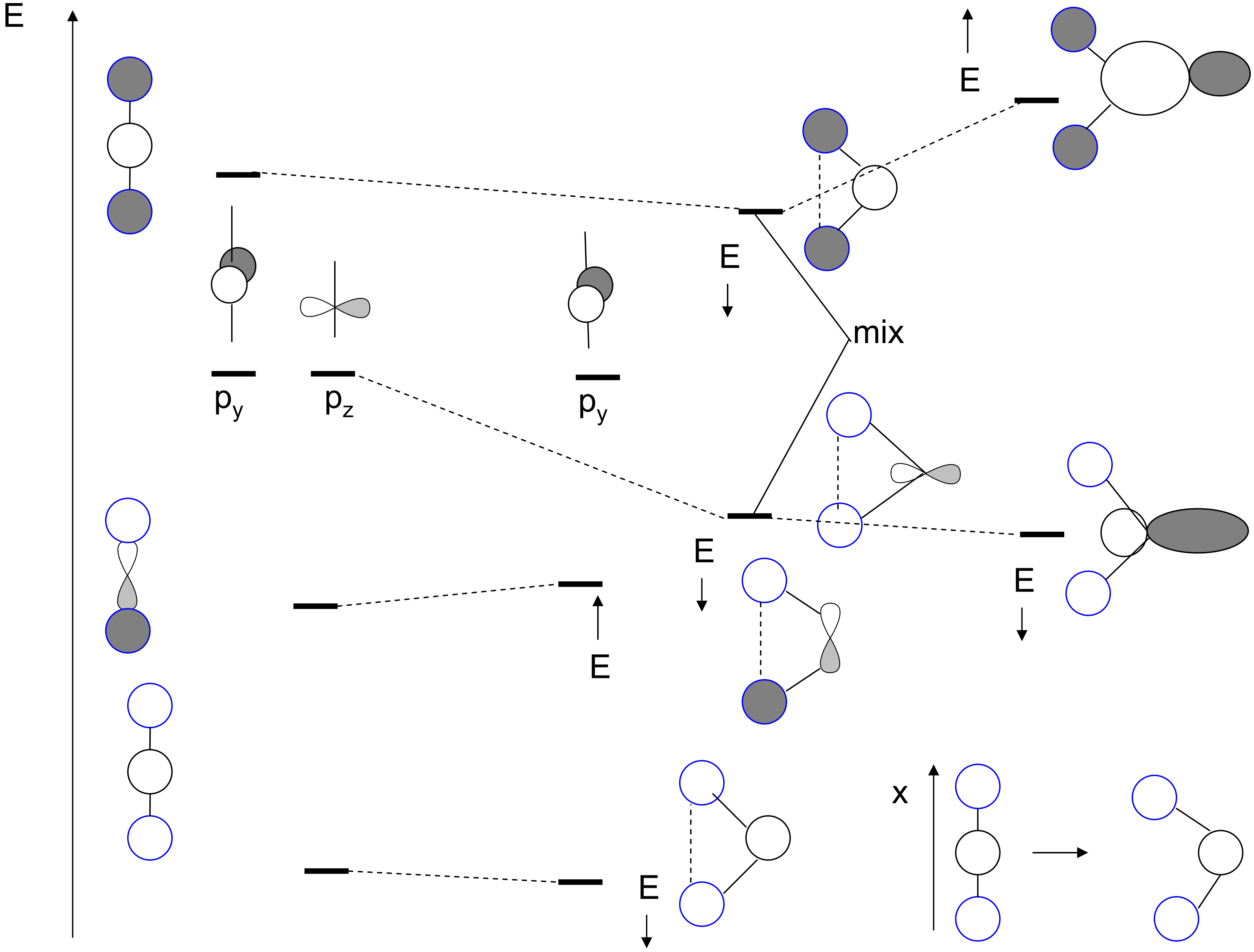
1. Build MOs for the system of highest symmetry- $D_{\infty h}$. Then bend it to C_{2V}. Upon the bending, the overlap between AOs in MOs will change. Thus, some MOs will go up in energy some down. The change in total energy of the system could be predicted.

