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 \( \text{N}_2 \) 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) \( s \) & \( p_\sigma \) AOs on the left overlap with those on the right (s-p hybrids); \( p_\pi \) AOs on the left overlap with those on the right, forming \( p_\pi \) 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)

\[
\begin{align*}
\varepsilon & \quad \text{H} \quad \text{H}_2 \quad \text{H} \\
1s & \quad 1\sigma \quad 1\sigma^* \quad 1s \\
\end{align*}
\]

Example: \( 2\text{H} \rightarrow \text{H}_2 \)

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

Here \( 1\sigma \) bond, symbol: \( \text{H} - \text{H} \)
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 $\sigma$ from 2s are shifted down by 2p-mixing
He$_2$ 2 LP; Li$_2$ 1$\sigma$ (weak: $1e^{-1/2}\sigma$ bond stronger than $2e^{-1}\sigma$ bond); 
Be$_2$ secondary bond of 2 LP; B$_2$ two $1/2\pi$ with parallel spins, 2 LP; 
C$_2$ 2 $\pi$, 2 LP (at similar energy $11/2\pi+1/2\sigma$); N$_2$ 2$\pi$ 1$\sigma$ 2LP; O$_2$ 1$\pi$ 1$\sigma$ 4LP; F$_2$ 1$\sigma$ 6LP; Ne$_2$ van der Waals attraction of 4+4 LP

$\sigma^2$ $\sigma^{*2}$: 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$_2$

$\pi^2$: 1 electron each in a real $\pi_x$ and $\pi_y$, or equivalently in a complex $\pi_{+1}$ and $\pi_{-1}$ orbital – density is cylindrical, 0 angular momentum, two $1/2\pi$ bonds

$\pi^4$ $\pi^{*2}$: 2 $\pi$ bonds, two $1/2\pi^*$ antibonds is equivalent to 1 $\pi$ bond and 2 $\pi$ 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$^{3p.7}$ H s$^1$ bonds: C s$^{1.2}$p$^{2.8}$, C has 0.8 s$\rightarrow$p, because 2s and 2p overlap similarly with H1s
4.4 Heteronuclear and Polyatomic Molecules

The 3+1 delocalized canonical symmetry-adapted MOs of \( \text{CH}_4 \) can be linear-combined to yield 4 localized equivalent C(s\(^1\)2p\(^3\))+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 \( \text{XeF}_2 \) the 3 AOs Xe5p\( \sigma \) and left and right F2p\( \sigma \) yield 3 canonical \( \sigma \)-MOs, 1 bonding, 1 nonbonding, 1 antibonding. They can be transformed into a Xe-LP and two polar F→Xe bonds: \( \text{F}^{-} \rightarrow \text{Xe}^{2\delta^{+}} \leftarrow \text{F}^{\delta^{-}} \).

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