

CALCULATION OF THE BAND STRUCTURE OF 2D CONDUCTING POLYMERS USING THE NETWORK MODEL

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The network model has been used to calculate the band structure the gap energy and Fermi level of conducting polymers in two dimensions. For this purpose, a geometrical classification of possible polymer chains configurations in two dimensions has been introduced leading to a classification of the unit cells based on the number of bonds in them. The model has been applied to graphite in 2D, represented by a three bonds unit cell, and, as a new case, the anti-parallel Polyacetylene chains (PA) in two dimensions, represented by a unit cell with four bonds. The results are in good agreement with the first principles calculations.

Key words: Polymer, network model, polyacetylene, band gap, tight binding model.

1. INTRODUCTION

More than half a century ago, the network model has been introduced to study the conjugated and aromatic molecules [1,2]. In this model, molecules are replaced by a network of straight lines joining adjacent atoms, and the π electrons are supposed to move entirely freely along these lines.

The results of this model have been found in good agreement with the tight binding ones. Coulson [3] has shown that in most cases the network and the tight binding models must give nearly equivalent results for the wave functions and energies of systems like polyene chains or ring molecules. Coulson [4] showed also the application of this model into two different examples of crystals; 2D graphite and 3D simple cubic lattices.

In this paper, the application of the network model into systems of conducting polymers that can be viewed as a 2D will be shown.

2. 2D POLYMERIC STRUCTURES

The crystal structure of some polymeric materials (Polyacetylene, Polyacene, Polyenes, PVV, etc.) can be viewed as being composed of parallel chains in

parallel planes. Neglecting the coupling between these planes, these materials can be described by a 2D structure, where the chains are aligned along say the x axis, Fig. (1). The 2D symmetry operations of polymeric materials are restricted to translations and reflections due to the low symmetry of polymers. The form of the possible unit cells for different structures will be determined by these symmetry operations and the inter- and intra- chains couplings. Restricting the coupling to the nearest neighbors in each chain and to the coupling between closest chains will result in only four possible different super cells.

1. A translation along S_1 or S_2 will lead to a cell containing 3 bonds for systems like polyacene chain or 4 bonds for polyacetylene as shown in Fig. (1a).

2. A translation along S_1 or S_2 and a reflection about X or Y axis will lead to a cell containing 6 or 8 bonds for systems like polyacetylene chains in phase, Fig. (1b).

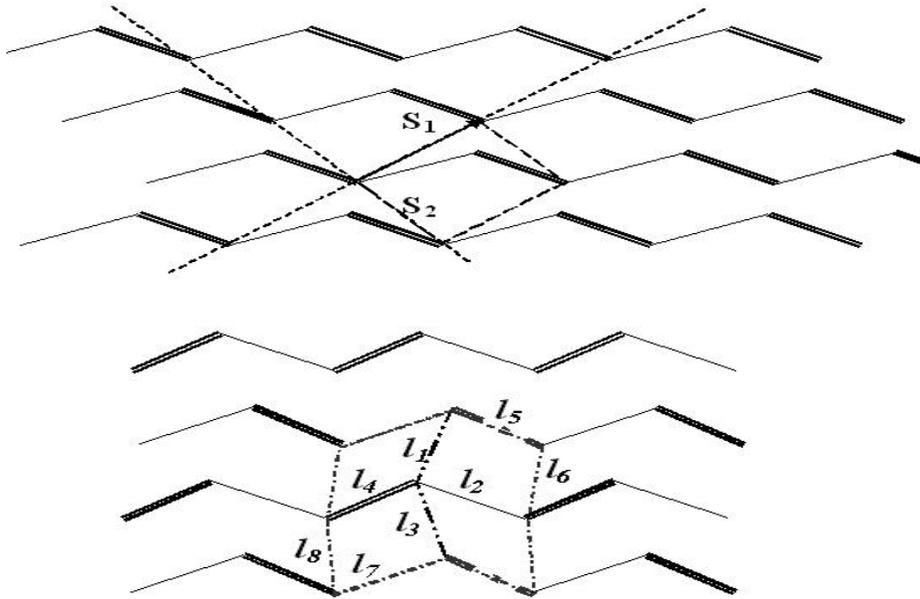


Fig. 1. (left) The 2D lattice. (right) Cell with 8 bonds, neglecting the l_1 and l_3 interaction we will result end with a 6 bond unit cell (polyacene chain for example).