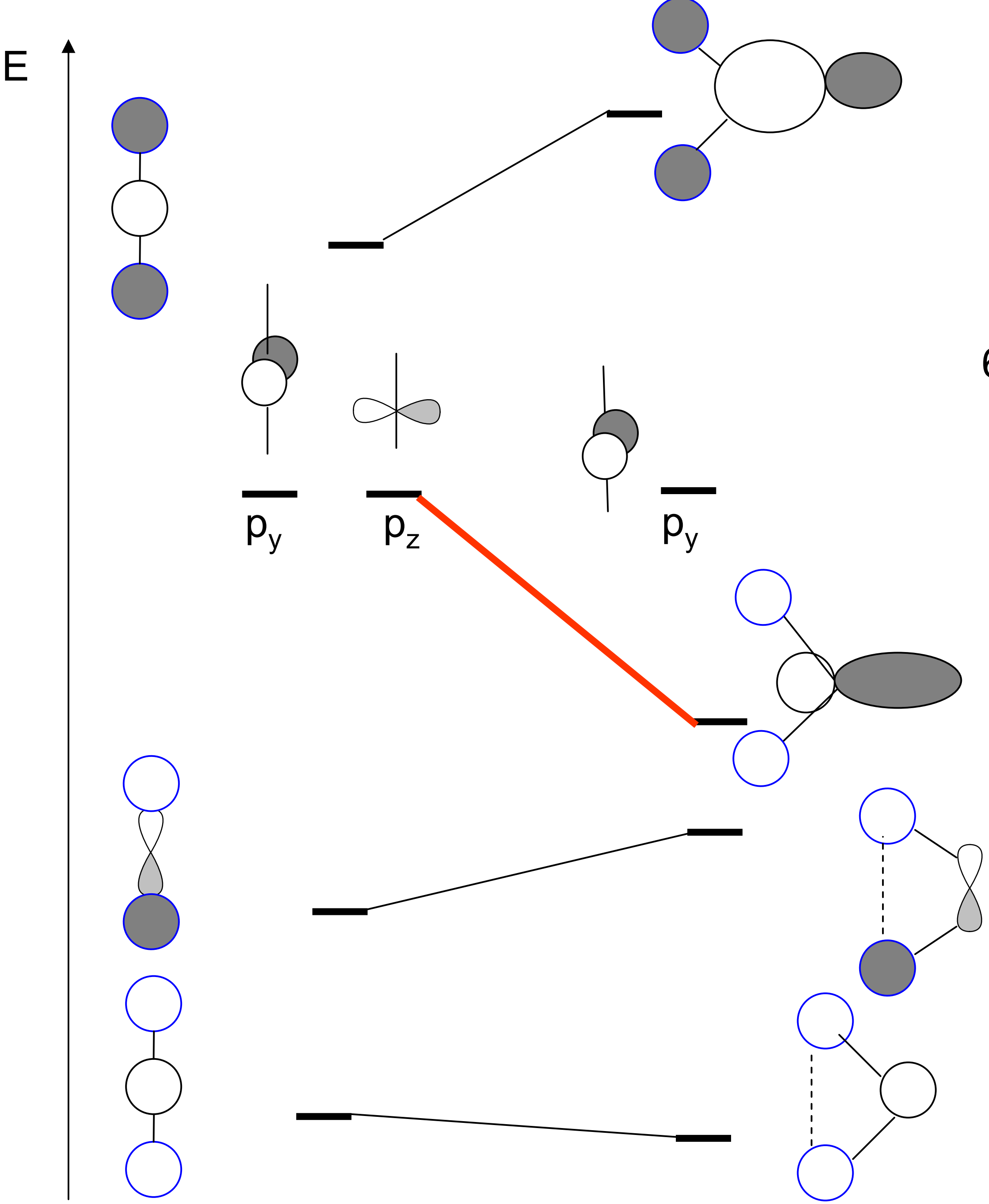
2. Place the system in the Cartesians (x, y, z) and DO NOT change the orientation!


E
p_x
p_y
p_z
p_y
p_z
2s
C-atom
1s
H-atom


x
$D_{\infty h}$
C_{2v}




E
E
E
mix
p_y
p_z
p_y
E
E
E
E
x



2e- bent (H_3^+)

3,4e-linear (BeH_2, BeH_2^+)

6,7 e-bent (CH_2, NH_2, NH_2^+)

8e-bent (OH_2, H_2F^+)

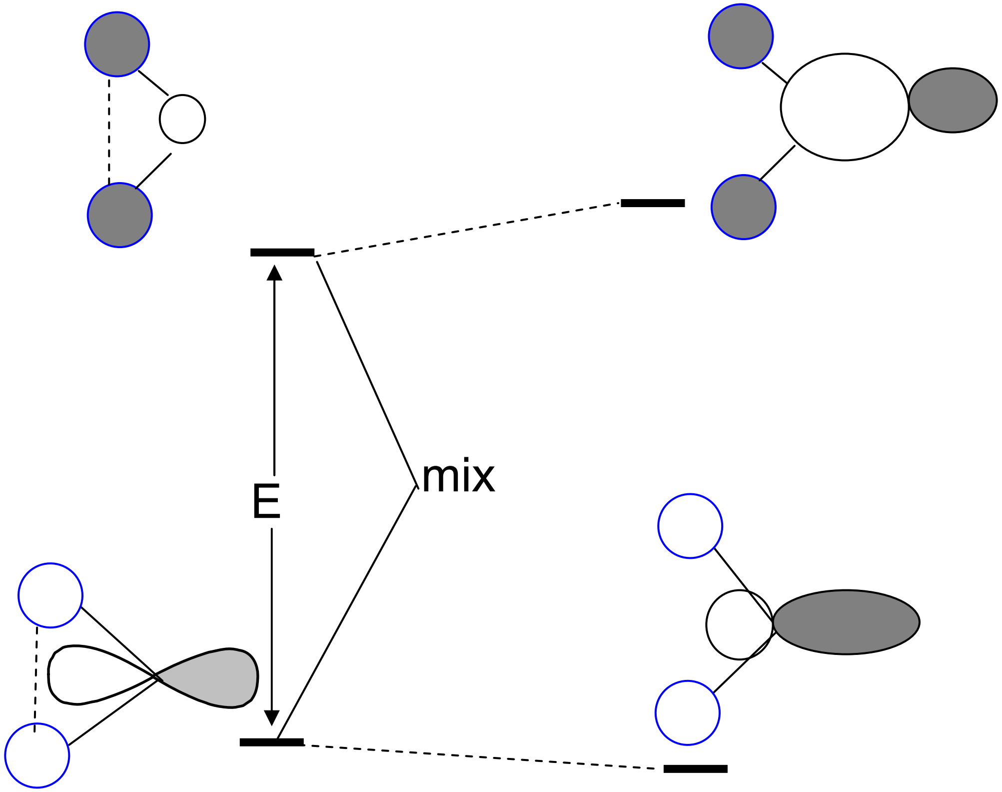
The most dramatic change: nonbonding orbital to bonding

