

Homework H35 Solution

1. The basis of the Woodward – Hoffmann rules is that eigenvalues and eigenvectors are continuous functions of the distance R . In this problem, you will prove that the eigenvalues vary continuously. Use the online diagonalizer you used for previous homework, to diagonalize the matrix

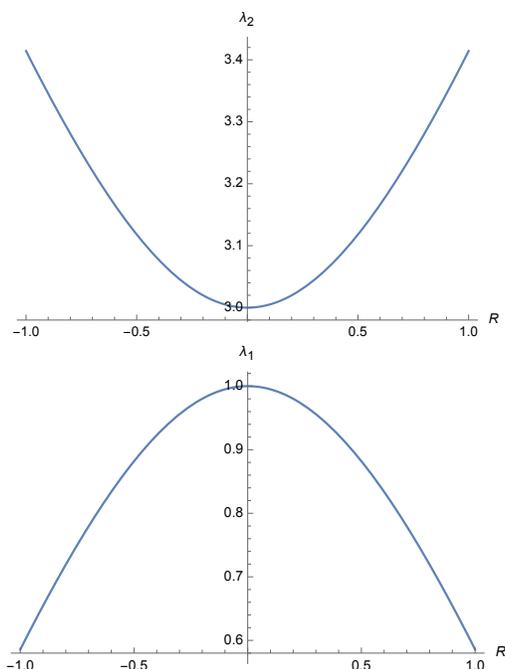
$$\begin{pmatrix} E - R & 1 \\ 1 & E + R \end{pmatrix}$$

for a range of values for $R = 1, 0.9, 0.8, \dots, -0.9, -1$. You can put in $E = 2$, and obtain a set of eigenvalues λ_1 and λ_2 for each value of R . Now plot these eigenvalues as a function of R to show that they are continuous functions.

Solution: Putting the value of $E = 2$, we diagonalize the matrix and find the eigenvalues in terms of R , to get,

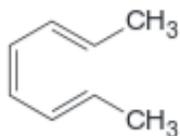
$$\begin{aligned} \lambda_2 &= 2 + \sqrt{1 + R^2} \\ \lambda_1 &= 2 - \sqrt{1 + R^2} \end{aligned}$$

Thus the eigenvalues vary with R as shown in the following plots:



This plot shows that the eigenvalues are continuous functions of the internuclear distance during bond formation. Note that the eigenvalues undergo a so-called “avoided crossing”: when the relative distance to the transition state is $R=0$ ($R<0$ is reactant, $R>0$ is product), the eigenvalues “repel” one another. If the off diagonal elements were 0 instead of 1, the eigenvalues would just cross through one another.

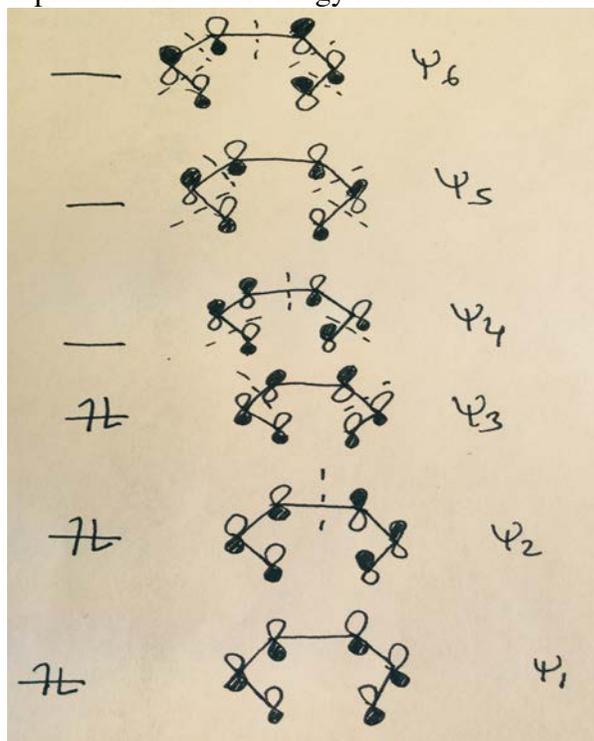
2. Draw the molecular orbital diagram (for 1 electron basis) for the electrocyclic ring closure reaction of the following molecule.



Show that the opposite happens compared to the cyclobutene case we did in class: with heat, both methyl groups end up pointing together, and with light, they point in opposite directions. [Hint : The reaction is controlled by the ‘frontier molecular orbital,’ which is the HOMO for this reaction. The +/- symmetry of the p basis functions making up the HOMO is different than for cyclobutene.]

Solution:

Note that even though this molecule looks similar to benzene, the molecular orbitals aren't exactly similar due to the lack of the ring symmetry. The easiest way to form the MOs is to realize that the number of nodes in ψ_n is $n - 1$. Thus ψ_1 has 0 nodes, and so on. Of course the separation between energy levels aren't drawn to scale.



As can be seen from the orbital energy diagram, ψ_3 is the HOMO of the molecule, in which the terminal p_z orbitals (the ones on C_1 and C_6) +/- symmetric, that is, the +/- phases of the two orbitals are on the same direction.

Clearly, to form a bonding orbital between C_1 and C_6 , the orbitals have to rotate in opposite directions (dis-rotatory motion). This leads to both methyl groups pointing along the same direction (above or below the plane of the molecule), with heat.

Under photochemical condition, one electron is excited from ψ_3 to ψ_4 . Now, ψ_4 is the HOMO, which has the +/- symmetry of the p_z orbitals in the opposite direction. This clearly has to undergo con-rotatory motion to form a bonding overlap. This leads to the methyl groups pointing in opposite directions.