3. NETWORK MODEL

Suppose a 3D lattice with one point in its unit cell connected with i bonds and the free electron moves along the bonds. ψ_i is the wave function along the bond i . These wave functions should satisfy:

1. Schrödinger equation

$$\frac{\partial^2 \psi_i}{\partial x^2} + q^2 \psi_i = 0 \quad (1)$$

where $q^2 = \frac{2mE}{\hbar^2}$, m is the electron mass and E its energy.

2. Current conservation

$$\sum \nabla \psi_i = 0 \quad (2)$$

where the gradient is along the bond.

3. Wave functions continuation:

$$\psi_i(x) = \psi_j(x) \Big|_{x \in \{\text{join points}\}} \quad (3)$$

4. Wave functions should be of the Bloch type

$$\psi_i(x) = e^{ikx} u_i(x). \quad (4)$$

The solution of Schrödinger equation leads to a wave function of the form

$$\psi_i(x) = b_i \cos(qx_i) + a_i \sin(qx_i). \quad (5)$$

It is clear that the number of variables is $2i$. Condition 3 at the node $x_i = 0$ reduces the number of independent variables to i and allows us to assume $b_i = 1$. Thus, i independent equations are needed to solve the model completely. This can be gotten from conditions 2, 3 and 4 at cell edges. Solving i equations and substituting the result in one of the rest, an implicit function $f(E, k_i) = 0$ is obtained which is called the dispersion relation; k_i is the wave vector along the bond. In some simple cases, an explicit function $E(k_i)$ can be determined from $f(E, k_i)$. Once the dispersion relation has been obtained, it is possible to apply some transformations to calculate the electronic density of states (DOS) [5] and the Fermi level.

Fermi level can be computed starting from the number of electrons $\nu(E)$ that occupy levels up to energy E . Since all electrons in a polymeric material must occupy levels below Fermi level, then we have

$$N(E_F) = \nu(E)/V = N. \quad (6)$$

Where V is the volume of the crystal, and, $\nu(E)$ is proportional to the possible combinations of k_x , k_y and k_z that satisfy $|\vec{k}| \leq |\vec{k}_F|$. k_F is the corresponding wave vector of the energy E_F . $N(E_F)$ becomes [6-8]

$$N(E_F) = \sum_{k \leq k_F} 2 = 2V_{uc} |k_F|^2 = mn_{uc}. \quad (7)$$

Where m is the number of unit cells in the crystal, n_{uc} is the number of electrons in the unit cell and V_{uc} is the volume of the unit cell. So, k_F is given by

$$|k_F|^2 = \frac{n_{uc}}{2V_{uc}} \quad (8)$$

Finally, E_F could be determined by substituting back Eq. (8) in the dispersion equation.

4. APPLICATION OF THE NETWORK MODEL INTO CONDUCTING POLYMERS

4.1. DISPERSION RELATION

3 bonds case:

Solving the network model in a unit cell like Fig. (2) (lower) with bond l_3 is missing off, the dispersion relation takes the form:

$$\sum_i \sum_{j>i} \frac{\cos(ql_i)\cos(ql_j)}{\sin(ql_i)\sin(ql_j)} - \frac{3}{2} = \sum_i \sum_{j>i} \frac{C_{ij}(k_1, k_2)}{\sin(ql_i)\sin(ql_j)} \quad (9)$$

where

$$C_{12} = \cos(k_2 S_2), C_{23} = \cos(k_1 S_1 + k_2 S_2), C_{13} = \cos(k_1 S_1) \quad (10)$$

Equation (9) represents the dispersion relation for any cell containing three bonds. For the special case when $l_1 = l_2 = l_4 = l$, it becomes

$$9 \cos^2(ql) = 3 + 2 \cos(k_1 S_1) + 2 \cos(k_2 S_2) + 2 \cos(k_1 S_1 - k_2 S_2) \quad (11)$$

which is the dispersion relation for graphite or (BN) lattice [4].