WALSH diagram

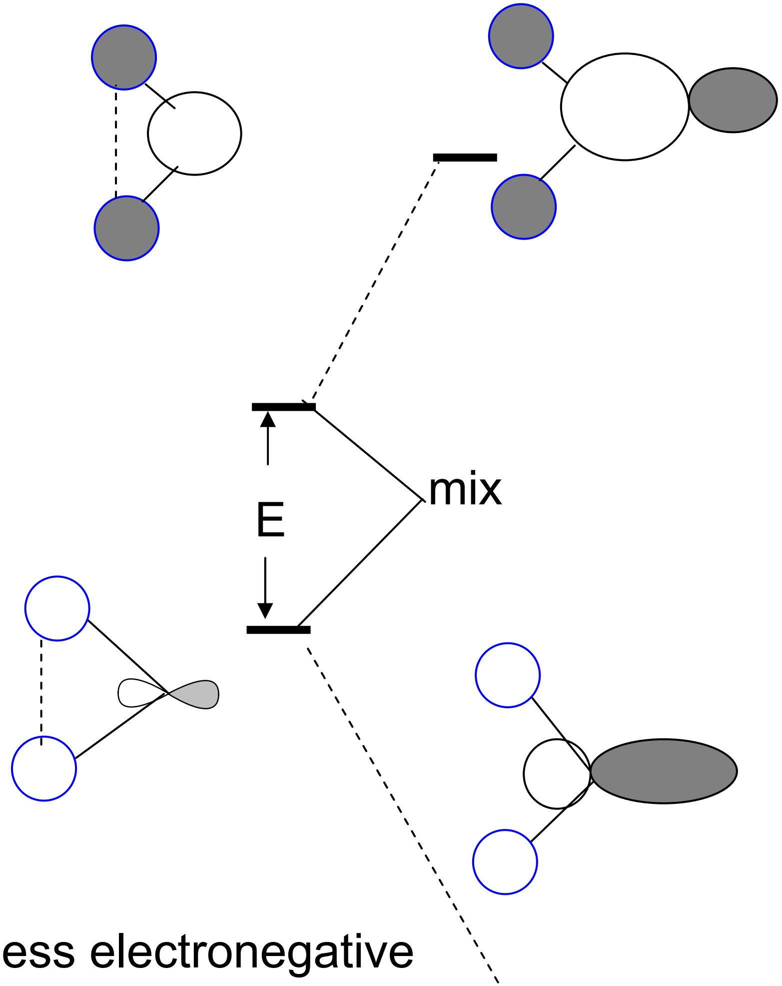
Could we predict the HAH angle?

Depending on the electronegativity of the central atom:

The smaller the electronegativity- the higher the p-orbitals-the smaller the gap between bonding and antibonding orbitals (often HOMO-LUMO) - the stronger the mixing- the more favorable the bent structure, i.e., the smaller the bond angle



