\( \pi \)-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 Between $D_{6h}$ and $C_6$

<table>
<thead>
<tr>
<th>$D_{6h}$</th>
<th>$E$</th>
<th>$2C_6$</th>
<th>$2C_3$</th>
<th>$C_2$</th>
<th>$3C_2'$</th>
<th>$3C_2''$</th>
<th>$i$</th>
<th>$2S_3$</th>
<th>$2S_6$</th>
<th>$\sigma_h$</th>
<th>$3\sigma_d$</th>
<th>$3\sigma_v$</th>
<th>$C_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_{1g}$</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{2u}$</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 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.

### Table

<table>
<thead>
<tr>
<th>$C_6$</th>
<th>$E$</th>
<th>$C_6$</th>
<th>$C_3$</th>
<th>$C_2$</th>
<th>$C_3^2$</th>
<th>$C_6^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1^a$</td>
<td>1</td>
<td>$\varepsilon$</td>
<td>-$\varepsilon^*$</td>
<td>-1</td>
<td>-$\varepsilon$</td>
<td>$\varepsilon^*$</td>
</tr>
<tr>
<td>$E_1^b$</td>
<td>1</td>
<td>$\varepsilon^*$</td>
<td>-$\varepsilon$</td>
<td>-1</td>
<td>-$\varepsilon^*$</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$E_2^a$</td>
<td>1</td>
<td>-$\varepsilon^*$</td>
<td>-$\varepsilon$</td>
<td>1</td>
<td>-$\varepsilon^*$</td>
<td>-$\varepsilon$</td>
</tr>
<tr>
<td>$E_2^b$</td>
<td>1</td>
<td>-$\varepsilon$</td>
<td>-$\varepsilon^*$</td>
<td>1</td>
<td>-$\varepsilon$</td>
<td>-$\varepsilon^*$</td>
</tr>
</tbody>
</table>

$\varepsilon = \exp(2\pi i/6)$
The \(A\) and \(B\) SALCs

<table>
<thead>
<tr>
<th>(C_6)</th>
<th>(E)</th>
<th>(C_6)</th>
<th>(C_3)</th>
<th>(C_2)</th>
<th>(C_3^2)</th>
<th>(C_6^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_f\phi_a)</td>
<td>(\phi_a)</td>
<td>(\phi_b)</td>
<td>(\phi_c)</td>
<td>(\phi_d)</td>
<td>(\phi_e)</td>
<td>(\phi_f)</td>
</tr>
<tr>
<td>(A)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\chi^a R_f\phi_a)</td>
<td>(\phi_a)</td>
<td>(\phi_b)</td>
<td>(\phi_c)</td>
<td>(\phi_d)</td>
<td>(\phi_e)</td>
<td>(\phi_f)</td>
</tr>
</tbody>
</table>

\[\Pi(A) = 1/\sqrt{6}(\phi_a + \phi_b + \phi_c + \phi_d + \phi_e + \phi_f) = \pi_1\]

<table>
<thead>
<tr>
<th>(C_6)</th>
<th>(E)</th>
<th>(C_6)</th>
<th>(C_3)</th>
<th>(C_2)</th>
<th>(C_3^2)</th>
<th>(C_6^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_f\phi_a)</td>
<td>(\phi_a)</td>
<td>(\phi_b)</td>
<td>(\phi_c)</td>
<td>(\phi_d)</td>
<td>(\phi_e)</td>
<td>(\phi_f)</td>
</tr>
<tr>
<td>(B)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(\chi^a R_f\phi_a)</td>
<td>(\phi_a)</td>
<td>(-\phi_b)</td>
<td>(\phi_c)</td>
<td>(-\phi_d)</td>
<td>(\phi_e)</td>
<td>(-\phi_f)</td>
</tr>
</tbody>
</table>

\[\Pi(B) = 1/\sqrt{6}(\phi_a - \phi_b + \phi_c - \phi_d + \phi_e - \phi_f) = \pi_6^*\]

Note: Both have the form

\[\chi_1^i \phi_a + \chi_2^i \phi_b + \chi_3^i \phi_c + \chi_4^i \phi_d + \chi_5^i \phi_e + \chi_6^i \phi_f\]

where the coefficients \(\chi_1^i, \chi_2^i, \ldots, \chi_6^i\) 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.

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

\[
\varepsilon - \varepsilon^* = \left(\cos \frac{2\pi}{6} + i\sin \frac{2\pi}{6}\right) - \left(\cos \frac{2\pi}{6} - i\sin \frac{2\pi}{6}\right) = 2i\sin \frac{2\pi}{6} = 2i\left(\frac{\sqrt{3}}{2}\right) = i\sqrt{3}
\]
Real-Number Degenerate SALCs - The $E_1$ Pair

Adding the two imaginary functions for $E_1$ gives

\[
P(E_1^a)\phi_a + P(E_1^b)\phi_a \propto \\
2\phi_a + (\varepsilon + \varepsilon^*)\phi_b - (\varepsilon + \varepsilon^*)\phi_c - 2\phi_d - (\varepsilon + \varepsilon^*)\phi_e + (\varepsilon + \varepsilon^*)\phi_f \propto \\
2\phi_a + \phi_b - \phi_c - 2\phi_d - \phi_e + \phi_f
\]

After normalization we obtain

\[
\Pi(E_1^a) = 1/(2\sqrt{3})\{2\phi_a + \phi_b - \phi_c - 2\phi_d - \phi_e + \phi_f\} = \pi_2
\]

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

\[
P(E_1^a)\phi_a - P(E_1^b)\phi_a \propto \\
i\sqrt{3}(0 + \phi_b + \phi_c + 0 - \phi_e - \phi_f) \propto \\
i\sqrt{3}(\phi_b + \phi_c - \phi_e - \phi_f)
\]

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

After normalization we obtain

\[
\Pi(E_1^b) = \frac{1}{2}\{\phi_b + \phi_c - \phi_e - \phi_f\} = \pi_3
\]
Real-Number Degenerate SALCs - The $E_2$ Pair

Do the same for the $E_2$ pair:

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

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

After normalization these yield

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

\[
\Pi(E_2^\beta) = 1/2\{-\varphi_b + \varphi_c - \varphi_e + \varphi_f \} = \pi_5^*
\]
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 $\chi_1^i \phi_1 + \chi_2^i \phi_2 + ... + \chi_n^i \phi_n$, where $\chi_1^i, \chi_2^i, ... \chi_n^i$ are the characters of the $i$th irreducible representation of the representation $\Gamma_\pi$ 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 $\pi$-SALCs of pendant atoms in planar MX$_n$ molecules with $D_{nh}$ symmetry.