

Simple model of conjugated polymers

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1 The Free Electron (FE) model

Experiments on conjugated polymers suggest that in these compounds π -electrons are “delocalised”. In the FE model, one considers an even number, N , of π -electrons delocalised over a polymers section of length L , say the interval $[-L/2, +L/2]$. If the averaged bond length is indicated by a , then $L = Na$, i.e., the length of the polymer section and the number of π -electrons are proportional.

From basic Quantum Mechanics (see your favourite textbook), we know that the Hamiltonian of a *single* free electrons is:

$$H_{FE} = \frac{\hbar^2}{2m_e} \hat{P}^2 \quad (1)$$

where \hbar is the reduced Plank constant, m_e is the electron mass, and \hat{P} is the quantum linear momentum operator. The wave functions, $\phi(R)$, with satisfy Eq.1 in the interval $[-L/2, +L/2]$ so that $\phi(-L/2) = \phi(L/2) = 0$ can be classified according to their parity as:

$$\begin{aligned} \phi_n(R) &= \sqrt{\frac{2}{L}} \cos(k_n R) \quad \text{if } n = 0, 2, 4, \dots \\ \phi_n(R) &= \sqrt{\frac{2}{L}} \sin(k_n R) \quad \text{if } n = 1, 3, 5, \dots \end{aligned} \quad (2)$$

and $k_n = (n+1)\pi/L$. By inserting Eq.2 in Eq.1, one verifies that the spectrum of a *single* free π -electrons is:

$$E_n = \frac{\hbar^2 k_n^2}{2m_e} = \frac{\hbar^2 \pi^2}{2m_e L^2} (n+1)^2$$

Assuming that all the single π -electron energy levels are doubly degenerate because of the electron spin, one can fill these levels with N free π -electrons according to the Pauli exclusion principle until the Highest Occupied Molecular Orbital (HOMO), $\phi_{N/2-1}(R)$. Therefore, the Lowest Unoccupied Molecular Orbital (LUMO) is $\phi_{N/2}(R)$.

The energy difference between the LUMO and the HOMO gives an estimate of the optical gap of the polymer section:

$$\Delta_N = E_{N/2} - E_{N/2-1} = \frac{\hbar^2 \pi^2}{2m_e L^2} (N + 1) \quad (3)$$

Eq. 3 provides a good estimate of the experimental optical gaps of *finite* polyenes (see e.g., N.S. Blyss J. Chem. Phys. 16 287 (1948) or chapter 8 of E.R. Bittner’s “Quantum dynamics” CRC press (2010)). However, the FE model fails to predict the correct gap saturation, $\Delta_N \rightarrow \text{constant}$, in the asymptotic limit $N \rightarrow \infty$. Instead, the FE model predicts $\Delta_N \rightarrow 0$ (remember that L and N are proportional).

In summary, despite its extreme simplicity, the FE model gives the correct $1/N$ trend of the optical gap for *finite* polyenes. This is a *a posteriori* confirmation that π -electrons are “delocalised” along a straight section of a conjugated polymer. The bonding structure of conjugated polymers is not accounted for by the FE model, which is a possible reason of its failure in giving the correct semiconducting behaviour (i.e., finite gap) of conjugated polymers.

2 The Hückel Molecular Orbital (HMO) model

Let us consider a model of straight conjugated polymer sections by assuming that:

1. The carbon and hydrogen atoms are lumped together to form effective C-H “pseudo-atoms”. This way, a straight conjugated polymer section can be graphically modelled by a linear sequence of C-H “pseudo-atoms”.
2. Only p_z orbitals are included in the calculation and there is just one π -electron per C-H “pseudo-atom”.
3. A constant α represents the on-site energy of an electron localised in the p_z orbital of the C-H “pseudo-atom”.
4. A constant β represents the energy gained by forming a π -bond between to nearest-neighbour “pseudo-atom”.
5. The use of Periodic Boundary Conditions (PBC), i.e., given an even number N of C-H “pseudo-atoms”, we introduce a fictitious extra bond between the last and the first “pseudo-atoms”. This way one neglects the details of the conditions at the ends of the conjugated section, e.g., twists, groups, etc., and focuses on the “bulk” of the polymer section.

According to these assumptions, one writes the HMO Hamiltonian operator as:

$$\begin{cases} H_{i,i} & = \alpha \\ H_{i,i+1} = H_{i+1,i} & = -\beta \\ H_{i,j} & = 0 \quad \text{otherwise.} \end{cases} \quad (4)$$

and solves the related Schrödinger eigenvalue problem:

$$\sum_{i=1}^L H_{i,j} \phi_k(j) = E_k \phi_k(i) \quad (5)$$

in order to find the Molecular Orbitals (MOs), $\phi_k(j)$, and their energies, E_k , where k is a yet to be assigned quantum number.

Taking the same constant β for all the “pseudo-atoms” is based on the fact that all the p_z orbitals are *a priori* equivalent. We shall discuss this point in Sec. 2.3.

