Coefficients of Butadiene Orbitals Using Kramer's Rule

Rule: The ratio of the coefficients = ratio of the corresponding minors

The secular determinant is:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \qquad \text{for } \Psi_i = c_{iA}\, p_{zA} + c_{iB}\, p_{zB} + c_{iC}\, p_{zC} + c_{iD}\, p_{zD} \qquad i = 1 \ldots 4$$

You can only find the ratio of coefficients. So for convenience find the ratio with respect to c_{iA}. For example, expand the minors for the first row:

$$\frac{c_{iB}}{c_{iA}} = \frac{-\begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{-(x^2-1)}{x^3-2x}$$

Use for each of the MO's in turn.

For the most bonding orbital, Ψ_1:

$x = -1.618 \qquad \dfrac{c_{1B}}{c_{1A}} = \dfrac{-1.618}{-1} = 1.618$

$$\frac{c_{iC}}{c_{iA}} = \frac{\begin{vmatrix} 1 & x & 0 \\ 0 & 1 & 1 \\ 0 & 0 & x \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{x}{x^3-2x}$$

for Ψ_1, $\qquad \dfrac{c_{1C}}{c_{1A}} = 1.618$

$$\frac{c_{iD}}{c_{iA}} = \frac{-\begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 0 & 0 & 1 \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{-1}{x^3-2x}$$

for Ψ_1 $\qquad \dfrac{c_{1D}}{c_{1A}} = 1$

For normalization, let $c_{1A} = N$ then $\Psi_1 = N\,(p_{zA} + 1.618\, p_{zB} + 1.618\, p_{zC} + p_{zD})$

$\int \Psi_1^*\Psi_1\, d\tau = N^2 \left[\int p_{zA}^2\, d\tau + 1.618^2 \int p_{zB}^2\, d\tau + 1.618^2 \int p_{zC}^2\, d\tau + \int p_{zD}^2\, d\tau \right] = 1$

Because cross terms like $\int p_{zA}\, p_{zB}\, d\tau = S_{AB} = 0$ in the Hückel approximation.

The p orbitals are normalized so $\int p_{zA}^2\, d\tau = \int p_{zB}^2\, d\tau = \int p_{zC}^2\, d\tau = \int p_{zD}^2\, d\tau = 1$

$\int \Psi_1^*\Psi_1\, d\tau = N^2 \left[1 + 1.618^2 + 1.618^2 + 1 \right] = 1 \qquad$ giving $N = 0.372$

$\Psi_1 = 0.372\, p_{zA} + 0.602\, p_{zB} + 0.602\, p_{zC} + 0.372\, p_{zD}$