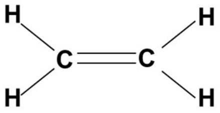
Exercise 13.1 (Hückel molecular orbitals)



ethene (or ethylene)

Calculate the energy levels and wave functions of the π molecular orbitals of ethylene using the Hückel model with the Coulombic integral α and transfer integral β as parameters.

a) Draw an energy level diagram and sketch the molecular orbitals
b) The lowest energy UV-absorption peak of ethylene gas is at a wavelength of about 170 nm. Estimate the value of the transfer integral $|\beta|$ in eV.

Exercise 13.1. Solution.

Here we start straight from the result obtained during lecture, for energy level and eigenfunctions we have:

$$E_k = \alpha + 2\beta \, cos\left(\frac{k\,\pi}{N+1}\right) \qquad k = 1,2, \dots N$$

$$\psi_k = \sum_{n=1}^{N} c_n^k \; \varphi_{2pz}(n) \qquad with \quad c_n^k = \sqrt{\frac{2}{N+1}}\, sin\left(\frac{kn\,\pi}{N+1}\right)$$

For Ethene we see that N=2, so:

$$E_1 = \alpha + 2\beta \cos\left(1 * \frac{\pi}{2+1}\right) = \alpha + \beta,$$

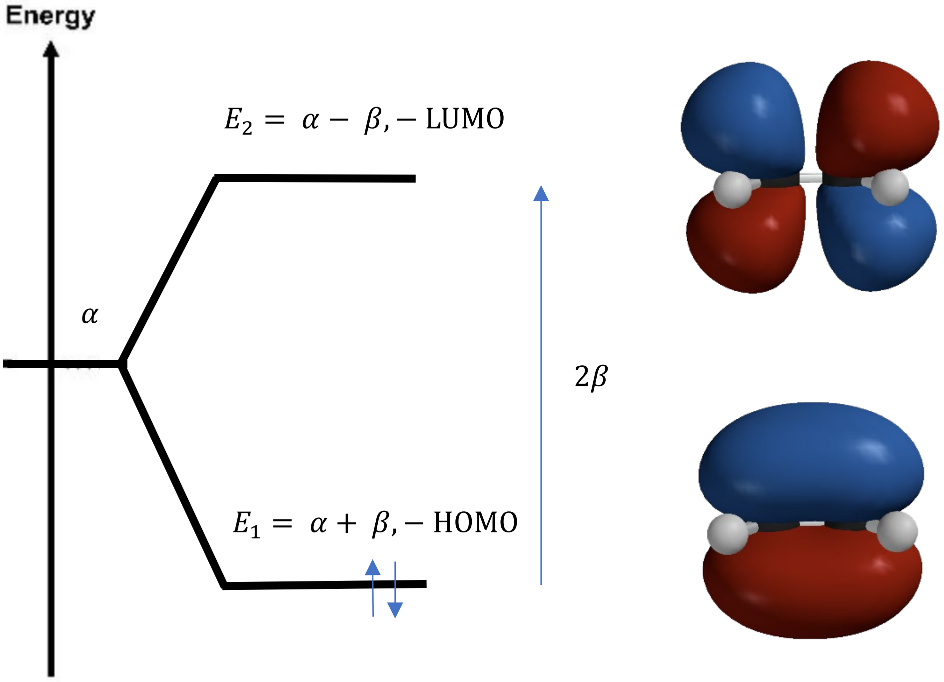
$$E_2 = \alpha - \beta$$

And:

$$\Psi_1 = \sqrt{\frac{2}{3}} \sin\left(\frac{\pi}{3}\right) \varphi_{2pz}(1) + \sqrt{\frac{2}{3}} \sin\left(\frac{2\pi}{3}\right) \varphi_{2pz}(2) = \frac{\varphi_{2pz}(1) + \varphi_{2pz}(2)}{\sqrt{2}},$$

$$\Psi_2 = \frac{\varphi_{2pz}(1) - \varphi_{2pz}(2)}{\sqrt{2}}$$

For the energy diagram:



For an estimation of β we have:

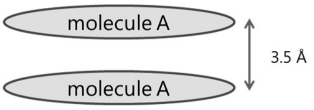
$$E_{abs} = \Psi_{LUMO} - \Psi_{HOMO} = -2\beta,$$

Thus, $|\beta|$ = E/2, converting 500 nm to eV, we get: $|\beta|$ = 3.65 eV

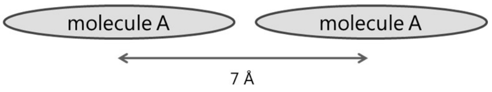
Exercise 13.2 (Exciton bands)

An isolated molecule A absorbs at a wavelength of 500 nm and has a transition dipole moment, which is oriented parallel to the long axis of the molecule, of 5 D. When two dye molecules are assembled to form a dimer, the absorption wavelength shifts due to excitonic coupling. Here we are looking at the two dimer structures I) and II).

