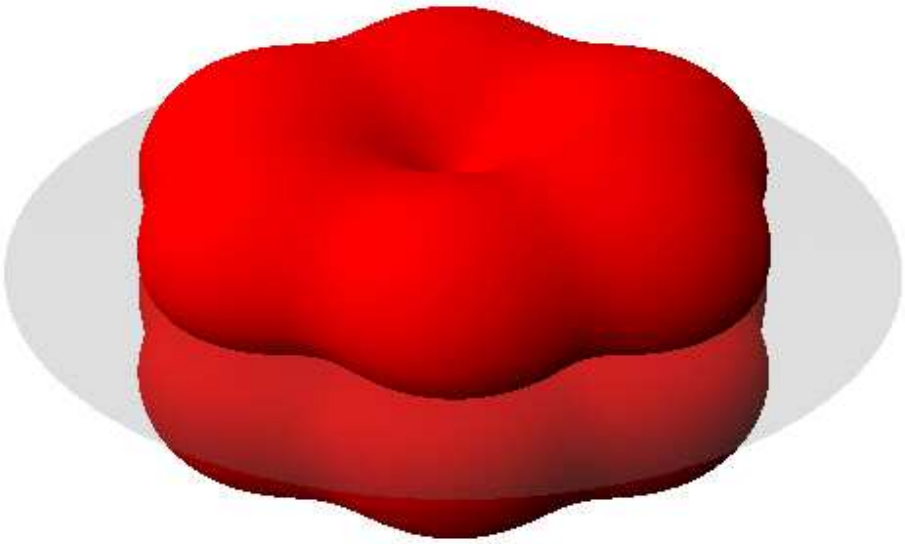
Pi MOs of Benzene, C_6H_6

- ✔ C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.

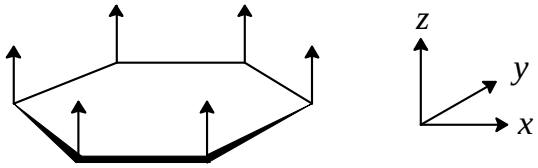


π electron density of benzene

- ✔ The six 2*p* 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 MOs of Benzene

✔ The symmetries and forms of these MOs can be deduced by applying the operations of the point group D_{6h} to a set of six vectors perpendicular to the ring, one at each carbon, to generate a reducible representation Γ_π.



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

$$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$$

Equations for Pi MOs of C_6H_6

a_{2u}: $$\pi_1 = \frac{1}{\sqrt{6}}(\varphi_a + \varphi_b + \varphi_c + \varphi_d + \varphi_e + \varphi_f)$$

$e_{1g:}$: $$\pi_2 = \frac{1}{2\sqrt{3}}(2\varphi_a + \varphi_b - \varphi_c - 2\varphi_d - \varphi_e + \varphi_f)$$

e_{1g}: $$\pi_3 = \frac{1}{2}(\varphi_b + \varphi_c - \varphi_e - \varphi_f)$$

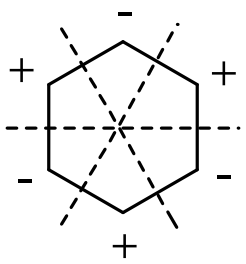
e_{2u}: $$\pi_4^* = \frac{1}{2\sqrt{3}}(2\varphi_a - \varphi_b - \varphi_c + 2\varphi_d - \varphi_e - \varphi_f)$$

e_{2u}: $$\pi_5^* = \frac{1}{2}(-\varphi_b + \varphi_c - \varphi_e + \varphi_f)$$

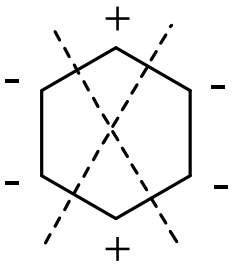
b_{2g}: $$\pi_6^* = \frac{1}{\sqrt{6}}(\varphi_a - \varphi_b + \varphi_c - \varphi_d + \varphi_e - \varphi_f)$$

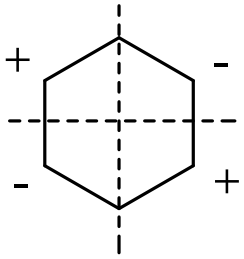
★ As we will see (Chapter 5), the mathematical forms of these MOs can be generated "automatically" by applying symmetry-based functions, called projection operators, to a single $2p_z$ wave function on one carbon in the ring.

