4.1 Rules for constructing MOs

1) Draw AO energy level schemes on the left and right side
2) Construct the MO energy level scheme in the middle
3) The atomic core levels are similar in the molecule
4) Valence AOs, overlapping, of similar energy, of same symmetry, combine to yield shifted MO levels (in N_2 etc. 1s are core AOs!)
5) n AOs yield n MOs (the highest valence MO is sometimes missing !)
6) The lowest MO is below the lowest AO, the highest MO is even more above the highest AO (nonsymmetric splitting !)
7) s & pσ AOs on the left overlap with those on the right (s-p hybrids); pπ AOs on the left overlap with those on the right, forming pπ MOs
8) The MO shifts are the larger the larger the overlap and the more similar the AO energies; s-p mixing-promotion for C (B,N; little:Be,O)
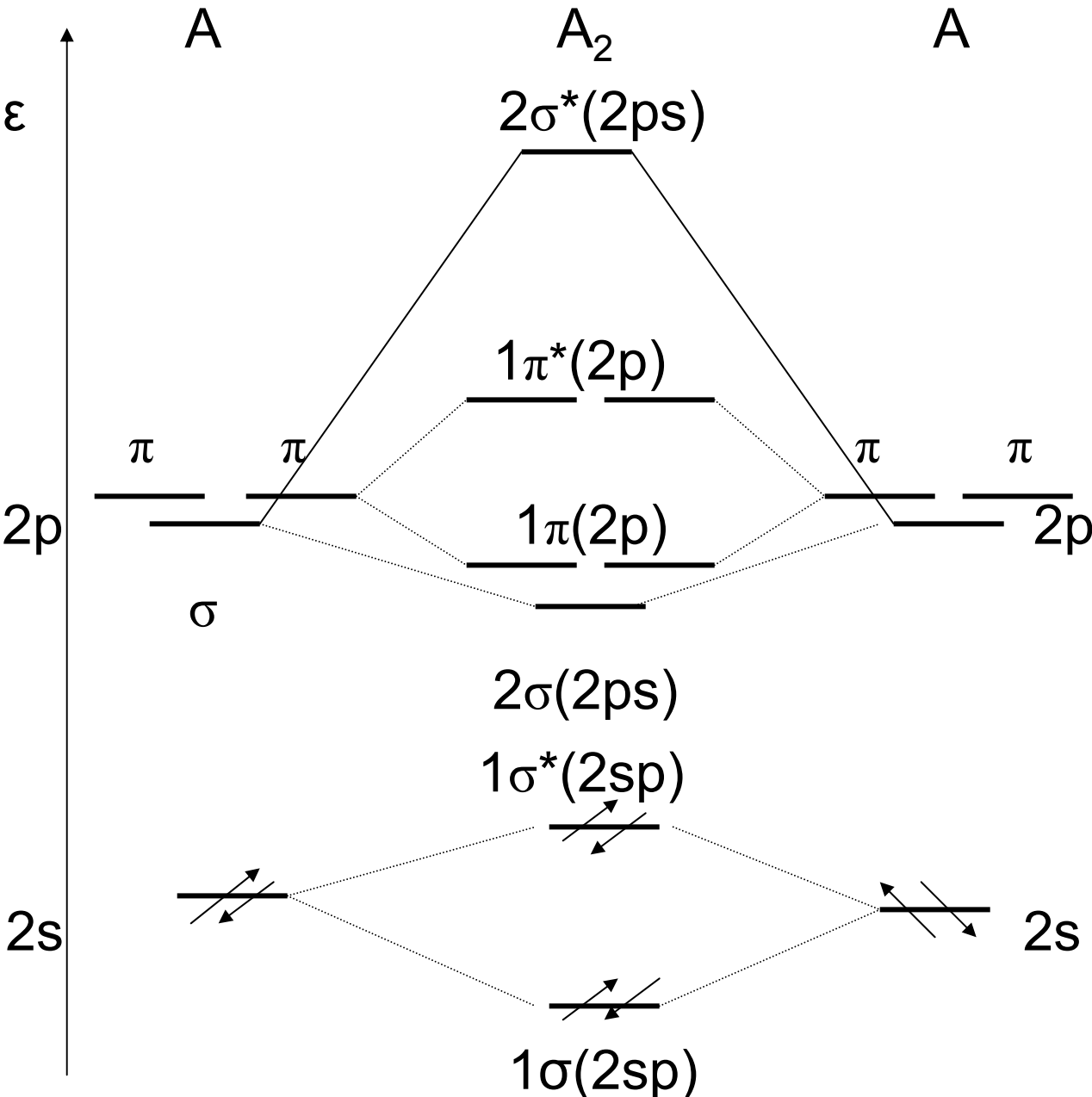
ε H H_2 H

1σ*

1s   1σ 1s
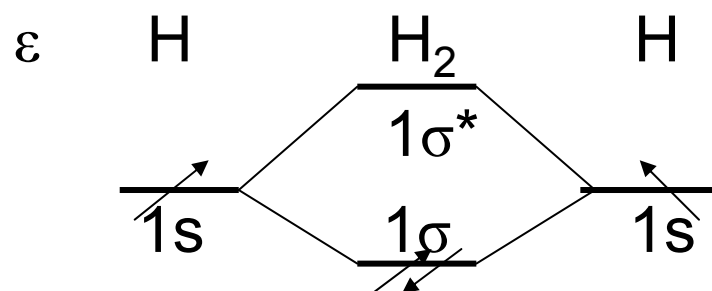
Example: $2H \rightarrow H_2$