More electronegative central atom



Less electronegative central atom

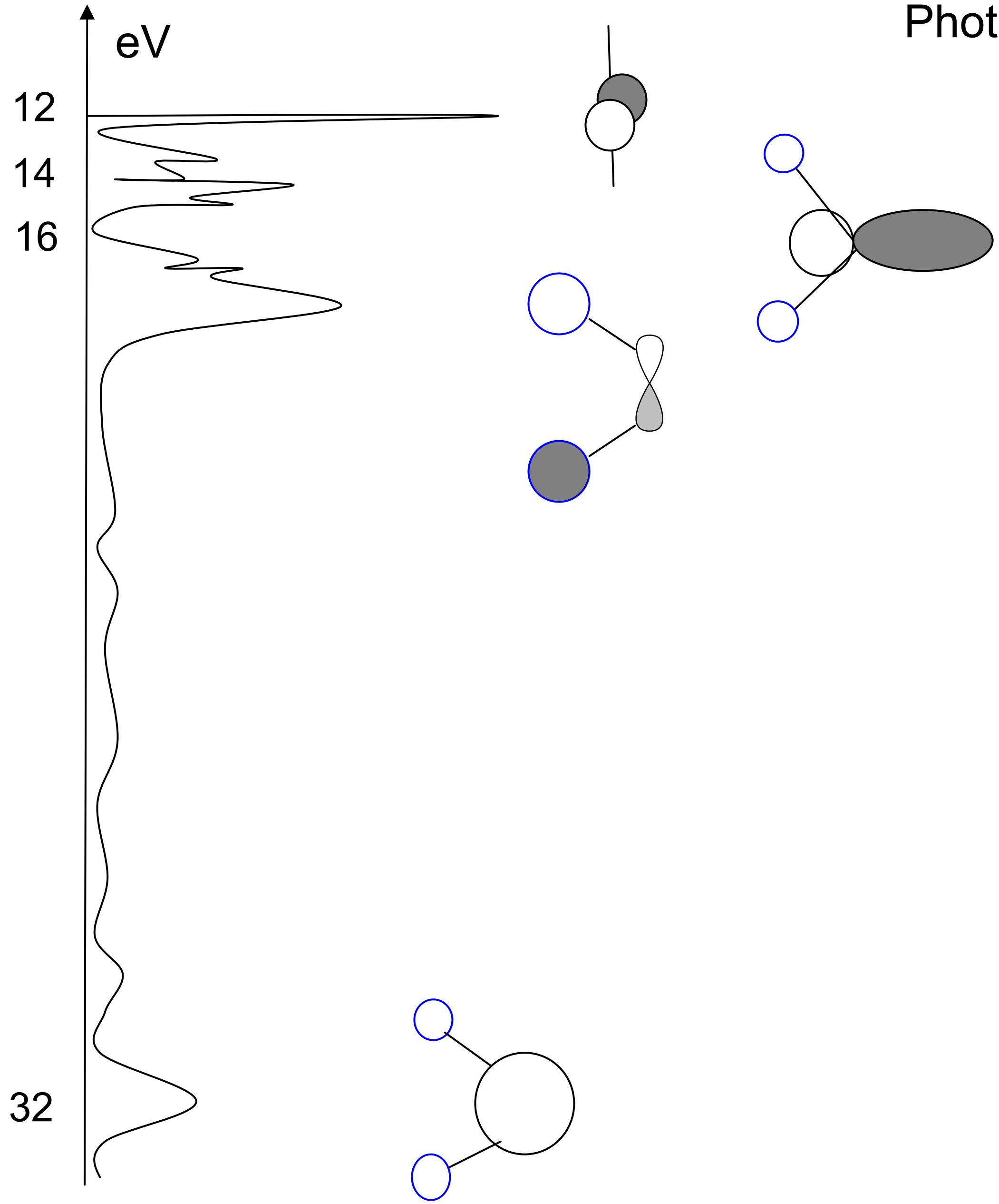
electronegativity

→

	H_2Te	H_2Se	H_2S	H_2N^-	H_2O	H_2F^+
HAH angle	90.3	90.6	92	104	104.5	118.1

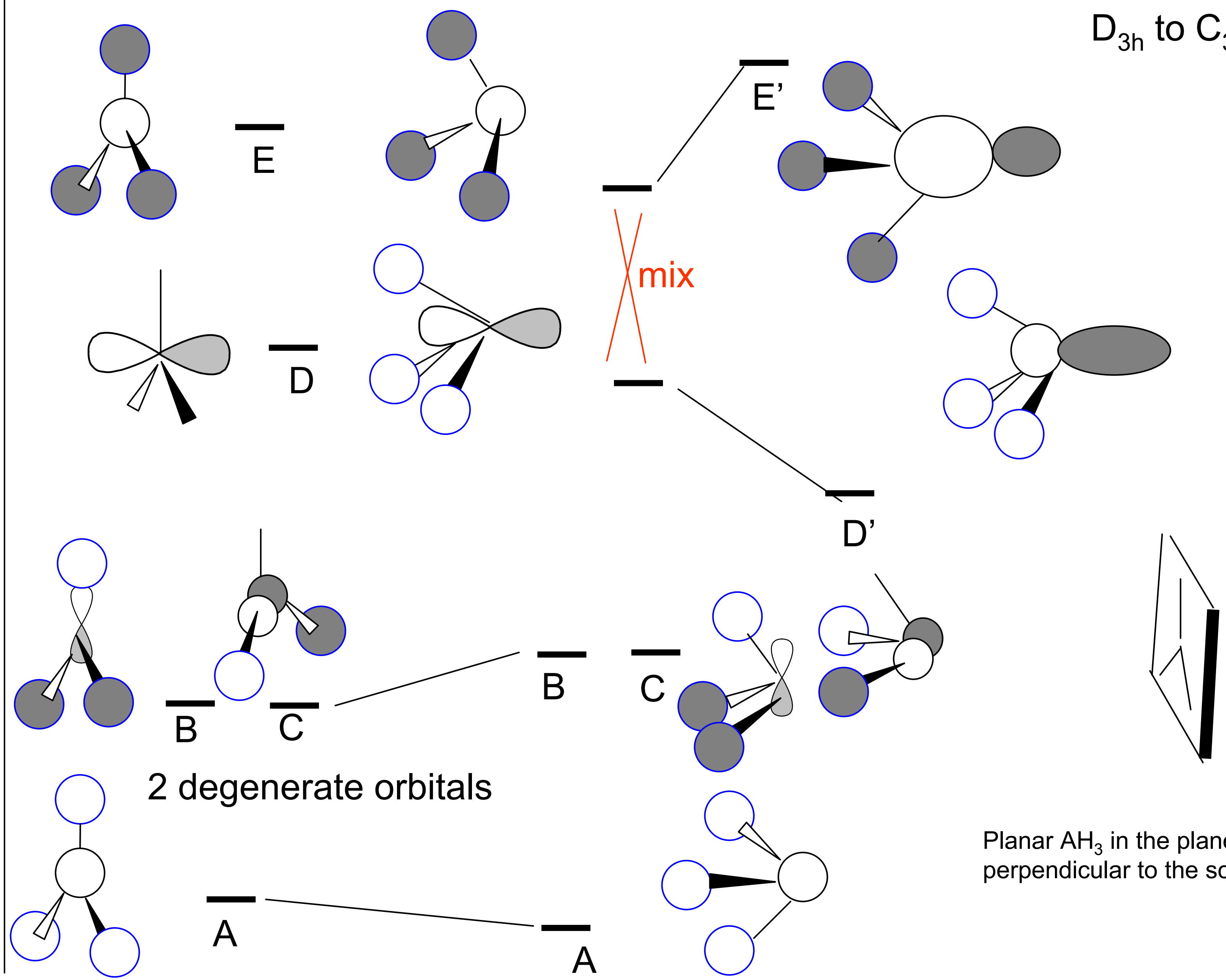
Photoelectron spectrum of water

Find 2 lone pairs



Walsh diagram for the AH_3 system (A is a second period element)

