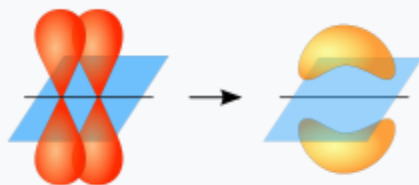


Pi bonds (π bonds) are **covalent chemical bonds** where two lobes of an **orbital** on one atom overlap two lobes of an orbital on another atom and this overlap occurs laterally. Each of these atomic orbitals has zero **electron density** at a shared **nodal plane**, passing through the two bonded **nuclei**. The same plane is also a nodal plane for the **molecular orbital** of the pi bond. Pi Bonds can form in double and triple bonds but do not form in single bonds in most cases.



Two p-orbitals forming a π -bond.

The Greek letter π in their name refers to **p orbitals**, since the **orbital symmetry** of the pi bond is the same as that of the p orbital when seen down the bond axis. One common form of this sort of bonding involves p orbitals themselves, though d orbitals also engage in pi bonding. This latter mode forms part of the basis for **metal-metal multiple bonding**.



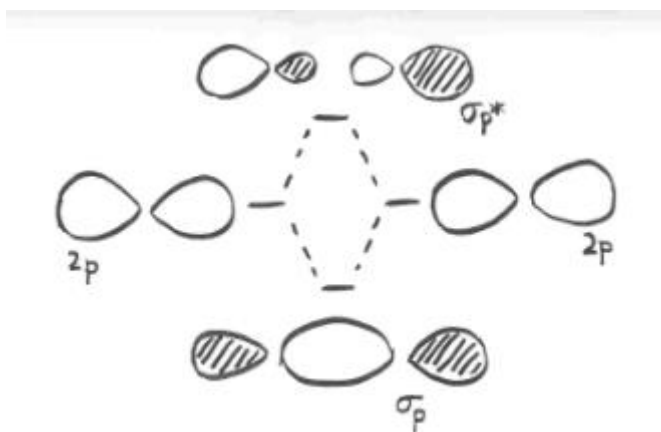
Ethylene (ethene), a small organic molecule containing a pi bond, shown in green.

Pi bonds are usually weaker than **sigma bonds**. The **C-C double bond**, composed of one sigma and one pi bond,^[1] has a bond energy less than twice that of a C-C single bond, indicating that the stability added by the pi bond is less than the stability of a sigma bond. From the perspective of **quantum mechanics**, this bond's weakness is explained by significantly less overlap between the component p-orbitals due to their parallel orientation. This is contrasted by sigma bonds which form bonding orbitals directly between the nuclei of the bonding atoms, resulting in greater overlap and a strong sigma bond.

Pi bonds result from overlap of atomic orbitals that are in contact through two areas of overlap. Pi bonds are more diffuse bonds than the sigma bonds. Electrons in pi bonds are sometimes referred to as **pi electrons**. Molecular fragments joined by a pi bond cannot rotate about that bond without breaking the pi bond, because rotation involves destroying the parallel orientation of the constituent p orbitals.

For **homonuclear diatomic molecules**, bonding π **molecular orbitals** have only the one nodal plane passing through the bonded atoms, and no nodal planes between the bonded atoms. The corresponding *antibonding*, or π^* ("pi-star") molecular orbital, is defined by the presence of an additional nodal plane between these two bonded atoms.

Earlier, we saw that p orbitals that lie along the same axis can interact to form bonds.



Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis. They can make an in-phase combination, as shown below.

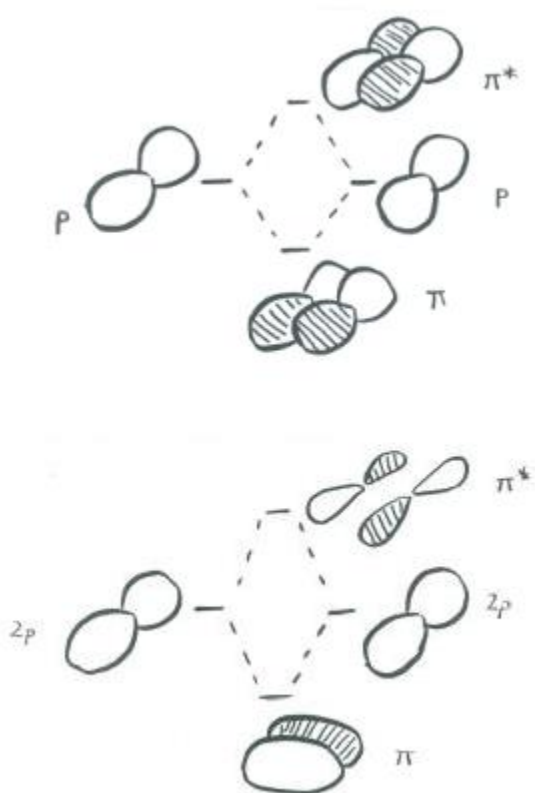


They could also make an out-of-phase combination, as shown below.



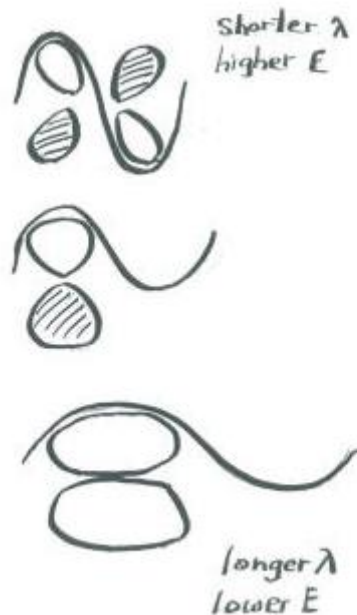
- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.



In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

Just as the sigma-bonding orbitals display progressively shorter wavelengths along the bonding axis as they go to higher energy, so do the pi bonding orbitals. In other words, there are more nodes in the higher-energy orbitals than in the lower-energy ones.



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. A s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.

