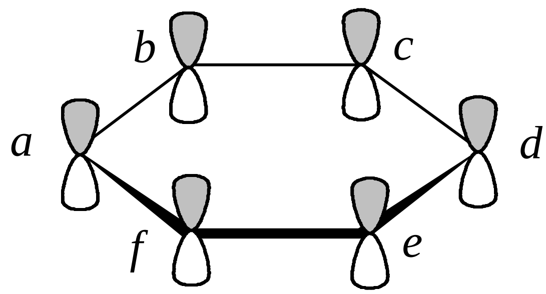
π-MOs of Benzene



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

✔ D_{6h} has h = 24, meaning that there are twenty-four terms in each projection operator. To save labor, do the work in C_6, for which h = 6.

Correlation Betwen D_{6h} and C_6

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	C_6
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	A
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	B
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$\{E_1\}$
E_{2u}	2	-1	-1	1	0	0	-2	1	1	-2	0	0	$\{E_2\}$

Advantages of working in C_6:

- Fewer terms in the projection operator.
- Differentiation among species preserved.
- Correlation with D_{6h} is obvious.
- Double degeneracies lifted, allowing separate generation of paired degenerate functions.

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5
E_1^a	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*
E_1^b	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε
E_2^a	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$
E_2^b	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$

$\varepsilon = \exp(2\pi i/6)$

The *A* and *B* SALCs

C_6	E	C_6	C_3	C_2	$C_3^{\,2}$	$C_6^{\,5}$
$R_j\varphi_a$	φ_a	φ_b	φ_c	φ_d	φ_e	φ_f
A	1	1	1	1	1	1
$\chi_i R_j\varphi_a$	φ_a	φ_b	φ_c	φ_d	φ_e	φ_f

$$\Rightarrow \Pi(A) = 1/\sqrt{6}(\varphi_a + \varphi_b + \varphi_c + \varphi_d + \varphi_e + \varphi_f) = \pi_1$$

C_6	E	C_6	C_3	C_2	$C_3^{\,2}$	$C_6^{\,5}$
$R_j\varphi_a$	φ_a	φ_b	φ_c	φ_d	φ_e	φ_f
B	1	–1	1	–1	1	–1
$\chi_i R_j\varphi_a$	φ_a	$-\varphi_b$	φ_c	$-\varphi_d$	φ_e	$-\varphi_f$

$$\Rightarrow \Pi(B) = 1/\sqrt{6}(\varphi_a - \varphi_b + \varphi_c - \varphi_d + \varphi_e - \varphi_f) = \pi_6^*$$

☞ Note: Both have the form

$$\chi_1^{\,i}\varphi_a + \chi_2^{\,i}\varphi_b + \chi_3^{\,i}\varphi_c + \chi_4^{\,i}\varphi_d + \chi_5^{\,i}\varphi_e + \chi_6^{\,i}\varphi_f$$

where the coefficients χ^i_1, χ^i_2, ..., χ^i_6 are the six successive characters of the *i*th irreducible representation of C_6.

☺ **Simply read off the forms of the nondegenerate SALCs from the characters of their irreducible representations.** (Works for any planar system in the appropriate rotational group C_n.)

Projections for the Degenerate SALCs

✔ From reading the characters of the irreducible representations:

$$P(E_1{}^a)\varphi_a \propto (\varphi_a + \varepsilon\varphi_b - \varepsilon^*\varphi_c - \varphi_d - \varepsilon\varphi_e + \varepsilon^*\varphi_f)$$

$$P(E_1{}^b)\varphi_a \propto (\varphi_a + \varepsilon^*\varphi_b - \varepsilon\varphi_c - \varphi_d - \varepsilon^*\varphi_e + \varepsilon\varphi_f)$$

$$P(E_2{}^a)\varphi_a \propto (\varphi_a - \varepsilon^*\varphi_b - \varepsilon\varphi_c + \varphi_d - \varepsilon^*\varphi_e - \varepsilon\varphi_f)$$

$$P(E_2{}^b)\varphi_a \propto (\varphi_a - \varepsilon\varphi_b - \varepsilon^*\varphi_c + \varphi_d - \varepsilon\varphi_e - \varepsilon^*\varphi_f)$$

✔ Make real functions from these imaginary pairs by adding and subtracting each pair, making use of the following relationships.