D_{3h} to C_{3v}



2 degenerate orbitals

Planar AH_3 in the plane perpendicular to the screen

We could apply the same Walsh diagram for substituted compounds, say for NF_3

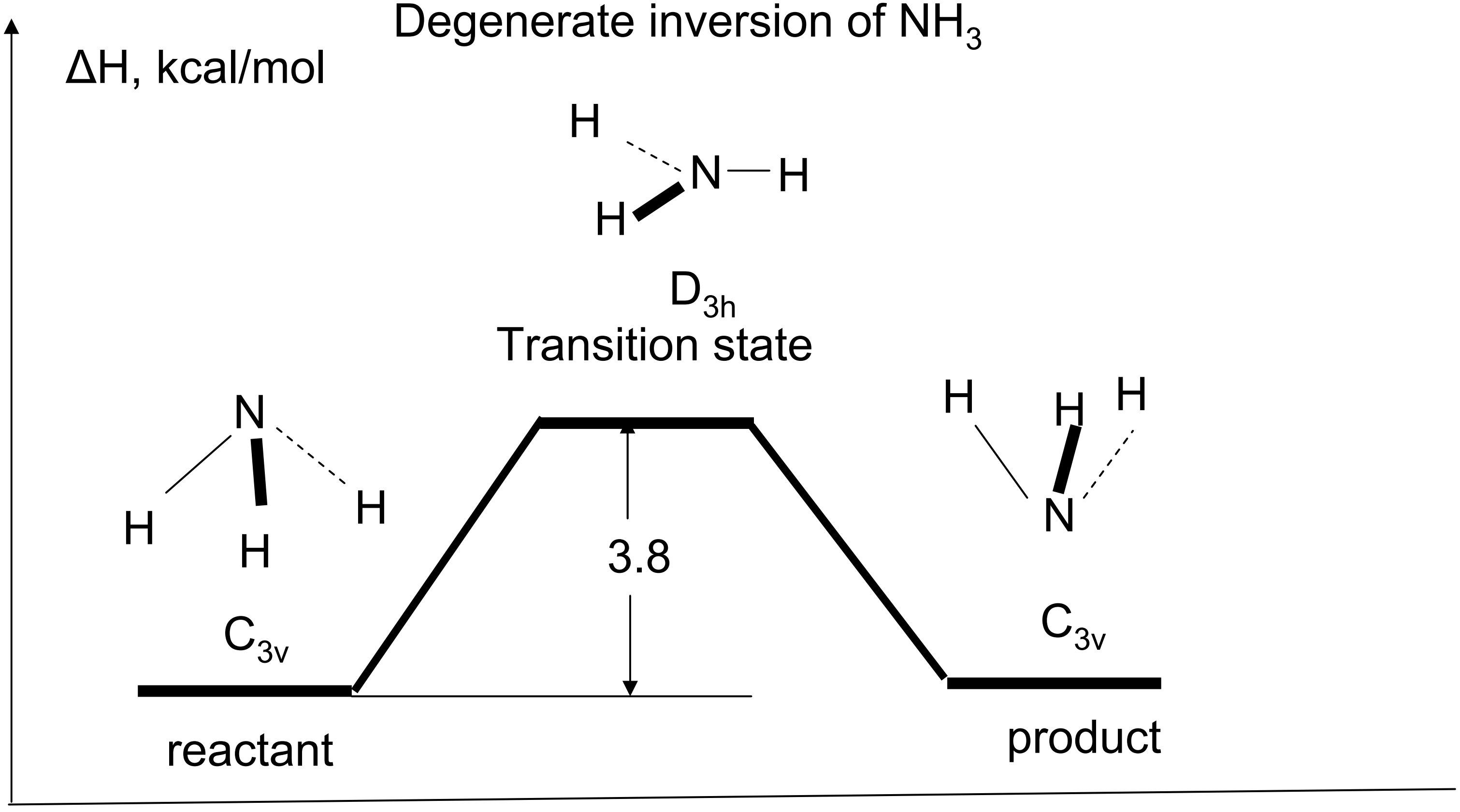
Halogen atoms are considered as one-valence electron substituents, similar to H but with p-orbital instead of s