Nodal Planes of π and π* MOs of Benzene

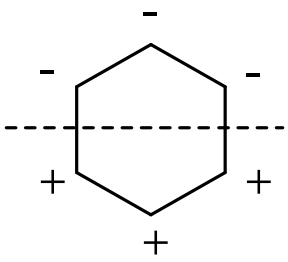


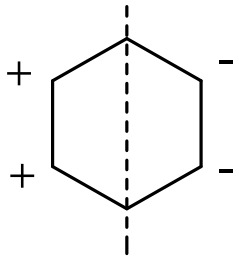
π_6^* (b_{2g})



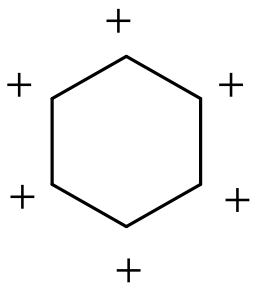


π_4^* (e_{2u}) π_5^*





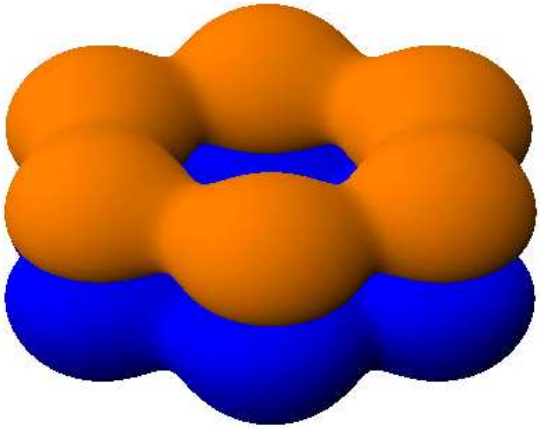
π_2 (e_{1g}) π_3



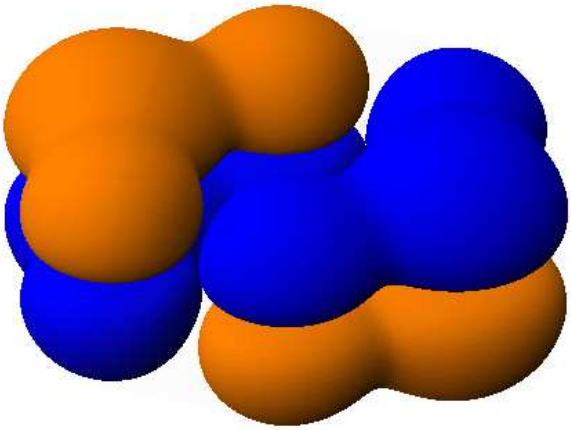
π_1 (a_{2u})

Occupied Bonding π MOs of Benzene, C_6H_6

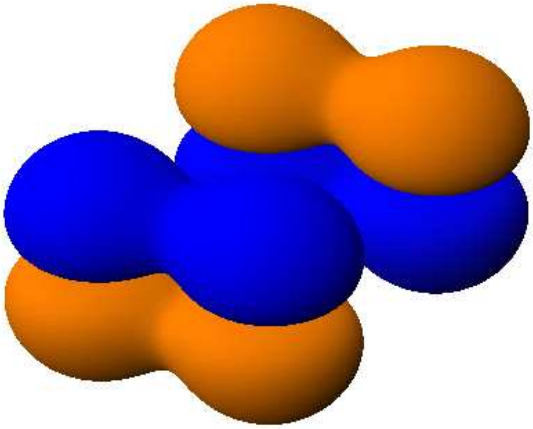
$\boldsymbol{\pi_1}$ (a_{2u})



$\boldsymbol{\pi_2}$ (e_{1g})

