

**Problem #7, 10 points, McQuarrie and Simon: Chapter 12, Problem 28 + Extra.**

Given the four symmetry orbitals of butadiene:

$$\phi_1 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_4)$$

$$\phi_2 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3)$$

$$\phi_3 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_4)$$

$$\phi_4 = \frac{1}{\sqrt{2}}(\psi_2 + \psi_3)$$

Derive the Hückel theory secular determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - \beta - E & 0 & 0 \\ 0 & 0 & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha + \beta - E \end{vmatrix} = 0$$

Which, given the substitution  $x = \frac{\alpha - E}{\beta}$ , reduces to

$$(x^2 - x - 1)(x^2 + x - 1) = 0.$$

Use this expression to solve for the four values of  $x$ , which yield four values of  $E$ . Specify these values, and plot them on an energy diagram.

# Mcquarrie Problem 7

**Marco Casella**



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