Influence of substituents:

Electronegative substituents stabilize the pyramidal form compared to planar.

Substituents do not affect the nonbonding D orbital of the planar form but they certainly “pull down” D’ MO of the pyramidal form since the p-AO of the electronegative atoms are lower in energy than s-AO of H.

Degenerate inversion of NH_3

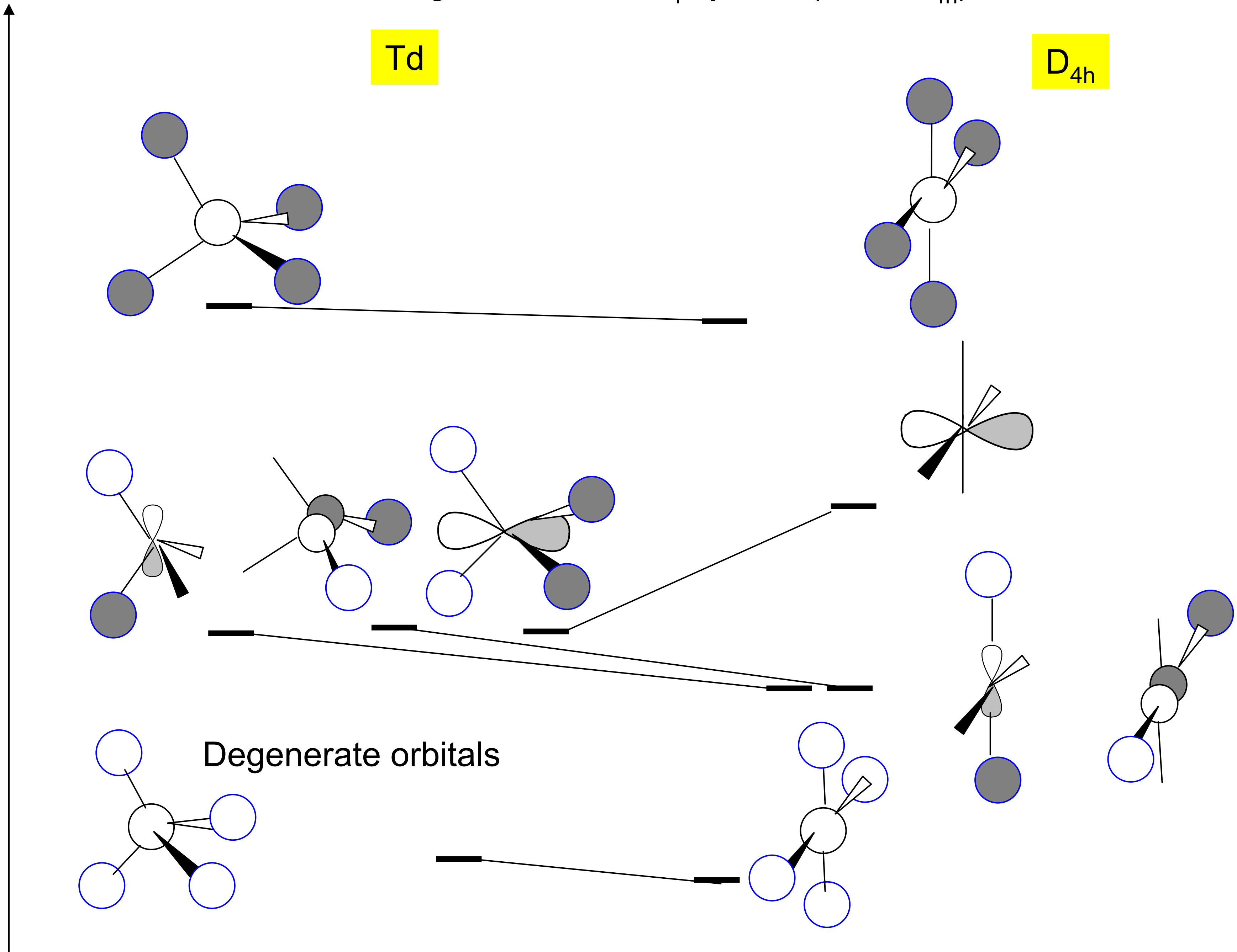


The reaction barrier to inversion is low- the process is very fast.

