NOTES ON MOLECULAR ORBITAL THEORY

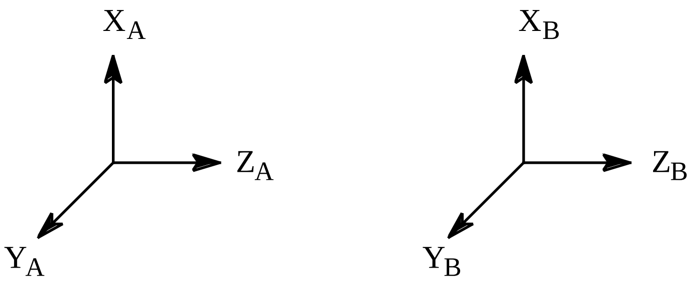
Five major points concerning molecular orbital theories for diatomic and polyatomic molecules are summarized. All of the material is covered in McQuarrie, but this outline should help organize the topics which I consider important.

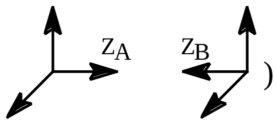
I. Energy-bonding-interactions

(1) Why don't a $2s_A$ and $2p_{xB}$ interact to form a bond ↔ antibond pair?

(2) Will there be *significant* $1s_A$ and $1s_B$ interaction sin the $1\sigma_g$ and $1\sigma_u$ orbitals of F_2 compared to the interactions between $2s_A$ and $2s_B$ in the $2\sigma_g$ and $2\sigma_u$ orbitals of F_2? How will the energies of $1\sigma_g$ and $1\sigma_u$ compare to the energy of a 1s electron in F atom?

(3) In a coordinate system with "consistent" z-axis direction:



(some sources use inconsistent ).

will $\psi = \frac{1}{\sqrt{2}}\,(2p_{ZA} + 2p_{2B})$ be bonding or antibonding?

What about $\psi = \frac{1}{\sqrt{2}}\,(2p_{ZA} - 2p_{ZB})$?

II. Classification Scheme

(1) A.O.'s used.

(2) Numbers of nodal planes passing through z-axis (σ, π, δ etc.).

Can you identify which *d orbital* components would contribute to σ-bonds, π-bonds, δ-bonds?

(3) Bonding or antibonding*

(4) Symmetry with respect to inversion (*g* gerade or *u* ungerade)

(5) Schemes 1 and 3 are only approximations while 2 and 4 are rigorous classifications.

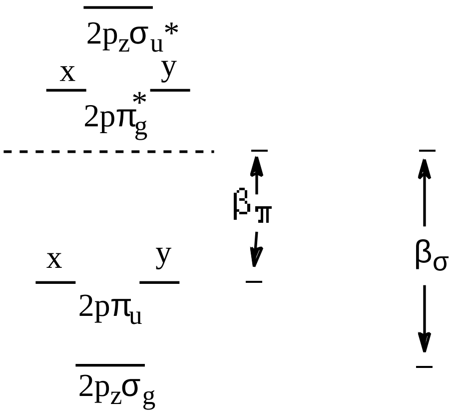
In complete calculations *more than two* a.o.'s can interact to form m.o.'s. Thus a $2\sigma_g$ could have in addition to $2s_A$ and $2s_B$ other types of σ orbitals *e.g.* $2p_{ZA}$, $2p_{BZ}$ and classification (1) would only be approximate. In addition if more than two a.o.'s are present, some a.o ↔ a.o. interactions could be bonding while others antibonding. Thus classification (3) is only approximate. The results of complex calculations therefore utilize only the inversion (*g* or *u*) and the plane symmetry (σ, π, δ etc.) as in figure 9-15 in McQuarrie.

III. Energy ordering, aufbau, and molecular properties.

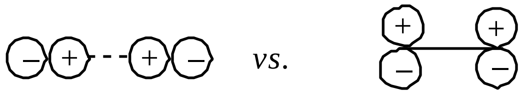
(1) Know the energy ordering appropriate for m.o.'s from the 1^{st}, 2^{st}, and 3^{rd} row a.o.'s.

(2) Understand the origin of the two different schemes for p-orbital m.o.'s.

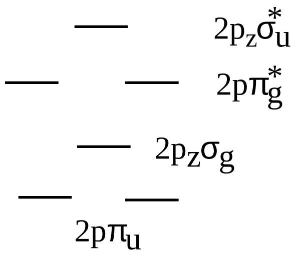
Type II



results from a greater interaction between the $2p_z\sigma$ orbitals on the two atoms. Type II energy ordering originates from greater $2p_z\sigma_A$ ↔ $2p_z\sigma_B$ overlap than $2p\pi_A$ ↔ $2p\pi_B$ overlap at bonding intermolecular distances.



Type I



Type I ordering results from interactions between 2s and 2pz orbitals in forming the “$2s\sigma_u^*$” and “$p_z\sigma_g$.” Although this σ_u^* is primarily 2s ↔ 2s destructive interference, there is a small 2s ↔ $2p_z$ *constructive* interference which *stabilizes* this σ_u^* m.o. Although the $2p_z\sigma_g$ is primarily $2p_z$ ↔ $2p_z$ constructive interfereence, *destructive* 2s ↔ $2p_z$ interference makes *destabilizing* energy contributions raising $E_{2p_z\sigma_g}$ above $E_{2p\pi_u}$. (2s orbitals cannot interact with $2p_x$ or $2p_g$ in π m.o.s.) This interaction is especially pronounced for the “larger” (less tightly bound) $2s\sigma$ orbitals in the lighter diatomics. The Type I scheme applies to He → N where the type II scheme applies to O^+ → Ne. Note that since the two are identical for the antibonding orbitals, the Type I will give the ground state configuration for all cases (ignoring “shift arounds” of closed shell orders).

