

Recipe for π bonds in polyatomic molecules

Notes on General Chemistry

<http://quantum.bu.edu/notes/GeneralChemistry/RecipeForPiBondsInPolyatomicMolecules.pdf>
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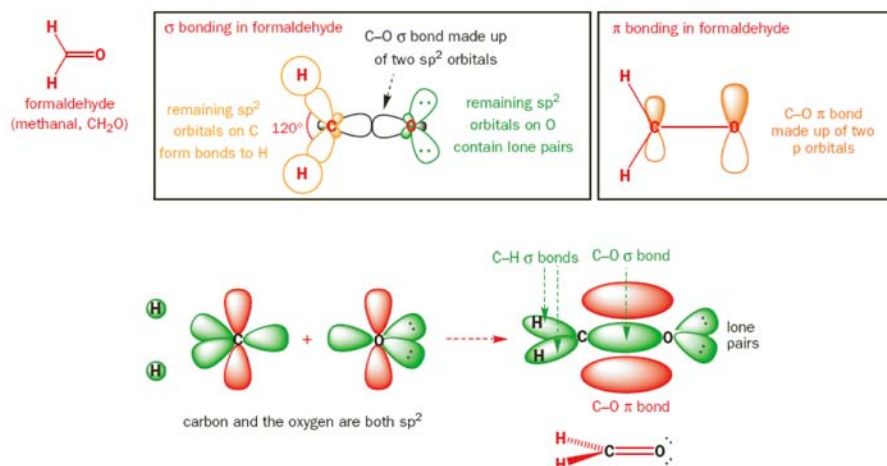
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Bonding in polyatomic molecules (molecules with more than two atoms) is treated in two parts.

The first part accounts for the *connectivity* of the atoms, that is the bonds between the atoms. This is treated as a framework of (localized) σ bonds built from overlapping *hybridized* AO's.

The second part accounts for *multiple bonds*. This is treated as a framework of π MO's built from overlapping *unhybridized* AO's.

Here are illustrations of these two aspects, for formaldehyde, $\text{H}_2\text{C}=\text{O}$.



Framework of σ bonds (left panel) and π bonds (right panel) in formaldehyde. The π antibonding orbital is not shown. The hybridization on the O is determined by the C. Adapted from Clayden et al., *Organic Chemistry* (Oxford University Press, 2000), pages 108 (bottom figure) and 136 (top figure). © Copyright Oxford University Press, 2007.

We have learned how to connect atoms with a σ framework built from sp , sp^2 , sp^3 hybrid orbitals. Here we describe how to treat multiple bonds, using a recipe for building π frameworks.

In the following, the distinction is made between a *central atom* and a *terminal atom*. A central atom has two or more atoms attached to it. A terminal atom is an atom (other than H) that is connected to a central atom.

Here are two examples of this distinction. In formaldehyde, $\text{H}_2\text{C}=\text{O}$, the C is the only central atom, and the double bonded O is the only terminal atom. In formic acid, $\text{HC}(=\text{O})\text{OH}$, the C and single bonded O are central atoms, and the double bonded O is a terminal atom.

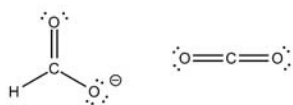
■ Recipe overview

The recipe is based on the Lewis structure of the molecule. If there are equivalent “resonance” Lewis structures, just one of these is needed.

- Step 1: Determine the number of p atomic orbitals (AO's) *not* used in the σ framework. This is the number of p AO's that are available to form the same number of π molecular orbitals (MO's).
- Step 2: Sketch the corresponding number of π MO's, and determine their bond character (bonding, nonbonding, or antibonding) and their relative energies.
- Step 3: Determine the number of electrons that there will be in the π MO's.
- Step 4: Assign all of the π electrons using aufbau and Hund rules, and calculate the π bond order.

■ Recipe details

Here is a description of how to carry out each step, using the examples of CO_2 and formate, HCOO^- , the conjugate base of formic acid, HCOOH .



Formate (left) and CO_2 (right) Lewis structures.

Step 1: Number of unhybridized p AO's available to form π MO's

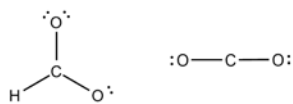
The key to this step is the following.

The hybridization on each terminal atom is determined by the central atom to which it is attached.

In formate, the C is sp^2 hybridized and in CO_2 the C is sp hybridized. The result is that then there will be one or more unhybridized AO's on each terminal atom that are perpendicular to the σ framework. The double bonded O's in formate and CO_2 illustrate that terminal atoms that look identical in Lewis structures do not have the same hybridization and do not form identical orbital interactions.

