MO Description of Pi-Delocalized Systems
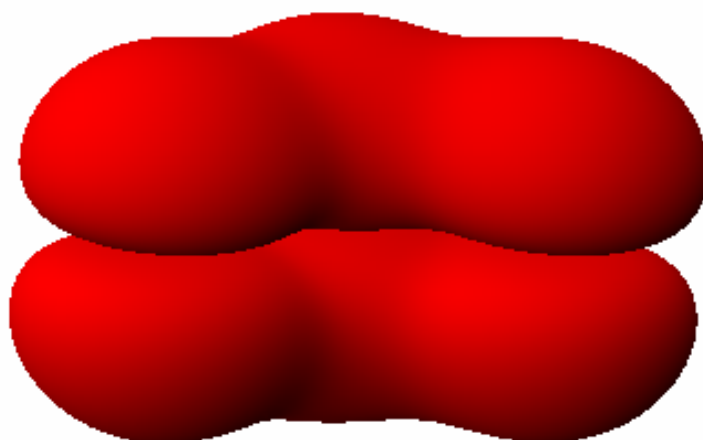
L   MO theory has no difficulty explaining the π-delocalized electron density implied by resonance forms, which VB theory cannot easily represent.
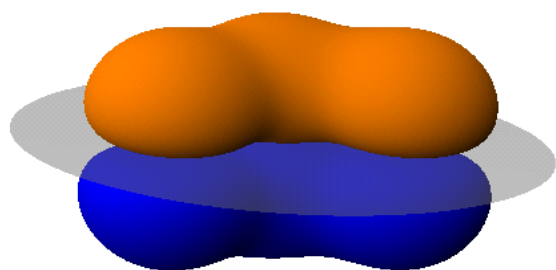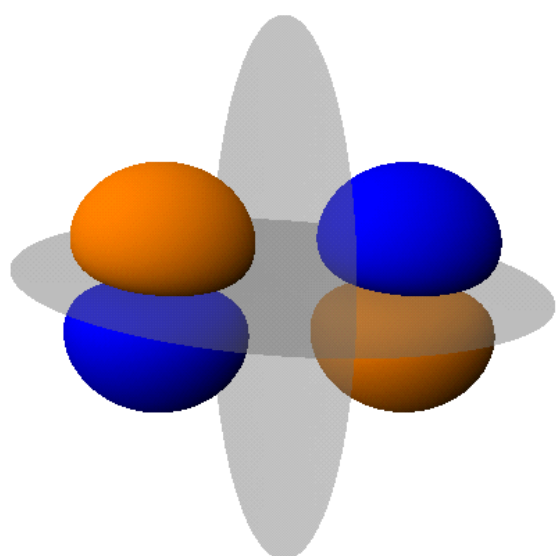

π electron density of O_3

Pi MOs of Ozone, O_3

U   The three $2p$ orbitals perpendicular to the molecular plane combine to form three π MOs:
    1. π – bonding MO
    2. π^n – nonbonding MO
    3. π^* – antibonding MO

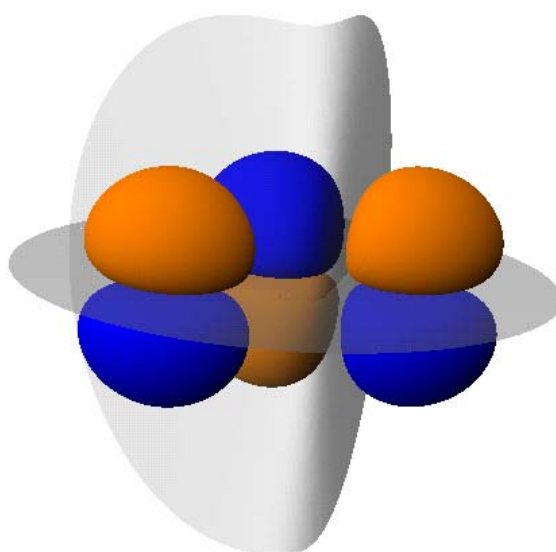U   A non-bonding MO neither builds nor destroys bonding between the oxygen atoms.

