

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

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Table of Contents Mcquarrie Problem 7

1. Understanding the eBook Mcquarrie Problem 7
 - The Rise of Digital Reading Mcquarrie Problem 7
 - Advantages of eBooks Over Traditional Books
2. Identifying Mcquarrie Problem 7
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Mcquarrie Problem 7
 - User-Friendly Interface
4. Exploring eBook Recommendations from Mcquarrie Problem 7
 - Personalized Recommendations
 - Mcquarrie Problem 7 User Reviews and Ratings
 - Mcquarrie Problem 7 and Bestseller Lists
5. Accessing Mcquarrie Problem 7 Free and Paid eBooks

- Mcquarrie Problem 7 Public Domain eBooks
- Mcquarrie Problem 7 eBook Subscription Services
- Mcquarrie Problem 7 Budget-Friendly Options
- 6. Navigating Mcquarrie Problem 7 eBook Formats
 - ePub, PDF, MOBI, and More
 - Mcquarrie Problem 7 Compatibility with Devices
 - Mcquarrie Problem 7 Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Mcquarrie Problem 7
 - Highlighting and Note-Taking Mcquarrie Problem 7
 - Interactive Elements Mcquarrie Problem 7
- 8. Staying Engaged with Mcquarrie Problem 7
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Mcquarrie Problem 7
- 9. Balancing eBooks and Physical Books Mcquarrie Problem 7
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Mcquarrie Problem 7
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Mcquarrie Problem 7
 - Setting Reading Goals Mcquarrie Problem 7
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Mcquarrie Problem 7
 - Fact-Checking eBook Content of Mcquarrie Problem 7
 - Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development

- Exploring Educational eBooks

14. Embracing eBook Trends

- Integration of Multimedia Elements
- Interactive and Gamified eBooks

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