

# Nanostructural properties 2010/11

## Simple models of conjugated polymers: Homework assignment

1. For a system on  $M$  interacting nuclei (with mass,  $m_1, m_2, \dots, m_M$ , and charges  $Z_1, Z_2, \dots, Z_M$ , respectively) and  $N$  electrons (of mass  $m_e$ ) in three dimensions, write down the most general Hamiltonian operator, i.e., including all the appropriate kinetic and Coloumbic terms.
2. Assuming  $N$  noninteracting electrons in an one dimensional box of size  $L$  (i.e., the free electron model of  $\pi$ -electrons), compute the energy gap,  $\Delta_m$ , between the HOMO- $m$  and LUMO+ $m$ . Remember that the HOMO is the Highest Occupied Molecular Orbital and the HOMO- $m$  is the  $m^{\text{th}}$  MO below the HOMO. Analogously, the LUMO is the Lowest Unoccupied Molecular Orbital and the LUMO+ $m$  is the  $m^{\text{th}}$  MO above the LUMO.
3. Assuming  $N$  noninteracting electrons in an one dimensional box of size  $L$  (i.e., the free electron model of  $\pi$ -electrons), compute the expectation value of the dipole of the HOMO- $m$  to LUMO+ $m$  transition:

$$d_m = \langle \phi_{HOMO-m} | \hat{R} | \phi_{LUMO+m} \rangle$$

where,  $\phi_{HOMO-m}(R)$  and  $\phi_{LUMO+m}(R)$  are the wave functions of the HOMO- $m$  and LUMO+ $m$ , respectively, and  $\hat{R}$  is the position operator. After you have computed  $d_m$ , plug it in the following expression

$$f_m = \frac{2}{3} \frac{m_e}{\hbar^2} \Delta_m |d_m|^2$$

to obtain the (adimensional) oscillator strength of the HOMO- $m$  to LUMO+ $m$  transition.

4. For the Hückel model of a homegeneous polyene of length  $L$  with periodic boundary conditions and an even number of carbon atoms,  $N$ , obtain the allowed values of the quantum number  $k$ , being

$$\phi_k(j) = \sqrt{\frac{1}{L}} \exp(+ikj)$$

the general functional form of a MO. [In the above equation  $i$  is the imaginary unit,  $i^2 = -1$ , and  $j$  is the carbon atom index,  $j = 1, 2, \dots, N$ . ]

The solutions of this homework assignment must be handled by each student separately, and preferably in electronic format to: [lorenzo.stella@ehu.es](mailto:lorenzo.stella@ehu.es) (and CC to: [angel.rubio@ehu.es](mailto:angel.rubio@ehu.es)) by 20/04/2011 5p.m.