Pi MOs of Ozone, O₃
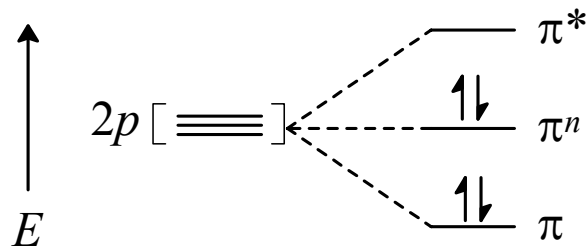
π (bonding)

π^n (nonbonding)

π^* (antibonding)

Pi MO Energy Level Scheme for O_3

U   The π system has two pairs of electrons, one pair in the π MO, and the other in the π^n non-bonding MO.

$$2p\,[\,\overline{\overline{\overline{}}}\,] \longleftarrow \begin{array}{c} \underline{} \quad \pi^* \\[4pt] \underline{\uparrow\!\downarrow} \quad \pi^n \\[4pt] \underline{\uparrow\!\downarrow} \quad \pi \end{array}$$

E

U   The configuration $(\pi)^2$ adds a bond order of 1 across the two O–O bonds (i.e., 0.5 to each bond).

U   When this is added to the sigma bond between each oxygen pair, the O–O bond order becomes 1.5.

U   The configuration $(\pi^n)^2$ neither adds nor subtracts from the overall strength of the bonds.

Pi MOs of Benzene, C_6H_6
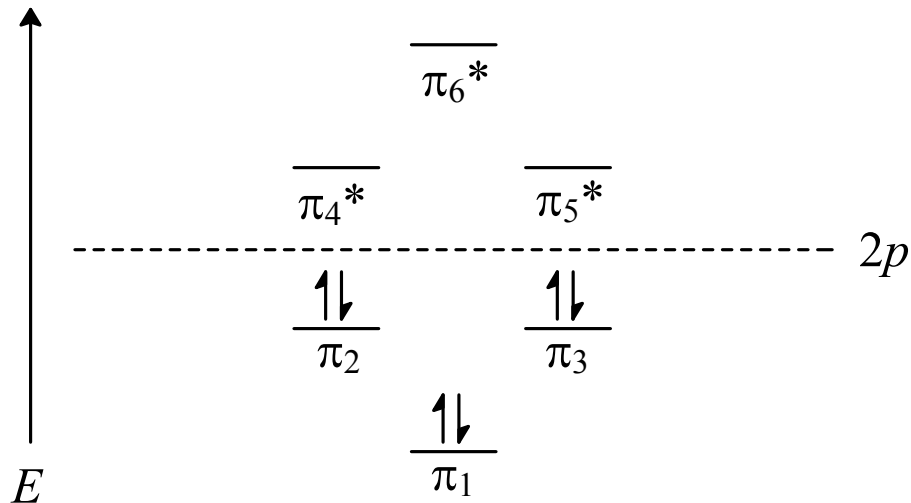
U C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.
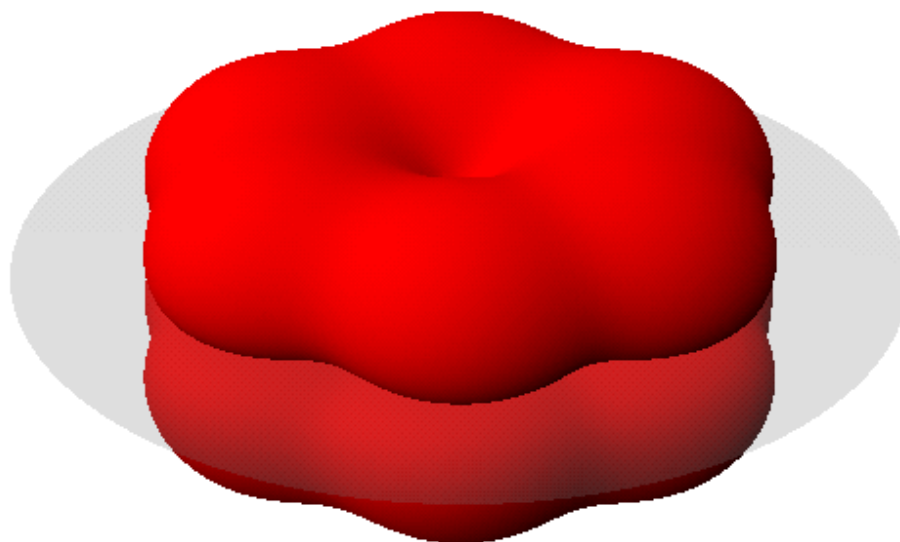
π electron density of benzene

U   The six $2p$ orbitals perpendicular to the ring on the six carbon atoms combine to form three bonding (π_1, π_2, π_3) and three antibonding (π_4^*, π_5^*, π_6^*) MOs.

