Pi MOs of Benzene, C₆H₆

✔ C₆H₆, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.

π electron density of benzene

✔ The six 2p orbitals perpendicular to the ring on the six carbon atoms combine to form three bonding (π₁, π₂, π₃) and three antibonding (π₄*, π₅*, π₆*) 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 $\Gamma_\pi$.

\[
\begin{array}{cccccccccccc}
D_{6h} & E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \\
\Gamma_\pi & 6 & 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & -6 & 0 & 2 \\
\end{array}
\]

\[\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}\]
Equations for Pi MOs of \( \text{C}_6\text{H}_6 \)

\( a_{2u}: \) \[
\pi_1 = \frac{1}{\sqrt{6}} (\phi_a + \phi_b + \phi_c + \phi_d + \phi_e + \phi_f)
\]

\( e_{1g}: \) \[
\pi_2 = \frac{1}{2\sqrt{3}} (2\phi_a + \phi_b - \phi_c - 2\phi_d - \phi_e + \phi_f)
\]

\( e_{1g}: \) \[
\pi_3 = \frac{1}{2} (\phi_b + \phi_c - \phi_e - \phi_f)
\]

\( e_{2u}: \) \[
\pi_4^* = \frac{1}{2\sqrt{3}} (2\phi_a - \phi_b - \phi_c + 2\phi_d - \phi_e - \phi_f)
\]

\( e_{2u}: \) \[
\pi_5^* = \frac{1}{2} (-\phi_b + \phi_c - \phi_e + \phi_f)
\]

\( b_{2g}: \) \[
\pi_6^* = \frac{1}{\sqrt{6}} (\phi_a - \phi_b + \phi_c - \phi_d + \phi_e - \phi_f)
\]

★ 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 $\pi$ and $\pi^*$ MOs of Benzene

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

$\pi_4^*$ ($e_{2u}$) $\pi_5^*$ ($e_{1g}$) $\pi_3$

$\pi_2$

$\pi_1$ ($a_{2u}$)
Occupied Bonding $\pi$ MOs of Benzene, $C_6H_6$

$\pi_1 (a_{2u})$

$\pi_2 (e_{1g})$

$\pi_3 (e_{1g})$
Unoccupied Antibonding $\pi^*$ MOs of Benzene, $\text{C}_6\text{H}_6$

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

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

$\pi_6^* (b_{2g})$
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.
The P.E.S. of benzene is consistent with the bonding MO scheme.