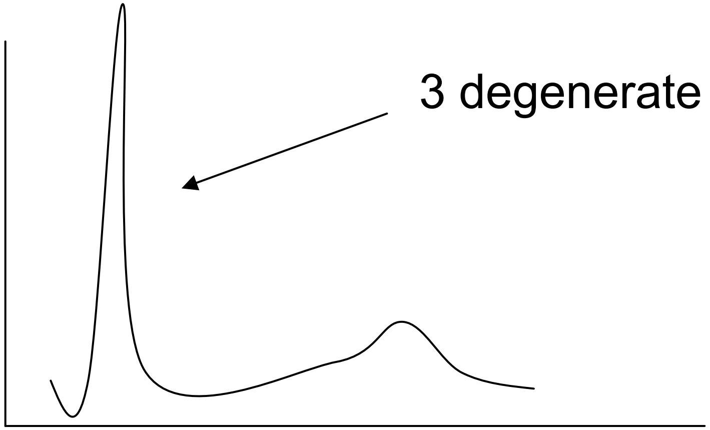
For NF_3 the barrier is much higher- ca. 80 kcal/mol

For PH_3 the barrier is significantly higher than for NH_3 - ca. 35 kcal/mol

Walsh diagram for the AH_4 system (Td to D_{4h})



MOs of CH_3 are consistent with its PER spectrum, hybrid orbitals are not

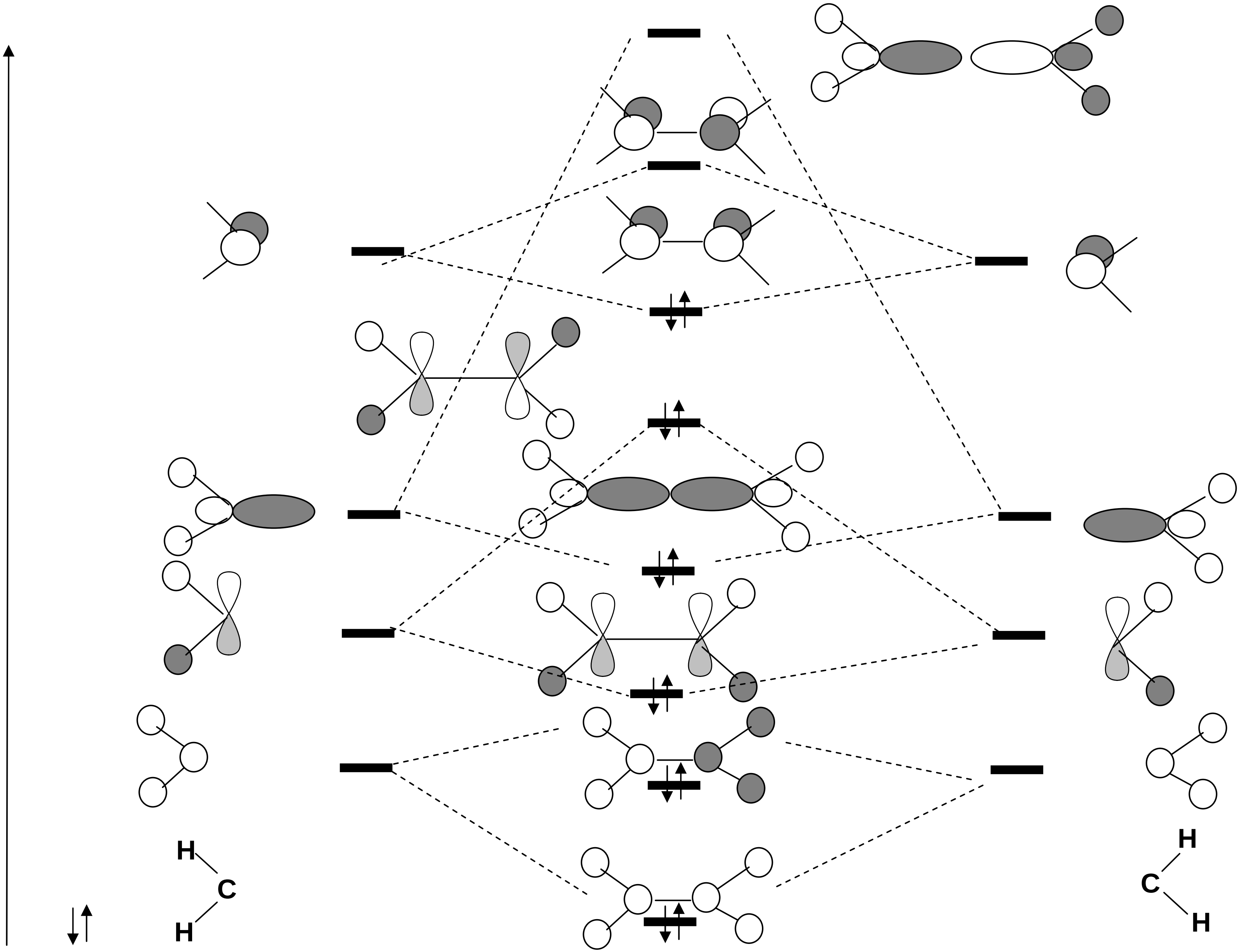


Problem of planar tetracoordinated carbon.