The lowered MO is bonding, the strongly raised MO is antibonding

Here 1 σ bond, symbol: H – H

4.2 Homonuclear Diatomics

Examples

"2 He" $1\sigma^2 1\sigma^{*2}$

Li–Li $1\sigma^2$

Be··Be· $1\sigma^2 1\sigma^{*2}$

|B⁻B| $1\sigma^2 1\sigma^{*2} 1\pi^2$

|C⁼C| $1\sigma^2 1\sigma^{*2} 1\pi^4$

|N≡N| $1\sigma^2 1\sigma^{*2} 1\pi^4 2\sigma^2$

O–·O $2\sigma^2 1\pi^4 1\pi^{*2}$

F–F $2\sigma^2 1\pi^4 1\pi^{*4}$

"Ne··Ne"

Note: The two lower σ from 2s are shifted down by 2p-mixing

4.3 Notes

He_2 2 LP; Li_2 1σ (weak:1e-½σ bond stronger than 2e-1σ bond); Be_2 secondary bond of 2 LP; B_2 two ½π with parallel spins, 2 LP; C_2 2 π, 2 LP (at similar energy 1½π+½σ); N_2 2π 1σ 2LP; O_2 1π 1σ 4LP; F_2 1σ 6LP; Ne_2 van der Waals attraction of 4+4 LP

σ^2 σ^{*2} : 1 deloc. bonding & 1 deloc. antibonding MO is equivalent to 2 localized nonbonding (one-center lone pair = LP) MOs; secondary bond for Be_2(s-p hybr.) ; none for He_2

π^2 : 1 electron each in a real π_x and π_y, or equivalently in a complex π_{+1} and π_{-1} orbital – density is cylindrical, 0 angular momentum, two ½π bonds

π^4 π^{*2} : 2 π bonds, two ½π* antibonds is equivalent to 1 π bond and 2 π lone pairs

s-p hybridization: SH_2 has two polar Sp/Hs bonds and 2s-LP, 2p-LP (=two 2sp-LPs =one cloud, not 2 'ears'): $S^{\delta-}$ $2s^2 2p^{4.4}$ $2H^{\delta+}$ $1s^{0.8}$

s-p promotion: CH_4 has 4 nonpolar C $s^{.3}p^{.7}$ H s^1 bonds: C $s^{1.2}p^{2.8}$, C has 0.8 s→p , because 2s and 2p overlap similarly with H1s

4.4 Heteronuclear and Polyatomic Molecules
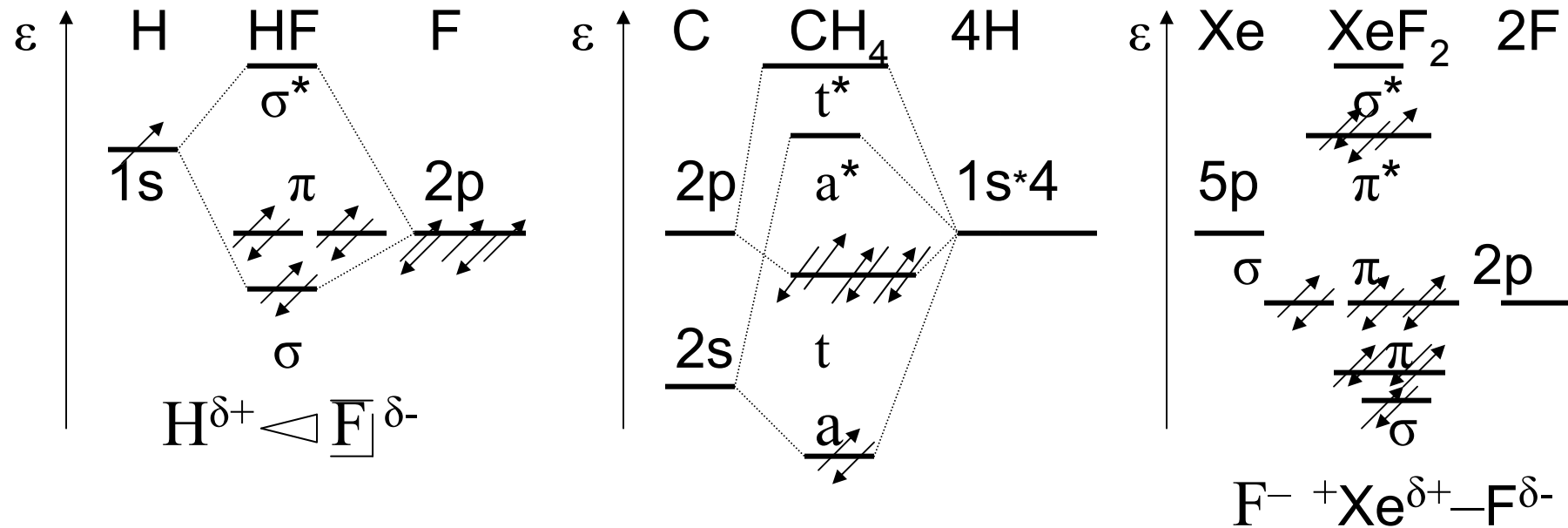
The 3+1 delocalized canonical symmetry-adapted MOs of CH$_4$ can be linear-combined to yield 4 localized equivalent C(s$^{1.2}$p^3)+H(s) MOs; in contrast to the VB assumption, the MO-SCF optimization gives a little more C2s 'population', since C2s is lower in energy than C2p and H1s.

In the case of XeF$_2$ the 3 AOs Xe5pσ and left and right F2pσ yield 3 canonical σ-MOs, 1 bonding, 1 nonbonding, 1 antibonding. They can be transformed into a Xe-LP and two polar F→Xe bonds: F$^{\delta-}$→Xe$^{2\delta+}$←F$^{\delta-}$.

Compare Atkins, PC^2 §14 (orbitals are neither slim nor touching spheres! tails are bigger! 1sσ-MO at r = 0 is smaller, etc.! But a few Figs. are correct)