Exercise 4.5
Pi Molecular Orbital Energy Level Diagrams: Lone Pairs

How to Decide Whether Lone Pairs Belong to the σ MOs or the π MOs

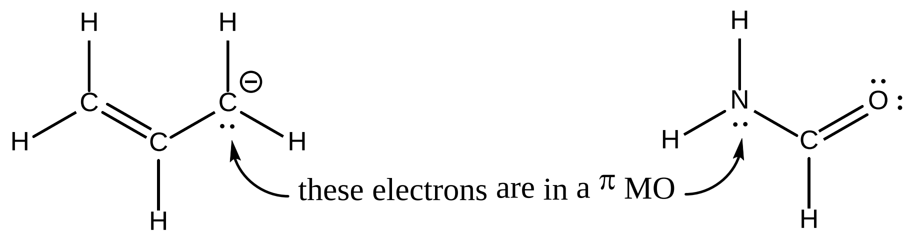
One of the most common questions when students are learning to construct pi molecular orbital energy level diagrams is how do we determine how many electrons to put in the pi molecular orbital energy level diagram.

Generally speaking,

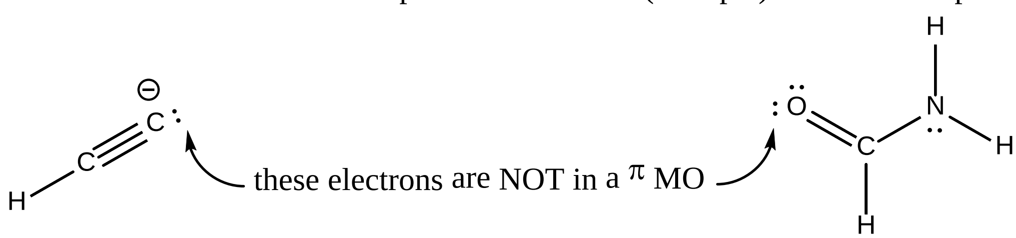
- every single bond corresponds to two electrons in σ MOs,
- every double bond corresponds to two electrons in σ MOs and two electrons in π MOs,
- every triple bond corresponds to two electrons in σ MOs, two electrons in one set of π MOs (one pi system) and two electrons in another set of π MOs (another pi system).

But this leaves the question of whether to put the lone pair electrons in σ MOs or π MOs.

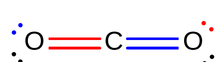
Looking at a Lewis diagram, if the atom next to the double (or triple) bonded atoms has at least one lone pair on it, then count one of those lone pairs as belonging to the pi system:



Lone pairs on one of the atoms that is part of the double (or triple) bond are not part of that pi system:

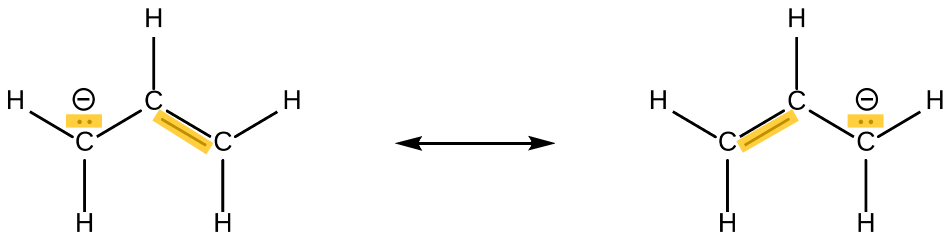


They might be part of a different pi system though. There are two perpendicular pi systems in CO_2 (one made from the $2p_x$ orbitals and one made from the $2p_y$ orbitals). They each contain four electrons. One pi system contains the lone pair shown in red plus one pair of electrons from the bond shown in red. The other pi system contains the lone pair shown in blue plus one pair of electrons from the bond shown in blue.

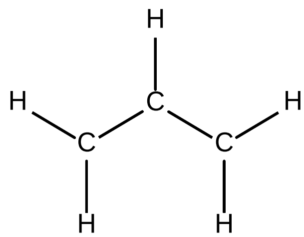


A useful test to help determine whether or not the electrons of a lone pair are in a π MO is to draw all reasonable resonance structures for the molecule. If the lone pair moves between any of the resonance structures, it is in a π MO. This approach is not as conclusive as the one on the previous page (since if cannot always recognize when electrons are <u>not</u> in a π MO), but it is nonetheless useful and it reinforces the concept that resonance structures are most often a tool for showing delocalization of π electrons.

For example, there are two resonance structures for the allyl anion ($C_3H_5^-$):



If we draw only the bonds and lone pairs that do not move (and show all bonds as single bonds), we get a "sigma skeleton" that looks like this:



The sigma skeleton includes 14 of the allyl anion's 18 electrons; those 14 electrons are in σ MOs. The remaining 4 electrons are in π MOs; they have been highlighted in yellow.

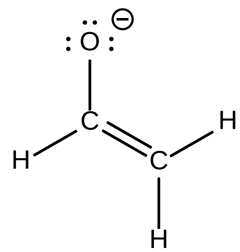
You would have come to the same conclusion using the method on the previous page. The lone pair is on the carbon atom <u>next to</u> the C=C bond, so those electrons are in a π MO.

1. Draw both resonance structures for ozone (O_3), and show that it has 4 electrons in π MOs.

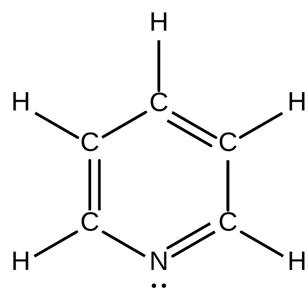
2. Each of the following species is planar and has one pi system.
For each species, identify the number of electrons in the pi system.

(a) NO_2^-

(b)



(c)



(d)