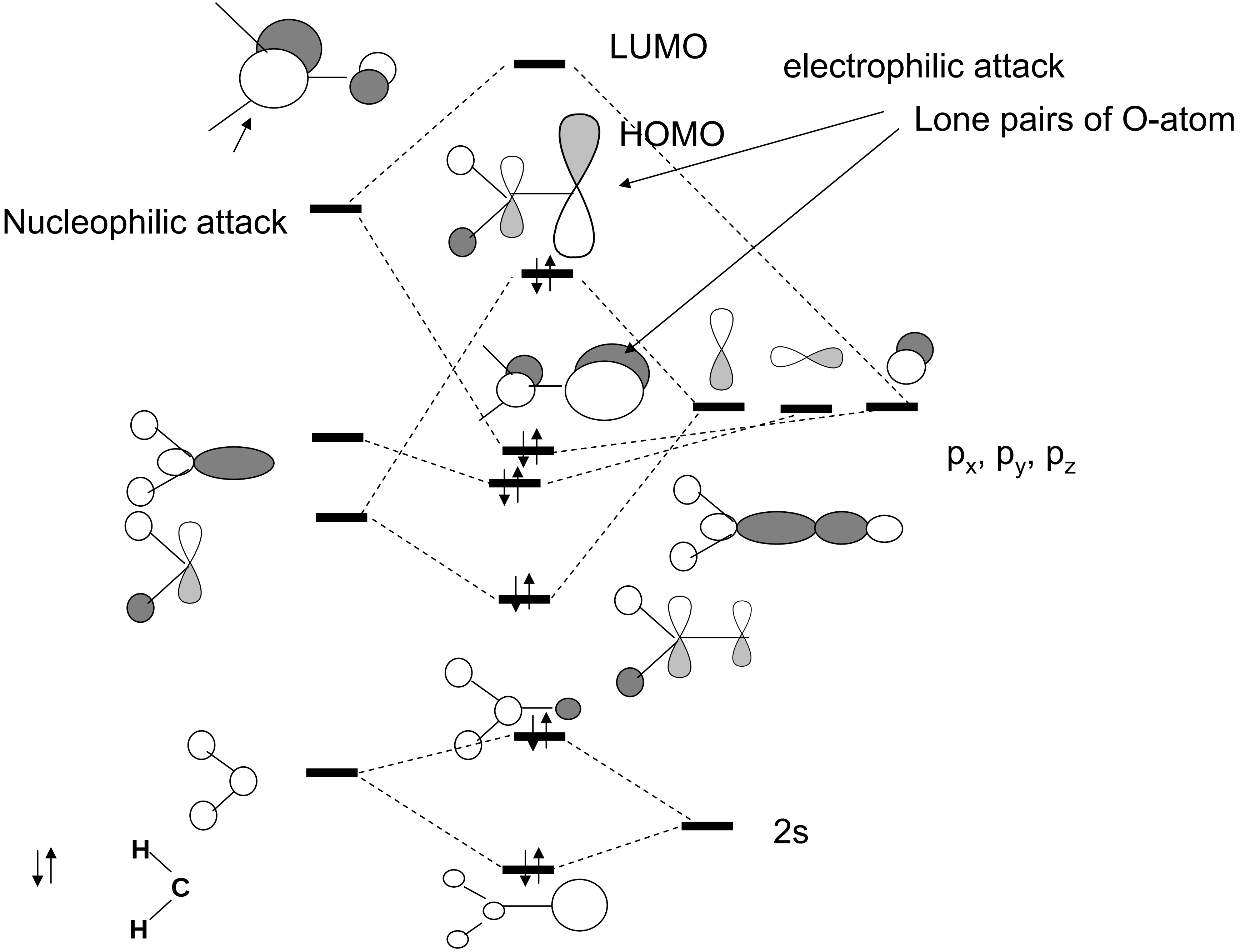
Is it possible to make a structure with planar carbon?

Making MOs of complicated systems using MOs of simple systems as fragments

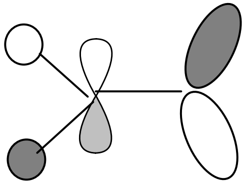
$H_2C{=}CH_2$. 12 e

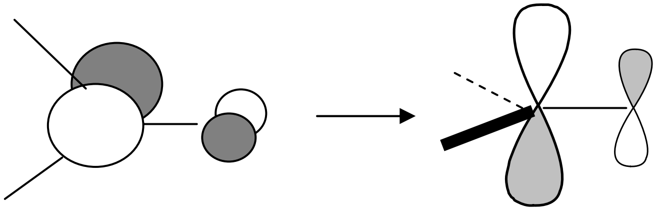


MOs of $H_2C=O$. It is isoelectronic to ethylene- MOs are the same, perturbed by O atom

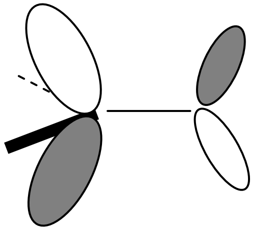


Orbital “tilting”





In fact



The direction of nucleophilic attack is not perpendicular to the plane but rather to by ca. 105^0 (the Bürgi-Dunitz angle).