The σ framework consists of the σ bonds and nonbonded hybrid AO's on terminal atoms.

Here are the σ frameworks of CO_2 and HCOO^- .



Formate (left) and CO_2 (right) σ frameworks.

Since the unhybridized p AO's on adjacent central atoms are perpendicular to the σ framework, all of these p AO's are available to form π MO's.

In CO_2 , since C is sp, both O's are sp. This means that there are two unhybridized, mutually perpendicular p AO's on each of the three atoms, for a total of six p AO's, which form six π MO's.

In HCOO^- , since C is sp^2 , both O's are sp^2 . This means that there is one unhybridized p AO on each of the three atoms, for a total of three p AO's, which form three π MO's.

Unhybridized p AO's on a terminal atom are closer to the other AO's on the same atom than they would be if all p AO's were hybridized. This means that there is an energy cost due to *increased*

electron cloud repulsion on the terminal atom.

This energy cost is overcome by the lowering of energy made possible by the formation of π MO's. There are two sources of the energy lowering due to π MO formation. First, bonding π MO's result in *increased electrical attraction* by shifting electron clouds toward pairs of nuclei. Second, the electron clouds of bonding π MO's will have *larger wavelength* than the individual p AO's, and so *smaller kinetic energy*. That is, the reason some lone pairs on terminal atoms are in unhybridized p AO's is the energy cost is paid for by the energy return made possible by π MO formation.

Step 2: Sketch the π MO's, and determine their bond character and relative energies

The general procedure is to use the number of loops that there must be in the MO electron wave to guide the relative phasing of the p AO's, and to use electronegativities to determine relative amounts of AO's. The lowest-energy MO must have one loop, the second-lowest must have two loops, etc. The *one-loop* (lowest-energy) MO will have greatest contribution from AO's on *most* electronegative atoms, and The *maximum-loop* (highest-energy) MO will have greatest contribution from AO's on *least* electronegative atoms.

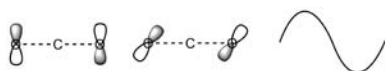
The lowest-energy (one-loop) MO has all of the p AO's in phase.



Degenerate pair of lowest energy (one-loop) π MO's in CO_2 . Formate has just a single one-loop π MO. The O AO's predominate, since O is more electronegative than C and these are *bonding* MO's (denoted by their blue color).

Since O is more electronegative than C, the O AO's predominate. For CO_2 , there are two degenerate (equal-energy), perpendicular one-loop MO's. This is because the unhybridized p AO's consist of two perpendicular sets of three AO's each. AO's from different sets have zero net overlap (that is incorrect relative symmetry) and so do not interact with each other. These are *bonding* MO's.

The two degenerate second lowest-energy (two-loop) MO's consist of a group of adjacent p AO's with one relative phase, and a group of adjacent AO's with the other relative phase.



Degenerate pair of second lowest energy (two-loop) π MO's in CO_2 . Formate has just a single two-loop π MO. There is no C contribution to these MO's. Because the AO's overlap hardly at all, these are *nonbonding* MO's (denoted by their black color).

The reason there is no C AO in these MO's is that such an MO electron cloud would be lopsided, which is inconsistent with the equal C–O bond lengths in these molecules. Because the O AO's are not adjacent, they overlap hardly at all and so these are *nonbonding* MO's.

The third lowest-energy (three-loop) MO's consist of AO's alternating in relative phase.



Degenerate pair of third lowest energy (three-loop) π MO's in CO_2 . Formate has just a single three-loop π MO. The C AO's predominate, since O is more electronegative than C and these are *antibonding* MO's (denoted by their red color).

These are *antibonding* MO's. Since O is more electronegative than C, the C AO's predominate.

Step 3: Number of electrons in the π MO's: visual method

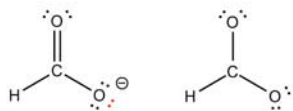
A visual way to determine the number of π electrons is to compare the full Lewis structure with just its σ framework part. For CO_2 the comparison is



CO₂ Lewis structure (left) and σ framework (right). One lone pair (shown in red) on each O and one pair from each double bond are the eight electrons in the π MO's

There are two lone pairs (shown in red) on the O's and two bond pairs that are not in the σ framework. These are the eight electrons that will be in the CO₂ π MO's.

The visual comparison for formate is



Formate Lewis structure (left) and σ framework (right). One lone pair (shown in red) and one pair from the double bond are the four electrons in the π MO's

There is one lone pair (shown in red) on the single bonded O and one bond pair that are not in the σ framework. These are the four electrons that will be in the formate π MO's.

