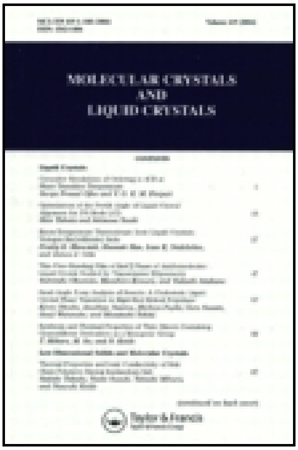

## Molecular Crystals and Liquid Crystals

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# THEORETICAL INVESTIGATION OF IMPURITIES AND INTERCHAIN COUPLING IN POLYACETYLENE

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In this work we study the effect of the interchain coupling on the electronic density of states in polyacetylene. First we show that a localized interchain coupling can be simulated by a single substitutional impurity scattering and introduces four symmetrical bound levels at the band edges. We then study the evolution of these levels in the presence of a soliton on the chains. Finally we consider a two-dimensional distribution of interchain interactions and study its effect on the broadening of the band edges. It is found that, when this coupling is taken into account, the semi conductor-metal transition found in charged soliton-lattices may occur at a concentration of solitons c $\sim$ 5 %.

## INTRODUCTION

The unusual characteristic properties of polyacetylene $(CH)_x$ have recently drawn a great interest on this polymer. It is now widely accepted$^{(1-2)}$ that solitons play an important role in its magnetic, optical and electrical properties. However little is known about the influence of the interchain coupling$^{(3)}$ on these properties. The object of the present work is to study theoretically the effects of such perturbations upon the purely one dimensional densities of states of such chains. We first study the case of a localized interchain coupling. Then a two dimensional interchain coupling distribution is investigated. Finally we discuss the possible effect of such a spatial distribution on the semi-conductor-metal transition in $(CH)_x$.

## LOCAL INTERACTION

Consider two polyacetylene chains and assume first that they do not interact. Let $H_0^A$ and $H_0^B$ be the one-electron Hamiltonians describing these two infinite chains A and B. These Hamiltonians are given, within the Hückel approximation as :

$$H_0^A = \sum_n \epsilon_n^A \, |n^A\rangle\langle n^A| + t^A_{n,n+1} \left( |n^A\rangle\langle n+1^A| + h.c \right) \qquad (1)$$

and similarly for $H_0^B$.

$|n^A\rangle$ denotes a $\pi$ electron state on the $n^{th}$ CH group of chain A ; $\epsilon_n^A$ and $t^A_{n,n+1}$ are respectively the self energies and the transfer integrals for this chain. The Hamiltonian of the whole system can thus be written as

$$H = \begin{pmatrix} H_0^A & 0 \\ 0 & H_0^B \end{pmatrix}$$

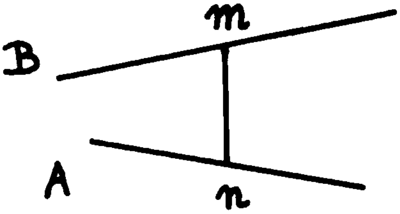

FIGURE 1 Model of the localized interchain coupling.

and the Green function is :

$$G_o = \begin{pmatrix} G^A & 0 \\ 0 & G^B \end{pmatrix}$$

where $G_o^A = (E - H_o^A)^{-1}$ and similarly for $G_o^B$.

Let us now allow these two chains to interact via a localized interchain coupling of strenght v connecting the state $|n^A\rangle$ on chain A to the state $|m^B\rangle$ on chain B. This perturbation V can thus be written in an operator form as :

$$V = v \, |n^A\rangle\langle m^B| \tag{2}$$

The usual theory of Green functions allows then us to obtain the energy levels, if any, introduced by such a perturbation. These correspond to zeros of the determinant

$$D\,(E) = \det \| \, 1 - G_o V \, \| \tag{3}$$

An important feature of this result is that the effective order of this determinant is equal to the order of the matrix V. In our case the only non-zero block of this matrix is the following 2 x 2 matrix.

$$\begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}$$

It is then easily found that the required energy levels are given as the solution of the following equation :

$$g^{oA}_{nn}(E)\; g^{oA}_{mm}(E) = \frac{1}{v^2} \tag{4}$$

$g^{oA}_{nn}(E)$ and $g^{oA}_{mm}(E)$ are respectively the n^th^ and m^th^ diagonal elements of $G_o^A$ and $G_o^B$.

In the particular case of two identical chains, this equation reduces to

$$g^{o}_{nn}(E) = \pm \frac{1}{v} \tag{5}$$

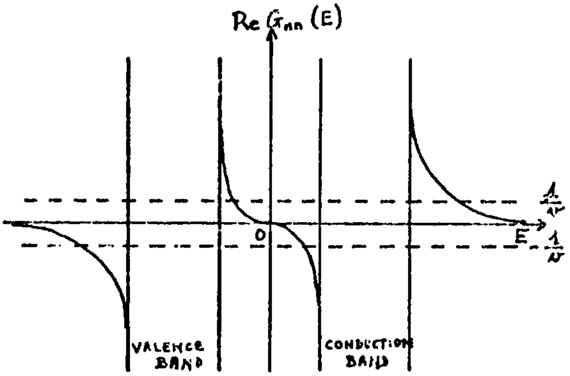

FIGURE 2 Real part of the diagonal element of the Green function for a perfectly dimerized chain.