$$\varepsilon + \varepsilon^* = \left(\cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6}\right) + \left(\cos\frac{2\pi}{6} - i\sin\frac{2\pi}{6}\right) = 2\cos\frac{2\pi}{6} = 2(½) = 1$$

$$\varepsilon - \varepsilon^* = \left(\cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6}\right) - \left(\cos\frac{2\pi}{6} - i\sin\frac{2\pi}{6}\right) = 2i\sin\frac{2\pi}{6} = 2i\left(\frac{\sqrt{3}}{2}\right) = i\sqrt{3}$$

Real-Number Degenerate SALCs - The E_1 Pair

✔ Adding the two imaginary functions for E_1 gives

$$P(E_1^{a})\varphi_a + P(E_1^{b})\varphi_a \propto$$
$$2\varphi_a + (\varepsilon + \varepsilon^*)\varphi_b - (\varepsilon + \varepsilon^*)\varphi_c - 2\varphi_d - (\varepsilon + \varepsilon^*)\varphi_e + (\varepsilon + \varepsilon^*)\varphi_f \propto$$
$$2\varphi_a + \varphi_b - \varphi_c - 2\varphi_d - \varphi_e + \varphi_f$$

☞ After normalization we obtain

$$\Pi(E_1^{\alpha}) = 1/(2\sqrt{3})\{2\varphi_a + \varphi_b - \varphi_c - 2\varphi_d - \varphi_e + \varphi_f\} = \pi_2$$

✔ Subtracting the two imaginary functions for E_1, remembering that $\varepsilon - \varepsilon^* = i\sqrt{3}$, gives

$$P(E_1^{a})\varphi_a - P(E_1^{b})\varphi_a \propto$$
$$i\sqrt{3}(0 + \varphi_b + \varphi_c + 0 - \varphi_e - \varphi_f) \propto$$
$$i\sqrt{3}(\varphi_b + \varphi_c - \varphi_e - \varphi_f)$$

Factor out $i\sqrt{3}$ prior to normalization.

☞ After normalization we obtain

$$\Pi(E_1^{\beta}) = ½\{\varphi_b + \varphi_c - \varphi_e - \varphi_f\} = \pi_3$$

Real-Number Degenerate SALCs - The E_2 Pair

✔ Do the same for the E_2 pair:

$$P(E_2{}^a)\varphi_a + P(E_2{}^b)\varphi_a \propto$$
$$\{2\varphi_a - (\varepsilon+\varepsilon^*)\varphi_b - (\varepsilon+\varepsilon^*)\varphi_c + 2\varphi_d - (\varepsilon+\varepsilon^*)\varphi_e - (\varepsilon+\varepsilon^*)\varphi_f\} \propto$$
$$2\varphi_a - \varphi_b - \varphi_c + 2\varphi_d - \varphi_e - \varphi_f$$

$$P(E_2{}^a)\varphi_a - P(E_2{}^b)\varphi_a \propto$$
$$\{0 - (\varepsilon-\varepsilon^*)\varphi_b + (\varepsilon-\varepsilon^*)\varphi_c + 0 - (\varepsilon-\varepsilon^*)\varphi_e + (\varepsilon-\varepsilon^*)\varphi_f\} \propto$$
$$\propto -\varphi_b + \varphi_c - \varphi_e + \varphi_f$$

☞ After normalization these yield

$$\Pi(E_2{}^\alpha) = 1/(2\sqrt{3})\{2\varphi_a - \varphi_b - \varphi_c + 2\varphi_d - \varphi_e - \varphi_f\} = \pi_4{}^*$$

$$\Pi(E_2{}^\beta) = ½\{-\varphi_b + \varphi_c - \varphi_e + \varphi_f\} = \pi_5{}^*$$

General Procedure for Degenerate SALCs of Planar D_{nh} Systems

1. Write down an initial set of SALCs by inspecting the character table C_n, which is a subgroup of the molecule's point group D_{nh}. These SALCs will have the form $\chi_1^i\varphi_1 + \chi_2^i\varphi_2 \ldots + \chi_n^i\varphi_n$, where $\chi_1^i, \chi_2^i, \ldots \chi_n^i$ are the characters of the *i*th irreducible representation of the representation Γ_π in the group C_n.

2. Make real functions for pairs of complex conjugate SALCs by adding and subtracting the imaginary functions. Factor out any overall coefficients containing *i* prior to normalization.

3. Normalize the functions.

☞ This method can also be applied to obtain the π-SALCs of pendant atoms in planar MX_n molecules with D_{nh} symmetry.