Step 3: Number of electrons in the π MO's: calculational method

A calculational method to determine the number of π electrons begins by writing that these electrons come from two places:

$$\begin{aligned} \text{number of } \pi \text{ electrons} &= \pi \text{ electrons from central atom multiple bonds} + \\ &\quad \pi \text{ electrons from terminal atom lone pairs} \end{aligned}$$

The number of π electrons from each central atom multiple bond is bond electrons $- 2$, that is, the number of electrons in the σ part of the multiple bond.

To compute the π electrons from terminal (non-H) atom lone pairs, subtract from the terminal atom lone pairs the number of pairs in the σ framework. The number of lone pairs in the σ framework is steric number $- 1$, since the terminal atom has one connection and so the remainder of the steric number (SN) must be made up of lone pairs. This means that the lone pairs left over, and so available as π electrons, is lone pairs $- (SN - 1)$.

Putting everything together, we get

$$\begin{aligned} \text{number of } \pi \text{ electrons} &= \text{sum of central atom (shared electrons} - 2) + \\ &\quad \text{sum of terminal atom (lone pairs} - (SN - 1)) \times 2 \end{aligned}$$

For CO₂, there are two double bonds, the steric number is SN = 2 (since each atom is sp), and there are two terminal atoms (ignoring the H), each with two lone pairs. Hence

$$\begin{aligned} \text{number of } \pi \text{ electrons} &= (4 - 2) + (4 - 2) + \\ &\quad (2 - (2 - 1)) \times 2 + (2 - (2 - 1)) \times 2 = 2 + 2 + 2 + 2 = 8 \end{aligned}$$

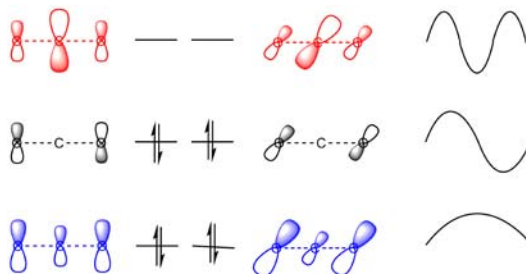
For HCOO⁻, there is one double bond, the steric number is SN = 3 (since each atom is sp²), and there are two terminal atoms, one with two lone pairs and one with three lone pairs. Hence

$$\begin{aligned} \text{number of } \pi \text{ electrons} &= 4 - 2 + \\ &\quad (2 - (3 - 1)) \times 2 + (3 - (3 - 1)) \times 2 = 2 + 0 + 2 = 4 \end{aligned}$$

Another method is to subtract all of the electrons in the σ framework from the total number of electrons. See if you can express this as a formula.

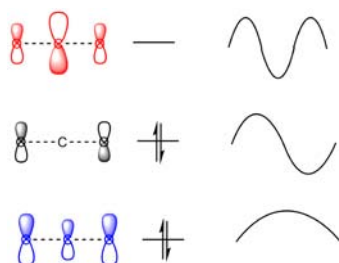
Step 4: Assign π electrons to MO's and calculate π bond order

In CO_2 we need to assign eight electrons to the π MO's. Four electrons are paired in the two one-loop MO's, contributing 2 to the π bond order. The remaining four electrons are paired in the two two-loop MO's; since these MO's are nonbonding, the contribution to the π bond order is 0. The net result is a π bond order = $2 + 0 = 2$, delocalized over C and the two O's.



CO_2 π MO's. The degenerate pair of bonding orbitals (in blue) corresponds to one loop in the π MO electron wave. The degenerate pair of nonbonding orbitals (in black) corresponds to two loops in the π MO electron wave. The degenerate pair of antibonding orbitals (in red) corresponds to three loops in the π MO electron wave.

In HCOO^- we need to assign four electrons to the π MO's. Two electrons are paired in the one-loop MO, contributing 1 to the π bond order. The remaining two electrons are paired in the two-loop MO; since this MO is nonbonding, the contribution to the π bond order is 0. The net result is π bond order = $1 + 0 = 1$, delocalized over C and the two O's.



Formate π MO's. The bonding orbital (in blue) corresponds to one loop in the π MO electron wave. The nonbonding orbital (in black) corresponds to two loops in the π MO electron wave. The antibonding orbital (in red) corresponds to three loops in the π MO electron wave.

■ Practice examples

For each of the following molecules,

- give the number of unhybridized p AO's,
- sketch that number of MO's,
- give the number of electrons in the π MO's, and
- compute the bond order.

SO_2

H_2CO

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