(3) Understand the Aufbau principle for filling these m.o.’s.

(4) Understand how net bonding electrons and bond orders determine stability bond length, *etc.* (*e.g.*, see Fig. 9-14).

IV. Application of m.o. theory to heteronuclear diatomics.

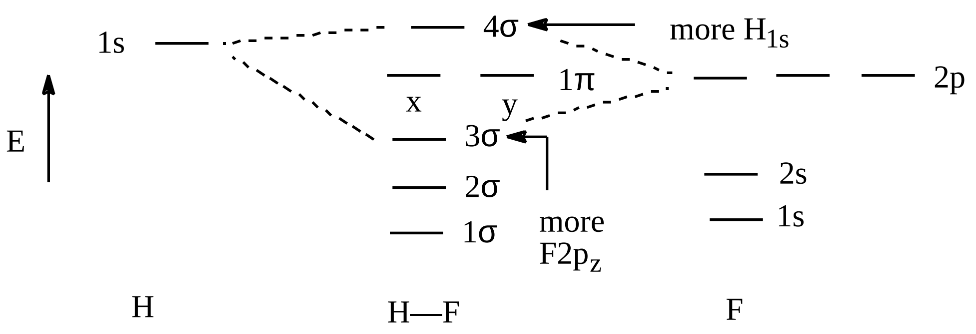
(1) When two a.o.’s of *differing* energies (e.g., B_{2s} and F_{2s} in B–F) interact to form an m.o., the *bonding* combination will have a greater proportion of the *more stable a.o.* and the **antibonding** combination will contain a greater proportion of the **less stable a.o.**

(2) Unequal a.o. contributions to the m.o.’s results in dipole moments.

(3) For molecules having atoms with nearly the same electronegativity (*e.g.* N–O, C≡O) one can use the homonuclear energy ordering scheme with the above [(2)] recognition of unequal contributions of the two a.o.’s.

(4) For atoms of greatly differing electronegativities, the a.o.’s most likely to interact (*i.e.*, which interact the most) are ones with the most similar energies, *e.g.*

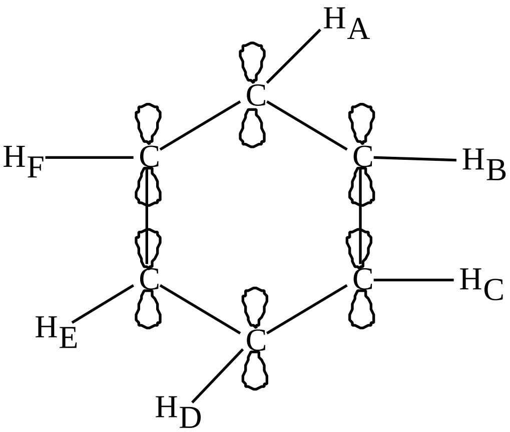
H• I.P. = 13.6 eV from 1s, :F̤̈• I.P. = 17.42 eV from 2p



V. Bonding in polyatomics

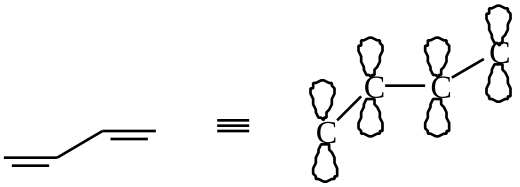
(1) Most chemical approach: hybrids for σ bonds, m.o.'s (delocalized) for π-bonds (like chem 1c, organic).

Conjugated systems require delocalized orbitals.



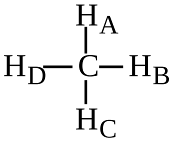
$$\varphi = C_A 2P_{zA} + C_B 2P_{zB} + C_C 2P_{zC} + C_D 2P_{zD} + C_E 2P_{zE} + C_F 2P_{zF}$$

One uses the variation theorem with $\hat{h}_f$ which takes into account K.E., average repulsion of the π-electrons for one another, and the attraction of C^+–H fragments (and C^+–C^+ framework) also for



The variation equations are written in terms of α's and β's and are solved using group theory and computers to get C's and E's.

Example: H–C bonds of methane:



$$\varphi_{(C-H)_A} = C_{1A}\chi_{2s} + C_{2A}\chi_{2px} + C_{3A}\chi_{2py} + C_{4A}\chi_{2pz} + C_{5A}\chi_{H1sA}$$

$$\varphi_{(C-H)_B} = \ldots$$

Finding best coefficients will give approximate sp^3 combinations for mixtures of a.o.'s on carbon. Note that this then combines with χ_{H1s} to form localized m.o. (φ_{mo} = hybrid + H1s).

Why doesn't the variation theorem just leave the a.o.'s unhybridized? Hybridization (1) increases the directionality and thus the overlap of the carbon orbital (hybrid) and the H_{1s} giving stronger bonding than if not hybridized and (2) the increased directionality reduces electronic repulsion between bonding regions.

The mathematical and pictorial combinations of a.o.'s which give various hybrids can be found in McQuarrie sp (9-120, 9-121) for sp^2 and (9-122, 9-125, 9-128) for sp^3 (example 9-10).