Problem III.S ... quantum of orbital   10 points; průměr 10,53; řešilo 47 studentů

1. *Similarly to the series, use the Hückel method to create the Hamiltonian matrix for the cyclobutadiene molecule and verify that its eigenvalues are $\alpha + 2\beta$, α, α, $\alpha - 2\beta$. Sketch the diagram of the final energies in the resulting orbitals. And show how the electrons will occupy them. (4 b)*
   Bonus   What is the main difference in the characterics of these orbitals and their occupancy compared to a benzene molecule we showed in the series? What are the consequences for the cyclobutadiene molecule? (2 b)
2. *Try going back to the beta-carotene molecule and calculate again at what wavelength it should absorb using the Hückel method. What should the value of the parameter β be equal to in order to be consistent with the experimental result?*
   Alternative   If you encounter a problem with the diagonalisation of the hamiltonian, solve the problem statement with the hexa-1,3,5-triene molecule. The experimentally determined absorption value in this case is at a wavelength of 250 nm. (4 b)
3. *What happens to a molecule (a molecule with only simple bonds is sufficient) if we use UV light to excite an electron from the σ to the σ^* orbital? (2 b)*
                      Mikuláš gives presents again, this time at the right time of the year, almost.

1. For the cyclobutadiene molecule, we construct the hamiltonian matrix according to the same rules as for benzene. The result is a very similar matrix, just scaled down to 4×4.

$$\begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix}$$

We decompose it, as in the series, into

$$\alpha \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \beta \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}.$$

The eigenvalues of the second matrix are $0, 0, 2, -2$. Thus, the eigenvalues of the Hamiltonian matrix are $\alpha, \alpha, \alpha + 2\beta, \alpha - 2\beta$. (Many apologies for the error in the problem statement, which was brought to our attention by a participant.) We have four orbitals into which we need to place four electrons. The first two are clear, and we will occupy them to the lowest level with energy $\alpha + 2\beta$. (The parameters α and β are negative.) The remaining two electrons are more complex. These must be placed in two orbitals that have the same energy α. At the level of the Hückel model, it doesn't matter how we will fill these orbitals. Whether we put both electrons into one of the orbitals or each orbital will be filled by one electron. However, if we want to account for effects such as repulsion between electrons, which we neglect in the Hückel model, we must occupy the electrons according to Hund's rules. Thus, we place one electron at a time in each orbital so that the spins of both electrons point in the same direction. The occupation of the orbitals will look like the figure.

The main difference from the benzene molecule is that at the highest occupied level, we only have two electrons in the two orbitals of the same energy (not fully occupied). That
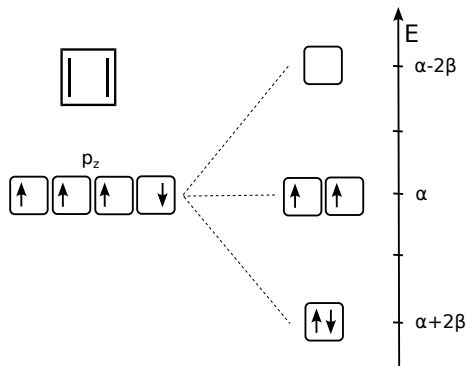
has some major implications. Firstly, the stabilization of delocalized π orbital is not the same as in benzene molecules, which is why cyclobutadiene does not behave as aromatic hydrocarbons. There is even a rule saying that for a cyclic hydrocarbon to be aromatic, it must have $4n+2$ π-electrons, where n is a natural number. At the same time, a specific geometric deformation of the molecule reduces the energy of one of the orbitals at the expense of increasing the other's energy. We can use that by occupying the orbital with reduced energy with two electrons and having lower total energy. In reality, the molecule of cyclobutadiene is not a square but rather a rectangle.

2. The Hamiltonian for $\beta - carotene$, given that we have 22 carbon atoms in the conjugated system, is a matrix of size 22×22. Despite its huge size, its shape is simple:

$$\mathbb{H} = \begin{pmatrix} \alpha & \beta & 0 & & 0 & 0 & 0 \\ \beta & \alpha & \beta & \dots & 0 & 0 & 0 \\ 0 & \beta & \alpha & & 0 & 0 & 0 \\ & \vdots & & \ddots & & \vdots & \\ 0 & 0 & 0 & & \alpha & \beta & 0 \\ 0 & 0 & 0 & \dots & \beta & \alpha & \beta \\ 0 & 0 & 0 & & 0 & \beta & \alpha \end{pmatrix}.$$

Diagonalizing the Hamiltonian gives a total of 22 eigenvalues. For us, the only significant ones are the 11th and 12th, in the order of magnitude, because they correspond to the orbitals between which the electron jumps during excitation. The energies of these orbitals are $\alpha+0.136\beta$ and $\alpha-0.136\beta$. The energy of the transition is -0.272β. If we substitute the value $\beta = -3\,\text{eV}$, we get a transition energy of approximately $0.816\,\text{eV}$, which corresponds to a wavelength of $1\,520\,\text{nm}$. That is even worse than the result from the last episode with the infinite potential pit, which gave us $1\,240\,\text{nm}$. To get an experimental value of $450\,\text{nm}$, which corresponds to the transition energy $2.76\,\text{eV}$, the β would have to be $-10.15\,\text{eV}$. Depending on the goal of our calculations, such large fluctuations of β indicate that Hückel's method is sometimes too drastic of an approximation to get accurate values.

If we are working with a hexa-1,3,5-triene molecule, we get the following diagonalized Hamiltonian

$$\mathbb{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

with energies of the corresponding levels $\alpha + 0.445\beta$ and $\alpha - 0,445\beta$. The transition energy then is -0.89β and with $\beta = -3\,\text{eV}$ we get a wavelength of $464\,\text{nm}$. If we wanted an experimental wavelength, we would need β with a value of $-5.57\,\text{eV}$.

3. If we excite an electron from a σ to a σ^* orbital, we must be able to assess what happens to the energy. Although the electron in the σ orbital will have a lower energy than if the atoms in the bond were infinitely distant, the penalty for the second electron in the σ^* orbitals will be even higher. The total energy of the molecule will therefore be higher than if the two atoms in the bond were infinitely distant. Thus, it is favorable to gradually increase the distance between the atoms in the bond to a lower energy state allowing the molecule to separate into two parts. The molecule could emit a photon and return to the original state with both electrons in the bonding orbital, but the photon emission takes place on much longer time scales than geometric changes, so the molecule will not "make it" before it decays. That is why the high energy photons radiation (UV, X-ray, and γ) is so damaging. It can destroy molecules, including those in our bodies. (It is important to note that the human body is particularly prone to DNA damage, for which excitation from the π to π^* is sufficient. It creates chemical bonds between molecules of two different bases, which disrupts the structure of the DNA so much that the body cannot repair it.)

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