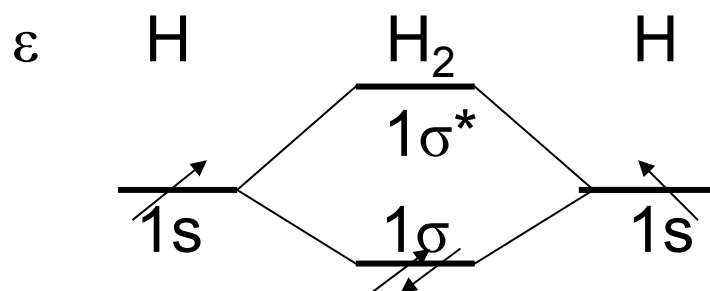


4.1 Rules for constructing MOs

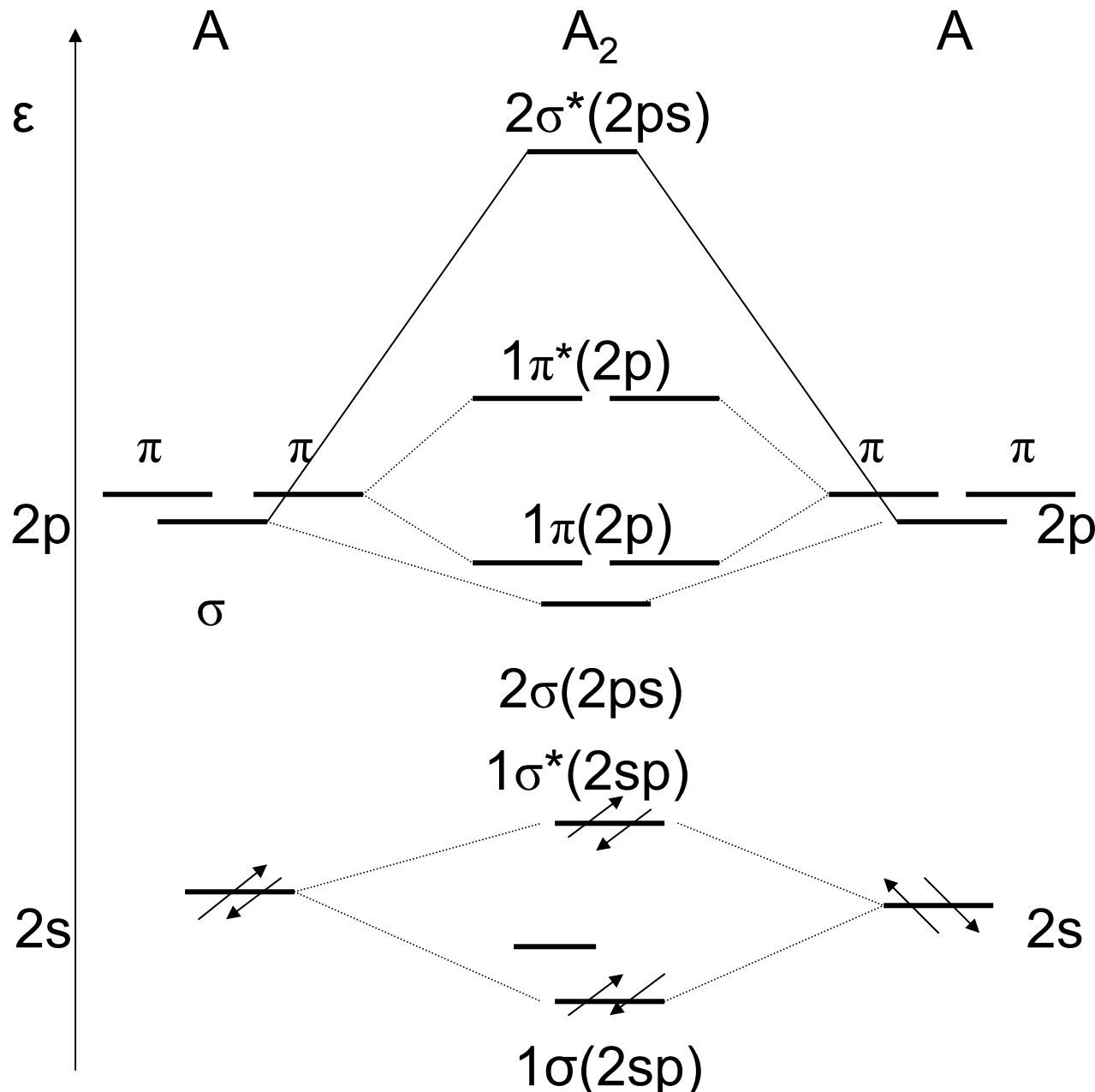
- 1) Draw AO energy level schemes on the left and right side
- 2) Construct the MO energy level scheme in the middle
- 3) The atomic core levels are similar in the molecule
- 4) Valence AOs, overlapping, of similar energy, of same symmetry, combine to yield shifted MO levels (in N_2 etc. $1s$ are core 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 & p_σ AOs on the left overlap with those on the right (s - p hybrids); p_π AOs on the left overlap with those on the right, forming p_π 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)



