Chem 442: Homework for lecture L35

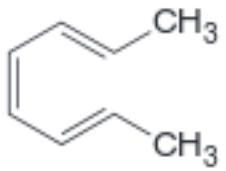
(only turn in **BOLD** assignment first lecture next week of classes; do <u>all</u> assignments)

1. Turn in 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 $R = 1, 0.9, 0.8, \ldots, -0.9, \ -1$. 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 of R.

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.]