I)



II)

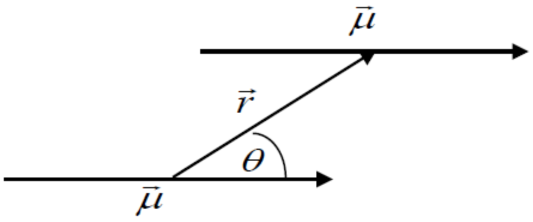


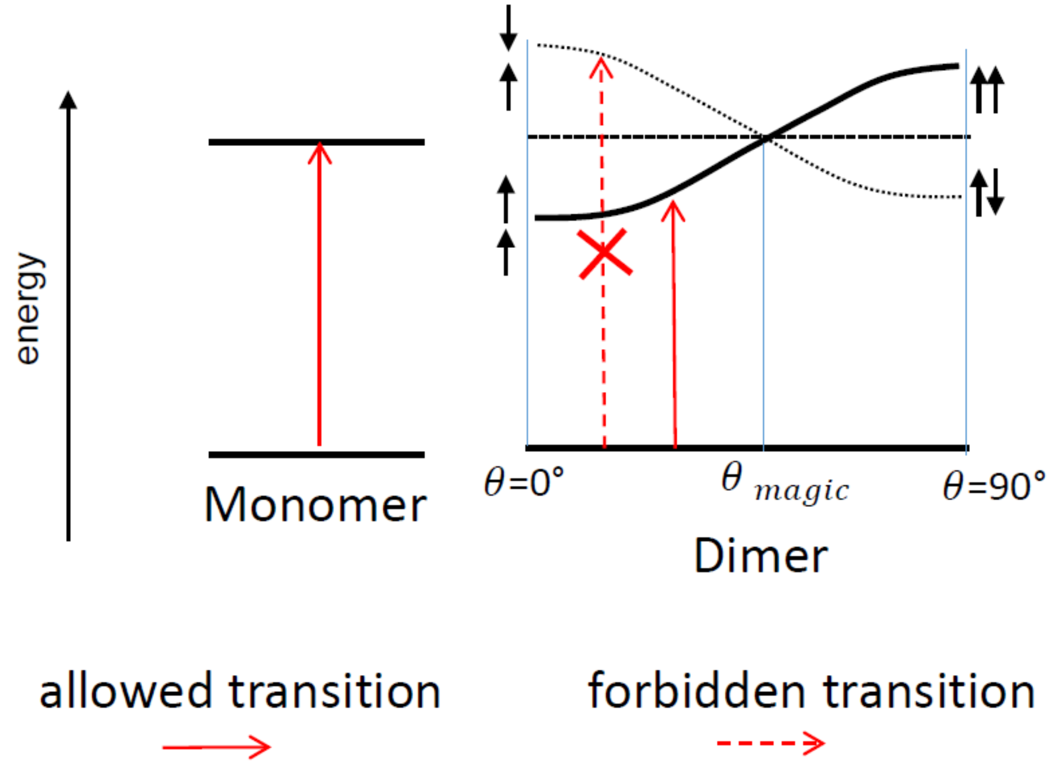
a) Which of the two structures leads to a blue resp. red shift of the absorption band?
b) Which of the two dimers is expected to fluoresce? Please explain.
c) Calculate the absorption wavelength for both dimers I) and II). Use the point dipole approximation and take ε = 3 for the dielectric constant.

Exercise 13.2. Solution

Let's consider results from the lecture:

$$J = \frac{\vec{\mu}^2}{4\pi\varepsilon\varepsilon_0 r^3}\left[1 - 3\cdot\cos^2\theta\right]$$





a) We see that 1st case corresponds to the $\theta = 90^o$, while 2nd to the $\theta = 0^o$. Transition to one of the levels is forbidden, and for the 2nd case in dimer transition would be allowed to the level that is energetically lower, than in monomer, thus resulting in the red shift. While for the 1st case, transition allowed to the higher level, resulting in the blue shift.

b) Dimer in the 2nd case is expected to fluoresce, because additionally to radiatively allowed transition, in the 1st case non-radiative transition is possible, as illustrated:

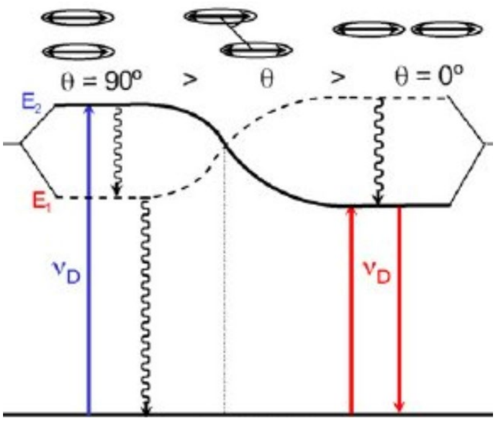


Figure. Exciton splitting of the electronic excited states of dimers with different geometries. (radiative deactivation: straight arrows, and non-radiative deactivation wavy arrows) [1].

c) Using expression above for the J, we find:

$$\begin{aligned} J_1 &= 363\, meV \\ J_2 &= -90\, meV \end{aligned}$$

For adjusted wavelengths we first convert 500 nm to eV, and then adjust by the values of J. For adjusted wavelengths we get:

$$\begin{aligned} \lambda_1 &= 436.2\, nm \\ \lambda_2 &= 518.9\, nm \end{aligned}$$

Reference:

[1] - Ferrnando López Arbeloa et al., Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Volume 8, Issue 2, 2007, Pages 85-108, ISSN 1389-5567, https://doi.org/10.1016/j.jphotochemrev.2007.03.003.