General MOs for CH$_4$

The four pendant H atoms in their sigma interactions with central C AOs can be represented by a set of four tetrahedrally oriented vectors point toward the center of a cube.

Counting nonshifted vectors after applying a representative operation from each class yields the following reducible representation:

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{SALC}$</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

$\Rightarrow A_1 + T_2$
Forming the Hydrogen SALCs

The following SALC equations have the requisite symmetries:

\[ A_1: \quad \Phi_1 = \frac{1}{2} \{1s_A + 1s_B + 1s_C + 1s_D\} \]

\[ T_2: \quad \Phi_2 = \frac{1}{2} \{1s_A + 1s_B - 1s_C - 1s_D\} \]
\[ \Phi_3 = \frac{1}{2} \{1s_A - 1s_B - 1s_C + 1s_D\} \]
\[ \Phi_4 = \frac{1}{2} \{1s_A - 1s_B + 1s_C - 1s_D\} \]

Carbon AO Symmetries

From vector transformation properties listed in the \( T_d \) character table:

\[ s = A_1 \quad (p_x, p_y, p_z) = T_2 \]

Assuming 1s orbital on C is nonbonding, LCAOs are formed between 2s and 2p AOs on C with the four SALCs defined above.
Representations of Bonding LCAO-MOs of CH₄

$\sigma_2$

$A_1$

$\sigma_3$

$\sigma_4$

$\sigma_5$

$T_2$
LCAO MO Equations for CH$_4$

$\sigma_1'' = c_0(1s)$  \hspace{1cm} \text{nonbonding core ($a_1$)}$

$a_1$ MOs:

$\sigma_2 = c_1(2s) + c_2 \Phi_1$  \hspace{1cm} \text{bonding}$

$\sigma_6^* = c_3(2s) - c_4 \Phi_1$  \hspace{1cm} \text{antibonding}$

$t_2$ MOs:

$\sigma_3 = c_5(2p_z) + c_6 \Phi_2$  \hspace{1cm} \text{bonding}$

$\sigma_7^* = c_7(2p_z) - c_8 \Phi_2$  \hspace{1cm} \text{antibonding}$

$\sigma_4 = c_9(2p_y) + c_{10} \Phi_3$  \hspace{1cm} \text{bonding}$

$\sigma_8^* = c_{11}(2p_y) - c_{12} \Phi_3$  \hspace{1cm} \text{antibonding}$

$\sigma_5 = c_{13}(2p_x) + c_{14} \Phi_4$  \hspace{1cm} \text{bonding}$

$\sigma_9^* = c_{15}(2p_x) - c_{16} \Phi_4$  \hspace{1cm} \text{antibonding}$
Qualitative MO Scheme for CH₄

C

CH₄

4 H (SALCs)

[2p₂, 2p₂, 2p₂, 2p₂]

[σ₂*]

[σ₁*]

[σ₃*]

[σ₄*]

[1½]

[1½]

[1½]

[1½]

[2s]

[a₁]

[1s]

[a₁ (core)]
Photoelectron Spectrum of CH$_4$

$\begin{align*}
\text{t}_2^6 & \\
\downarrow & \\
\text{a}_1^2 & \\
\downarrow & \\
\end{align*}$

\(\text{IE}(\text{eV})\)}