

Construction of Molecular Orbitals

The most common approach to constructing molecular orbitals, $\{\psi_{\sigma}; \sigma = 1, \dots, N\}$, is to build them up from **Linear Combinations of Atomic Orbitals**, $\{\phi_i; i = 1, \dots, N\}$:

$$\psi_{\sigma} = \sum_{i=1}^N c_{\sigma i} \phi_i = c_{1\sigma} \phi_1 + c_{2\sigma} \phi_2 + \dots + c_{N\sigma} \phi_N.$$

In this so-called LCAO expression, the coefficients $c_{1\sigma}, c_{2\sigma}, \dots, c_{N\sigma}$ give the contributions that each of the individual AOs $\phi_1, \phi_2, \dots, \phi_N$ make to the MO ψ_{σ} . There are three features of the MOs that are worth noting:

- (1) Starting with N atomic orbitals, we can construct N molecular orbitals. No more and no less.
- (2) The MOs are mutually *orthogonal* and *normalized*. This means that the net overlap between any two MOs is zero and the net overlap of any MO with itself = 1.
- (3) As a result of the Pauli exclusion principle, each MO can accommodate two electrons. One is spin-up ($m_s = +1/2$), the other is spin-down ($m_s = -1/2$).

In qualitative treatments, a minimal set of valence atomic orbitals is generally used for MO construction.

Homonuclear diatomic molecules (X_2 , $X = H, He, Li, \dots, Ne$). Notes:

(H_2 vs. He_2):

- mixing of atomic orbitals leads to formation of *bonding* and *antibonding* orbitals; the *destabilization of antibonding orbitals* is slightly greater than the *stabilization of bonding orbitals*. This leads to slight net destabilization of molecules for which both bonding and antibonding orbitals are doubly occupied.

(2nd row diatomics):

- the separation of the σ and π bonding problem arises from symmetry controlled zero overlap. π orbital manifold remains pure p in character.
- net bond order = $(1/2)[(\# \text{ bonding electrons}) - (\# \text{ antibonding electrons})]$
- s-p mixing (hybridization) is the result of s-p overlap and its magnitude is inversely proportional to the s-p orbital energy gap. As a consequence, there is no fixed s-p hybridization ratio — as was assumed by Pauling.

Heteronuclear diatomic molecules.

(HF):

- mixing of atomic orbitals is inversely proportional to the energy difference between them and roughly proportional to the square of the overlap between them. The F 2p orbital is closer in energy to the H 1s orbital than is the F 2s orbital. The F 2s orbital is also more contracted than is 2p and its overlap with the H 1s is poorer. Most of the H-F bonding involves the 1s-2p interaction.
- the bonding 1s-2p combination is localized more on the electronegative fluorine atom, the antibonding combination is localized more on the more electropositive hydrogen.
- the π orbitals on the fluorine remain localized on the fluorine atom - they have no valence orbitals on hydrogen with which they can overlap.

(CO):

- as for the other diatomics, the separation of the σ and π bonding problem arises from symmetry controlled zero overlap. π orbital manifold remains pure p in character. This π manifold remains fairly simple — note that π is localized more on oxygen, π^* (the LUMO) is more localized on carbon.
- each of the σ levels possesses a more complex mixture of carbon and oxygen s & p orbital contributions. The pictures give a qualitative indication of their orbital character; try to understand how each of these orbital wavefunctions arises.
- the HOMO has predominantly carbon lone pair character. The HOMO and LUMO are important in understanding the chemistry of CO in binding to transition metals.

Simple polyatomics.

(linear and cyclic H_3):

- We can build up MOs for polyatomic molecules from simpler fragments. A “fragmentation” of H_3 molecules into $H_2 + H$ has been chosen in these cases.
- symmetry is very useful in delimiting interactions. Note that the antisymmetric H_2 fragment orbitals have no overlap with the symmetric H orbital and thus remain unperturbed when the molecule is “assembled”.
- A “correlation diagram” can be constructed to relate the molecular orbitals and energies of the linear and cyclic forms.
- bonding “patterns” present in these simple-minded cases can be recognized in many more realistic cases, e.g., $2e^-$ systems: $C_3H_3^+$, $[CH_2=CH-CH_2]^+$, $B_2H_7^-$ (= $[H_3BHBH_3]^-$) & $4e^-$ systems: bifluoride (= FHF^-), $RCOO^-$, SO_2 , CO_2 (twice).

(H_n systems):

- as the size of the systems increase, number of orbitals increases and their spacing decreases.
- MOs for two familiar cyclic systems are illustrated. Note that orbitals increase in energy as the number of nodes increases (and the number of antibonding interactions increases).
- the Hückel $4n+2$ rule can be deduced from inspection of the cyclic systems.

(H_2O):

- symmetry adaptation of hydrogen orbitals greatly simplifies the interaction diagram. Note that only one of the symmetry types involves the mixing of more than two orbitals.
- the molecular orbitals can be approximately divided into two sets: two O-H bonding MOs and two with (inequivalent) lone-pair character.
- the HOMO has pure oxygen p character.