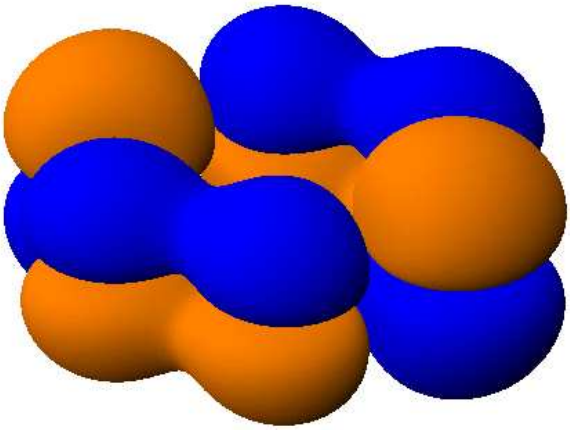


$\boldsymbol{\pi_3}$ (e_{1g})

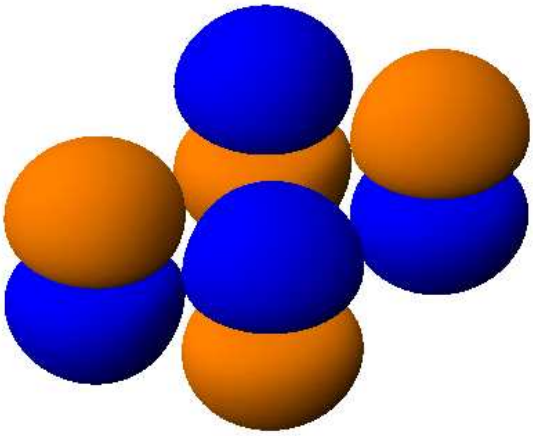


Unoccupied Antibonding π* MOs of Benzene, C_6H_6

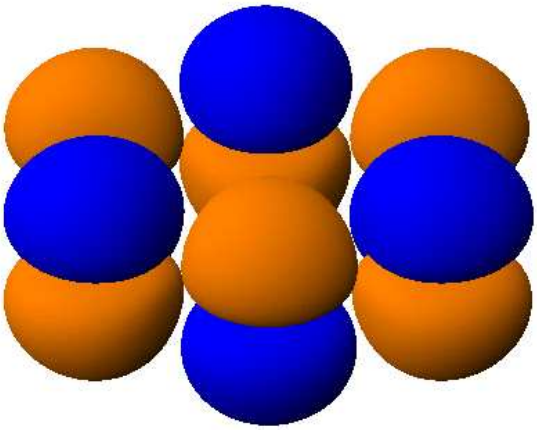
$\boldsymbol{\pi_4^*}$ (e_{2u})



$\boldsymbol{\pi_5^*}$ (e_{2u})

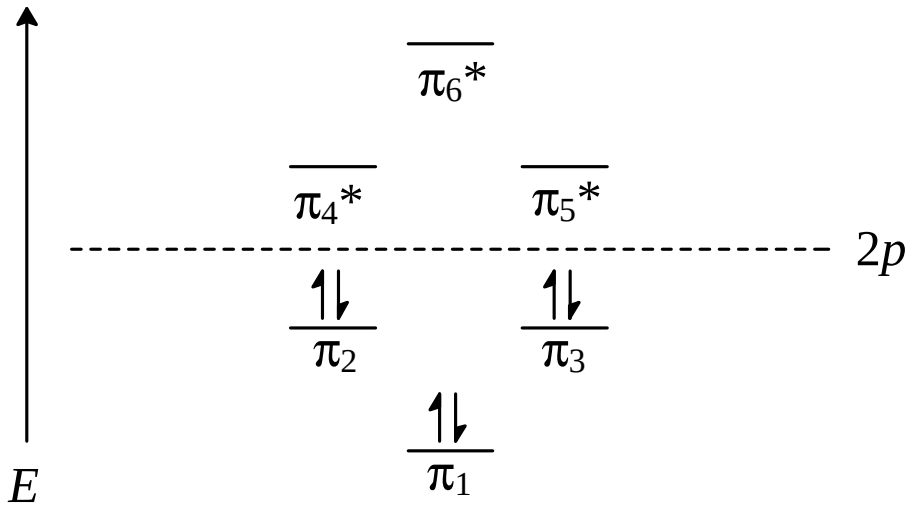


$\boldsymbol{\pi_6^*}$ (b_{2g})



