Exercise 2.1 (Molecular Orbitals)

Please describe (preferably as a PPT presentation with 3-4 slides):

- The orbitals of a cyclic aromatic compound with N atoms are described by the Coulson formula:

$$E_q = \alpha + 2\beta\cos\left(\frac{2\pi q}{N}\right) \qquad q = 1,2,...N$$

$$\psi_q = \sum_{n=1}^{N} a_n^q \psi_{2p_z}(n) \qquad a_n^q = \sqrt{\frac{1}{N}}\; e^{\left(\frac{2i\pi qn}{N}\right)}$$

a) Calculate the energies of the π molecular orbitals of benzene and represent them in an energy level diagram.

b) Applying the Pauli exclusion principle, calculate the energy lowering of the system (as compared to the isolated carbon atoms) induced by the bonding of the π electrons.

c) Calculate the wavefunctions with highest and lowest energy and sketch all the Hückel molecular orbitals.

Hint: the remaining wavefunctions are given by

$$\psi_5 = \frac{1}{\sqrt{12}}(2\psi_{p_z}(1) + \psi_{p_z}(2) - \psi_{p_z}(3) - 2\psi_{p_z}(4) - \psi_{p_z}(5) + \psi_{p_z}(6))$$

$$\psi_1 = \frac{1}{2}(\psi_{p_z}(2) + \psi_{p_z}(3) - \psi_{p_z}(5) - \psi_{p_z}(6))$$

$$\psi_2 = \frac{1}{\sqrt{12}}(2\psi_{p_z}(1) - \psi_{p_z}(2) - \psi_{p_z}(3) + 2\psi_{p_z}(4) - \psi_{p_z}(5) - \psi_{p_z}(6))$$

$$\psi_4 = \frac{1}{2}(\psi_{p_z}(2) - \psi_{p_z}(3) + \psi_{p_z}(5) - \psi_{p_z}(6))$$

Exercise 2.2 (Exciton theory)

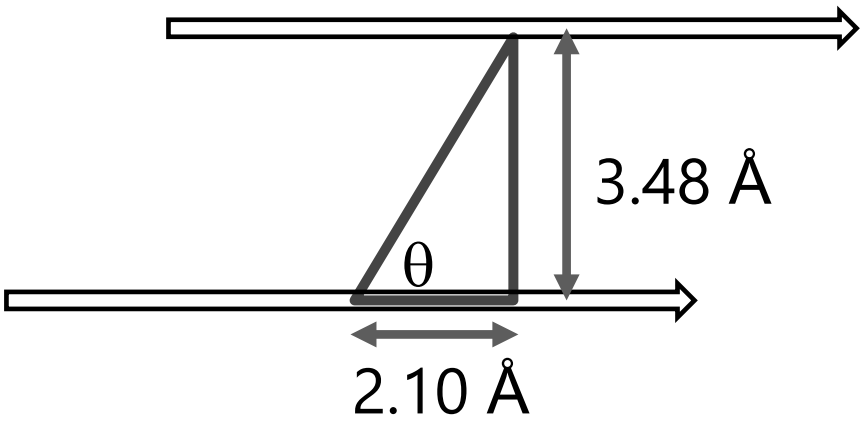
Please describe (preferably as a PPT presentation with 3-4 slides):

In the exciton theory developed by McRae and Kasha the change of absorption when going from the monomer to the (physical, not chemical) dimer can be calculated as a function of the orientation between the transition dipole moments of the two interacting molecules. For co-linear dipole moments a simple expression depending on the slipping angle θ is derived.

a) Calculate the magic angle and explain its meaning.

A merocyanine molecule (Mc2) has a transition dipole moment of 10.2 D and a maximum absorption wavelength of 540 nm in water.

b) By knowing the dimer geometry and the orientation and position of the transition dipole moment within the dye (see figure below), estimate the wavelength of the absorption maximum expected for the dimer using the expression obtained from exciton theory (use the point dipole approximation).

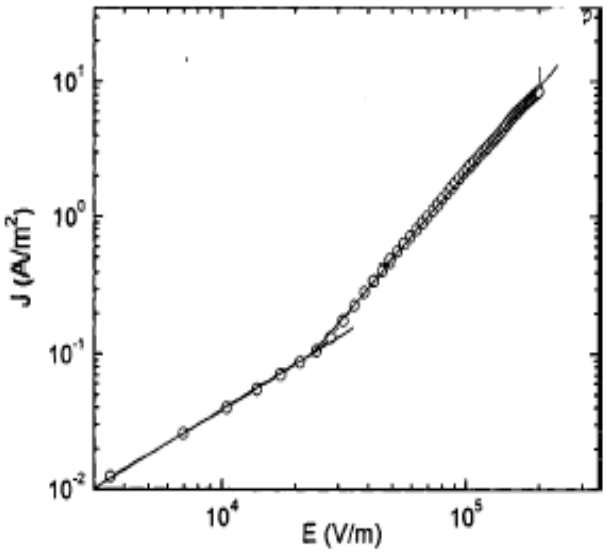


c) Taking the dipole length of l=9.1Å for the extended dipole approximation, calculate a refined value for the spectral shift and compare it to the one found in exercise b). (Note: 1D = 3,3•10^{-30} Cm)

Exercise 2.3 (Mobility)

Please describe (preferably as a PPT presentation with 3-4 slides):

a) Estimate the charge carrier mobility in a conjugated organic single crystal from the current-voltage plot on the right. The data was obtained by sandwiching the 20 μm thick crystal between two gold electrodes. First determine which region of the current-voltage characteristics is governed by ohmic behavior and which is governed by space charge limited current. Explain why.



b) You expect to have measured the hole or electron mobility?
(Take ε=3 as the dielectric constant of the molecular solid)

c) How will the curve change in the presence of traps?

d) Suggest another experiment to test if you are really in the SCLC regime.

Exercise 2.4 (Open circuit voltage)

Please describe (preferably as a PPT presentation with 3-4 slides):

Efficiencies losses in organic solar cells are in many cases related to the Open Circuit Voltage V_{oc}. For optical bandgaps in the range of 1.7 to 2.1 eV, V_{oc} rarely exceeds 1V. So it is important to understand the origins of theses losses.

a) Derive the following expression for V_{oc} from an equivalent circuit model for solar cells and explain the individual terms:

$$V_{\mathrm{OC}} = \frac{nk_{\mathrm{B}}T}{q} \ln\left(\frac{J_{\mathrm{ph}}}{J_0} + 1\right)$$

b) Draw an energy level diagram with HOMO and LUMO levels of donor and acceptor and indicate ΔE_{HL}

c) Following Kippelen et al., which relation exists between V_{oc} and reverse saturation current J_0?

Literature: W. J. Potscavage, Jr., S. Yoo, B. Kippelen, Origin of the open-circuit voltage in multilayer heterojunction organic solar cells; Applied Physics Letters 93, 193308 (2008).