2.1 The wave function

Solving Eq. 5 is in general a difficult task. In practise, one is guided by his/her previous experience. For instance, one can start from a FE solution, as in Sec.1:

$$\phi_k(j) = \frac{1}{\sqrt{L}} e^{+ikj} \quad (6)$$

This particular kind of wave function is called plane wave and k is its wave number. As a consequence of the PBC, only discrete values of the quantum number k are allowed (see the Homework assignment).

2.2 The undimerised solution

By inserting Eq. 6 in to Eq. 5, one finds that:

$$-\beta \phi_k(j-1) + \alpha \phi_k(j) - \beta \phi_k(j+1) = E_k \phi_k(j)$$

(remember the PBC) which, after a few simplifications, reads:

$$-\beta e^{+ik} + \alpha - \beta e^{-ik} = E_k$$

This can be then rewritten in a more convectional way as

$$E_k = \alpha - 2\beta \cos(k) \quad (7)$$

which gives the HMO energies of a conjugated polymer section.

2.3 Discussion

As usual, the derivation of Eq. 7 is not the end of the story. We still have to understand the physical meaning of this equation. We start with noticing that:

1. In the $N \rightarrow \infty$ limit, there is only one band, defined for $k \in (0, 2\pi]$, while we expected at least two bands, one for the π -electrons (conduction band) and the other for the holes (valence band).

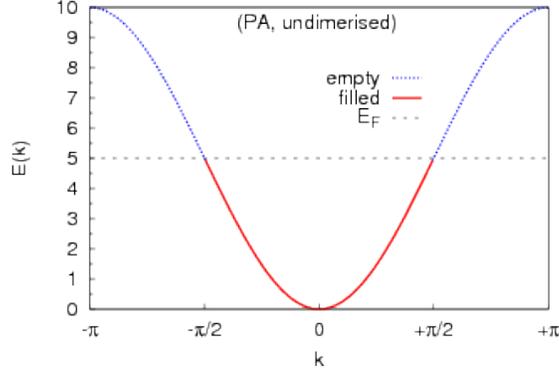


Figure 1: Band structure PA, undimerised

2. The only model parameter with a physical meaning is the β constant because the energy E_k can be always defined apart from an arbitrary constant, e.g., α .

The band structure from Eq. 7 is depicted in Fig. 1. Since in each state one can put two π -electrons, one with spin up and the other with spin down, just half of the N possible levels (see Sec. 2.1) are filled. Once again, in the $N \rightarrow \infty$ limit conjugated polymers are erroneously predicted to be metallic.

Knowing that in this limit conjugated polymers have an experimental finite gap, we conclude that there something wrong in our assumptions, see Sec.2. In particular, although all the p_z orbitals are equal, we also know that conjugated polymers show alternating single and double bonds. Therefore, it might be interesting to introduce two constants, β_s and β_d , one for the single and the other for the double bonds.

2.4 The dimerised solution

One can solve the Schrödinger Eq. 5 with the following Hamiltonian:

$$\begin{cases} H_{i,i} & = \varepsilon \\ H_{i,i+1} = H_{i+1,i} & = -\beta_s \quad \text{if } i \text{ is odd} \\ H_{i,i+1} = H_{i+1,i} & = -\beta_d \quad \text{if } i \text{ is even} \\ H_{i,j} & = 0 \quad \text{otherwise.} \end{cases} \quad (8)$$

i.e., by allowing two different β constants, for single and double bonds, respectively. One can use the following combination of plane waves as a tentative solution:

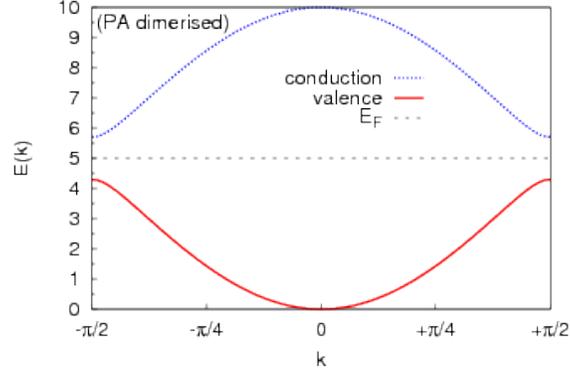


Figure 2: Band structure PA, dimerised

$$\begin{cases} \phi_k(j) = e^{+ikj} & \text{if } j \text{ is odd} \\ \phi_k(j) = e^{+ikj+i\phi} & \text{if } j \text{ is even.} \end{cases} \quad (9)$$

The phase factor ϕ is another unknown quantity, along with the energy E , but note that it does not depend on k . Therefore, by inserting Eq. 9 and Eq. 8 into Eq. 5, one obtains a system of two equations (remember the PBC). The detailed solution is left to the student, while the HMO energies for this case are depicted in Fig. 2. As one can see, the correct semiconducting behaviour of conjugated polymers is finally retrieved if their bond alternation is correctly described in the HMO Hamiltonian, as in Eq.8.