Example: $2H \rightarrow H_2$

The lowered MO is bonding, the strongly raised MO is antibonding
Here 1σ 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| $1\sigma^2 1\sigma^{*2} 1\pi^4 2\sigma^2$
 - $\overline{\text{O}}-\underline{\text{O}}$ $2\sigma^2 1\pi^4 1\pi^{*2}$
 - $\underline{\text{F}}-\underline{\text{F}}$ $2\sigma^2 1\pi^4 1\pi^{*4}$
 - “Ne·Ne”
- Note: The two lower σ from 2s are shifted down by 2p-mixing*

4.3 Notes

He₂ 2 LP; **Li₂** 1σ (weak: 1e-1/2σ bond stronger than 2e-1σ bond);
Be₂ secondary bond of 2 LP; **B₂** two 1/2π with parallel spins, 2 LP;
C₂ 2 π, 2 LP (at similar energy 1 1/2π+1/2σ); **N₂** 2π 1σ 2LP; **O₂** 1π 1σ
4LP; **F₂** 1σ 6LP; **Ne₂** van der Waals attraction of 4+4 LP

σ² σ*² : 1 deloc. bonding & 1 deloc. antibonding MO is equivalent to 2 localized nonbonding (one-center lone pair = LP) MOs; secondary bond for Be₂(s-p hybr.) ; none for He₂

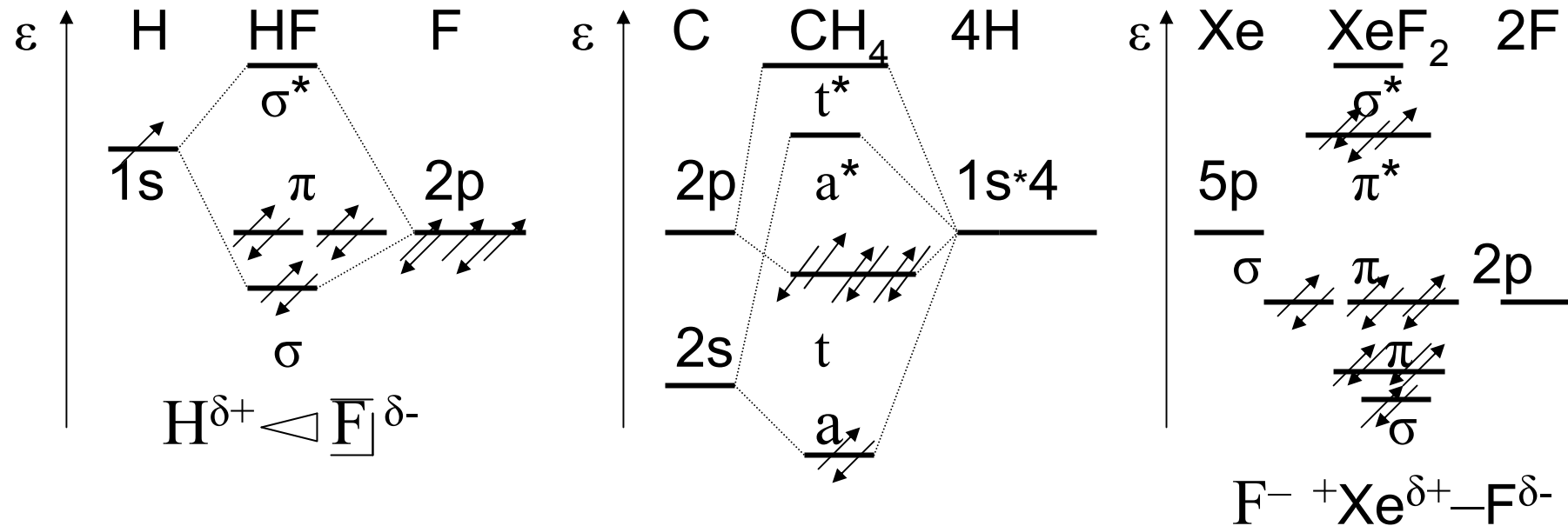
π² : 1 electron each in a real π_x and π_y, or equivalently in a complex π₊₁ and π₋₁ orbital – density is cylindrical, 0 angular momentum, two 1/2π bonds

π⁴ π*² : 2 π bonds, two 1/2π* antibonds is equivalent to 1 π bond and 2 π lone pairs

s-p hybridization: **SH₂** has two polar Sp/Hs bonds and 2s-LP, 2p-LP (=two 2sp-LPs =one cloud, not 2 'ears'): S^{δ-} 2s²2p^{4.4} 2H^{δ+} 1s^{0.8}

s-p promotion: **CH₄** has 4 nonpolar C s^{.3}p^{.7} H s¹ 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 CH₄ can be linear-combined to yield 4 localized equivalent C(s^{1.2}p³)+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 XeF₂ the 3 AOs Xe5p σ and left and right F2p σ yield 3 canonical σ -MOs, 1 bonding, 1 nonbonding, 1 antibonding. They can be transformed into a Xe-LP and two polar F \rightarrow Xe bonds: F^{δ-} \rightarrow Xe^{2δ+} \leftarrow F^{δ-}.

Compare Atkins, PC² §14 (orbitals are neither slim nor touching spheres! tails are bigger! 1 σ -MO at r = 0 is smaller, etc.! But a few Figs. are correct)