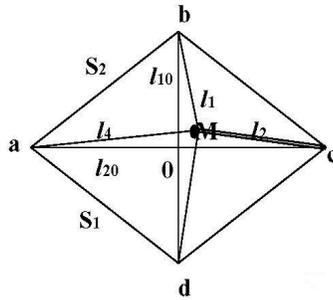


Fig. 2. Cell with 4 bonds, if one of the bonds is missing (according to the material structure) we will get the 3 bonds unit cell.

4 bonds cell:

The dispersion relation for a general 4 bond unit cell is:

$$\sum_i \sum_{j>i} \frac{\cos(ql_i)\cos(ql_j)}{\sin(ql_i)\sin(ql_j)} - 2 = \sum_i \sum_{j>i} \frac{C_{ij}(k_1, k_2)}{\sin(ql_i)\sin(ql_j)} \quad (12)$$

where

$$\begin{aligned} C_{12} &= \cos(k_1 S_1), C_{13} = \cos(k_1 S_1 - k_2 S_2), C_{14} = \cos(k_2 S_2) \\ C_{23} &= \cos(k_2 S_2), C_{24} = \cos(k_1 S_1 + k_2 S_2), C_{34} = \cos(k_1 S_1). \end{aligned} \quad (13)$$

In case of $l_1 = l_2 = l_3 = l_4 = l$, $S_1 = S_2 = l\sqrt{2}$ and

$$k_1 = \frac{1}{\sqrt{2}}k_x + \frac{1}{\sqrt{2}}k_y, \quad k_2 = \frac{1}{\sqrt{2}}k_x - \frac{1}{\sqrt{2}}k_y \quad (14)$$

Eq. (12) will become

$$2 \cos(ql) = \cos(k_x l) + \cos(k_y l), \quad (15)$$

which it is the dispersion relation for a square lattice as a special case of the simple cubic lattice [4].

6 and 8 bonds unit cells:

The dispersion relation can be found with similar procedures in the form of

$$F(k_1, k_2, q) / H(k_1, k_2, q) = 0 \quad (16)$$

However, the F and H functions are rather lengthy functions, suggesting not to present them here.

5. RESULTS AND DISCUSSION

The study of the above dispersion relations leads to the energy levels and wave functions, which consequently lead to the density of states, Fermi level and optical properties, etc. The network model equations for each unit cell have been solved analytically using Maple, the well-known computer algebra software. The dispersion relation has been found in form of explicit or an implicit function of the wave vectors.

5.1. THREE BONDS UNIT CELL

As an example, graphite in 2D has been studied to verify the written program using Maple. It is clear from Eq. (11) that there are two bands. The upper represents

conduction band and the lowest one is the valance. Fig. (3) shows the density curve in terms of $(ql)^2$. The lower band one is filled up to 2.45 since there is one π electron per atom and the upper one is empty. The DOS at energy 2.45 is very low which means that graphite is a poor conductor. Our results are identical to the results obtained in [4].