Pi MO Energy Level Scheme for Benzene, C_6H_6

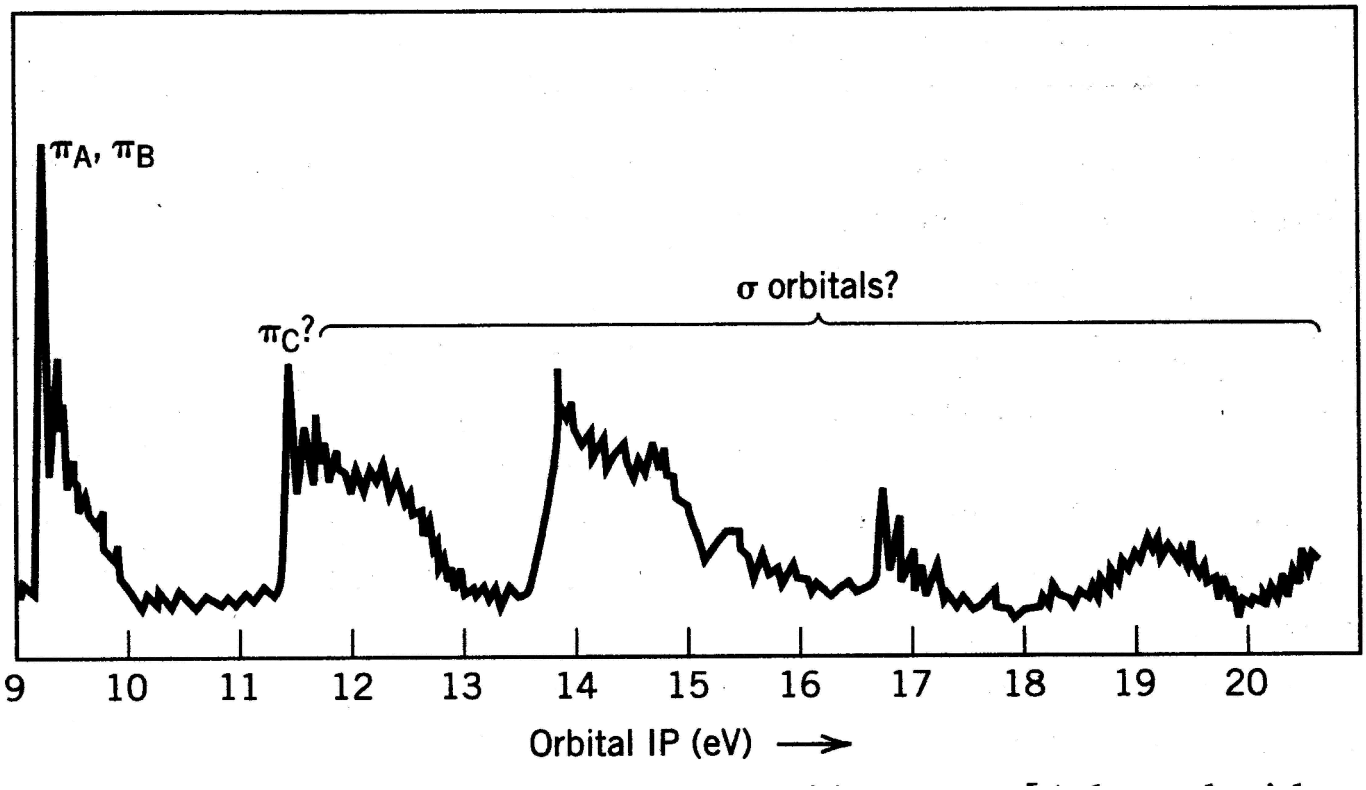
☞ By the "shadow method" we can anticipate that the pi-MO scheme will look like the following:



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

✔ When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.

P.E.S. of Benzene



✔ The P.E.S. of benzene is consistent with the bonding MO scheme.