Pi MO Energy Level Scheme for Benzene, C_6H_6

$$\overline{}\ \pi_6{}^*$$

$$\overline{}\ \pi_4{}^* \qquad \overline{}\ \pi_5{}^*$$

- $2p$

$$\underline{\uparrow\downarrow} \qquad \underline{\uparrow\downarrow}$$
$$\pi_2 \qquad\qquad \pi_3$$
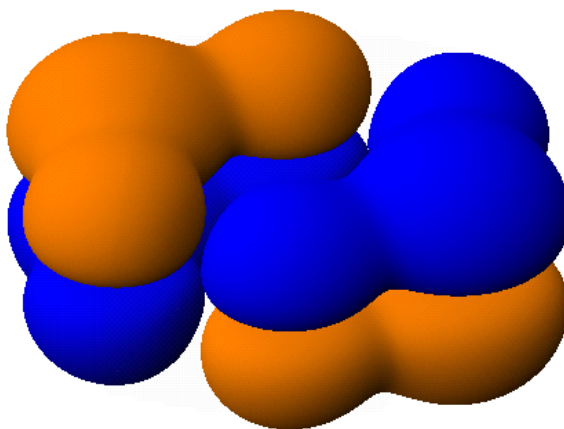
$$\underline{\uparrow\downarrow}$$
$$\pi_1$$

E

U Three pairs in bonding MOs add a total of three bond orders over six C–C linkages, or 0.5 for each.

U When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.
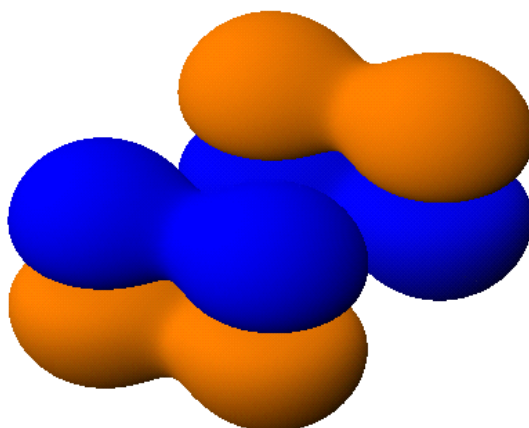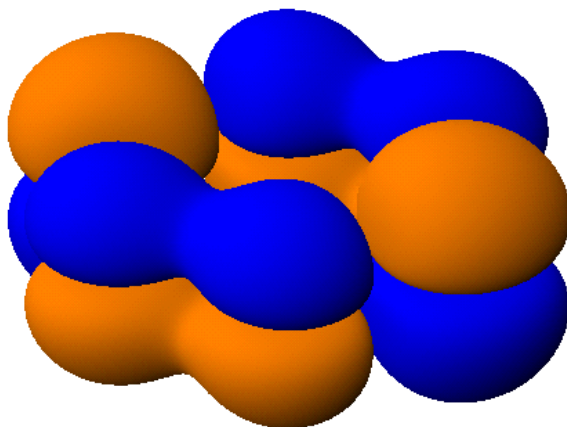
Occupied Bonding π MOs of Benzene, C₆H₆

π_1
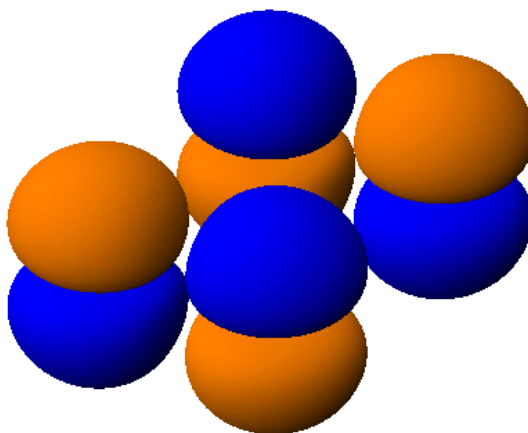
π_2
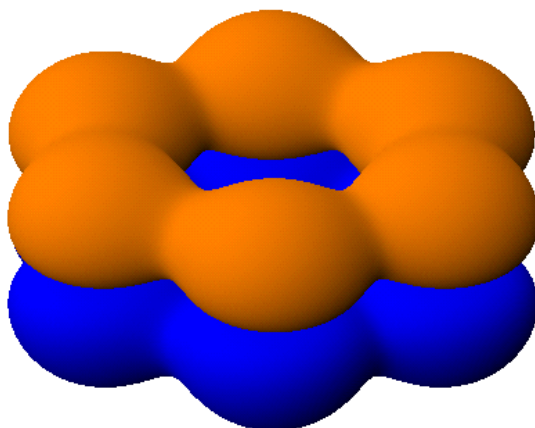
π_3

Unoccupied Antibonding π* MOs of Benzene, C₆H₆

π_4^*

π_5^*

π_6^*