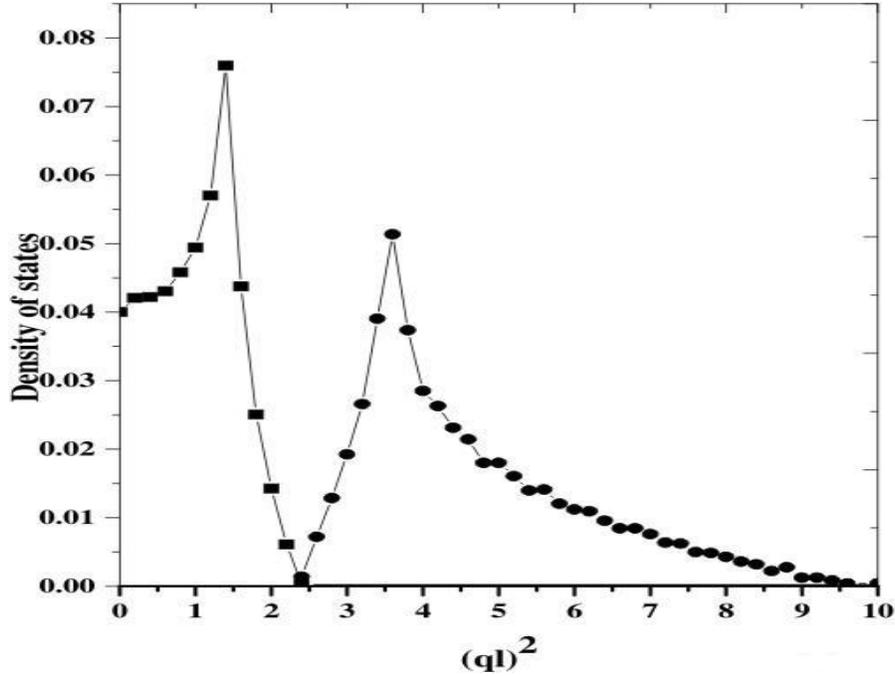


Fig. 3. The density of states of graphite in 2D in terms of (ql) .

5.2. FOUR BONDS CELL

Fig. (2) shows the four bonds cell which represents two chains of trans-polyacetylene in the out of phase order, where all lengths are measured by angstrom (see Fig. (6) of Ref. 11). Since the model is very sensitive to bond length, the geometry of the cell will be given a particular attention. It is obvious from the figure that the cell is rhombus $abcd$ with two different diagonals meeting at the origin point O of the coordinates x axis along Oc and y axis along Ob . The length of the long diagonal is $2l_{10}$ and the short one is $2l_{20}$. Now moving from O the point M we get the bonds $l_1 = \overline{bM}$, $l_2 = \overline{cM}$, $l_3 = \overline{dM}$ and $l_4 = \overline{aM}$. Their lengths can be given in terms of the M coordinates (x,y) and l_{10} and l_{20} as:

$$\begin{aligned}
 l_1 &= \sqrt{x^2 + (l_{10} - y)^2}, & l_2 &= \sqrt{y^2 + (l_{20} - x)^2} \\
 l_3 &= \sqrt{x^2 + (l_{10} + y)^2}, & l_4 &= \sqrt{y^2 + (l_{20} + x)^2}
 \end{aligned}
 \tag{17}$$

Substituting these parameters in Eq. (12), the effect of bond alternation into the energy bands of the system can be studied. Fig. (4) shows the energy bands in terms of the wave vectors k_1 and k_2 for $l_{10}=7.23$, $l_{20}=1.2$ and $M(0.055,0.5)$ and therefore $l_1=6.73$, $l_2=1.25$, $l_3=7.23$, $l_4=1.35$. These bands are nearly flat for some points in k space, which leads to some singularities in the density of states plot.

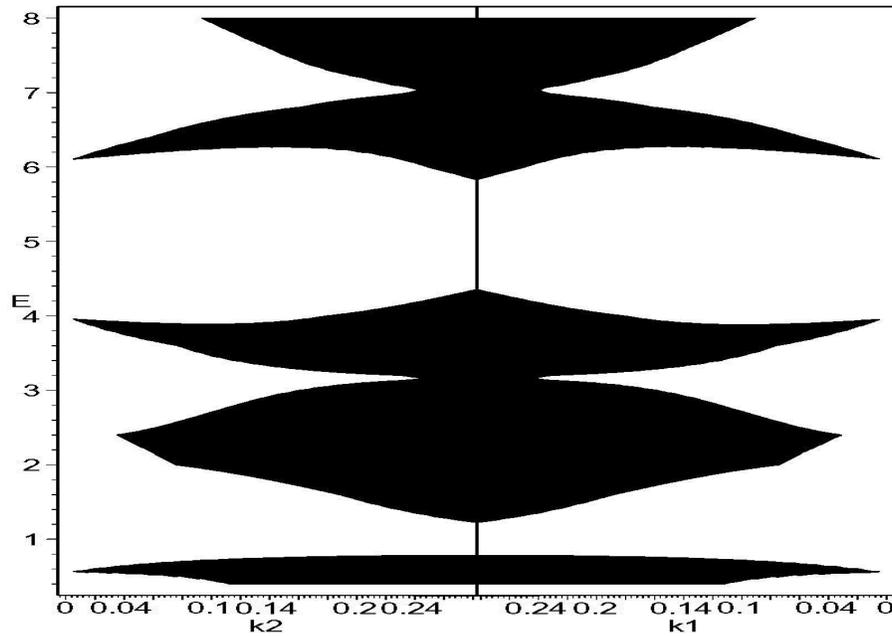


Fig. 4. Energy bands of PA chains in terms k_1 and k_2 for $l_1=6.73$, $l_2=1.25$, $l_3=7.23$, $l_4=1.35$ and E is in eV unit.

5. 2.1. Density of States

Since the density of states is related to a number of experimental observable, it is an important quantity to calculate in any theoretical study. A Fortran program has been written to find the energy levels and the possible combinations of k_x and k_y . A step of 0.002 along k_x and k_y axis and 0.001 along q axis were used. The corresponding density of states curve is plotted in Fig. (5). A gap is noticed between 4 and 6 eV. The finite peaks indicate the flatness of the energy surfaces. These peaks are saddle points of type M_1 .

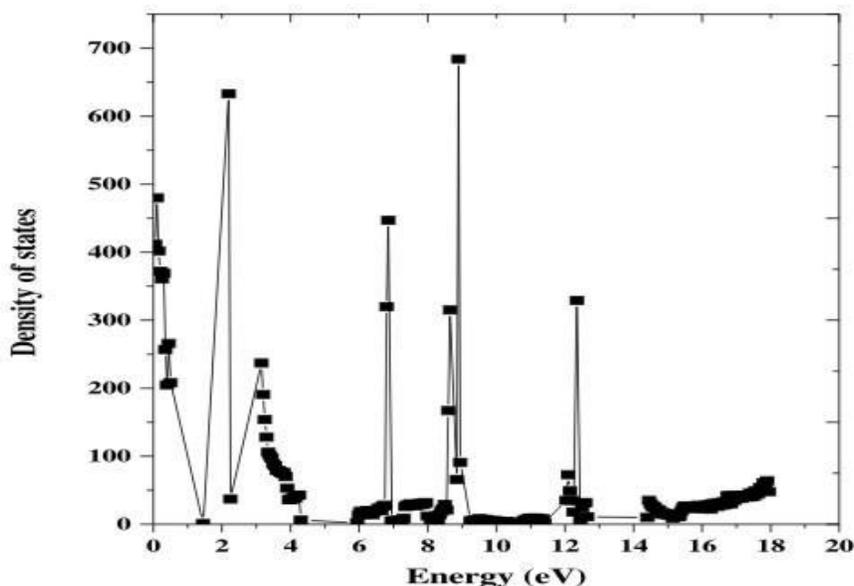


Fig. 5. The density of state of PA chains in 2D.

5. 2.2. Fermi Level

Fermi level can be obtained from Eq.(8) and the dispersion relation Eq. (12). The area of the unit cell is $2 \times l_{10} \times l_{20}$. Number of electrons in the unit cell is 2. Hence Fermi level is 4.3 eV measured from the bottom of the valance band. This level is positioned at the top of the valance band below the conduction band by 1.5 eV. This band gap is similar to the obtained one through measurements of the pressure dependence of absorption edge [13] and references therein. On the other hand Vogl et. al. [14] have carried out a first-principles local density functional calculation of the electronic structure of the 3D PA. They found a band gap about 1.4 eV for the out of phase crystalline structure, which is a little bit smaller than our results due to the fact that the overlapping between the wave functions in 3D reduces the band gap.

6. CONCLUSION

The network model of organic molecules has been used to calculate the band structure of conducting polymers in 2D. According to chain geometry, four different unit cells with respect to the number of bonds have been deduced. The dispersion relations of three and four bonds unit cells have been solved analytically using the algebraic maple package, while the six and eight bonds should be solved

numerically. Graphite, as a special case of the three bonds unit cell, has been considered. The obtained results are in good agreement with the literature. The dispersion relation for the general case of a four bonds unit cell has been found. The polyacetylene chains in the anti parallel ordering in 2D, as an example of four bonds unit cell, have been studied. The band structure and consequently the band gap, the density of state and Fermi level have been found. The result that can be compared with experiment is the band gap which was not far from the experimental and the sophisticated theoretical models values given in the literature.

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