The $\pm$ sign excepted, this equation appears to be the same as that giving the extra levels introduced in the chain by a substitutional impurity with self energy v. In the following we shall focus specially on the particular case of two identical chains. First we can note that equation (5) has no solutions inside the energy bands since it is known that, within these bands, $g^0_{nn}(E)$ has a non-zero imaginary part. An analysis of the qualitative features of the solutions of (5) can be better carried out with the help of figure 2 where we have plotted schematically the Green function $g^0_{nn}(E)$ of a perfectly dimerized $(CH)_x$ chain.

The roots of equation (5) are given by the intersections of the curves representing $g^0_{nn}(E)$ with the horizontal lines $y = \pm \frac{1}{v}$. Whatever is the value of v, there are four such intersections which appear symmetrically with respect to the gap center. In the case of a substitutional impurity, note that only two levels appear which are not symmetrical. When we deal with perfectly dimerized chains, the diagonal elements of the Green function are independant of the site index n and thus the energies of the bound states introduced by the localized interchain coupling are independant of n. However, when the periodicity is lost, for example with the introduction of defects such as solitons into the chains, these energies may depend upon the relative position of the sites involved in the coupling and of the soliton. To get an insight into this dependance, let us consider two identical chains interacting via the coupling.

$$V = |0^A\rangle v \langle 0^B|$$

Now let us consider the two following cases : in the first one we put a soliton on each chain at the n = 0 site and in the second one we put it at an infinitely removed position. (n = 50 is in fact sufficient for computations).

The soliton is described by the bond alternation amplitude

$$u_n = (-1)^n u_o \tanh \frac{n}{\ell}$$

The transfer integrals in (1) is as usually expanded in linear order with respect to the $u_n$'s as :

$$t_{n,n+1} = t_o - \alpha (u_n - u_{n+1})$$

The numerical values for the involved parameters are those used by Su, Schrieffer and Heeger(1). The Green functions are obtained by a recursive method specially suited to the study of one dimensional solids(4). In figure 3 we have plotted the calculated values of $|g_{oo}(E)|$ corresponding to these two cases for energies within the gap. It can be seen that as the soliton moves from infinity towards the coupling site, the bound level

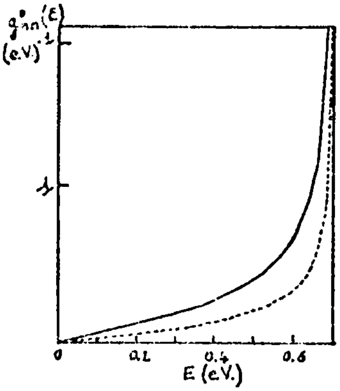

FIGURE 3 Diagonal element of the Green functions within the band gap. The upper curve corresponds to a chain with a soliton centered on the coupling site, the lower one to a chain with a soliton at infinity.

shifts from the edge of the gap towards its center. However, for realistic values of the strenght of the interchain coupling i.e $v \sim 0.04$ eV this shift is less than 1 meV, which is quite negligeable. It can thus be said that the bound levels introduced by the interchain coupling lie practically at the band edges. Indeed, we can expect that there exists a distribution of such interchain interactions along the chains which can thus give a continuum of such states.

To perform a more precise analysis of this effect, we study in what follows a simple model of a spatial distribution of interchain coupling.

## THREE DIMENSIONAL INTERCHAIN COUPLING

Consider a two dimensional squared lattice of periodicity c of idendical parallel chains of $(CH)_x$ which we assume for simplicity to be perfectly dimerized along the z direction. The electronic system is described by identical transfer integrals along the x and y directions, $t_\perp$ which we assume to be much smaller than the transfer integrals along the z direction.

It can be shown that the Green function corresponding to this lattice may be written as :(5)

$$G\,(E) = \sum_{k_x,k_y} G_o\left(E-2t_\perp\,(\cos k_x c + \cos k_y c)\right) \qquad (6)$$

where $G_o\,(E)$ is the one dimensional Green function and the summation runs over the transverse components of the wave vector in the 2D Brillouin zone which corresponds to the periodicity along the x and y directions.

The 3D density of states for such a lattice is thus :

$$N\,(E) = -\frac{2}{\pi}\sum_{kx,ky} \mathrm{Im}\; g^{o}_{nn}\left(E-2t_\perp(\cos k_x c + \cos k_y c)\right) \qquad (7)$$

For numerical calculations we choose $t_\perp = 0.04$ eV in accordance with the work of Grant and Batra(6). The summation in the 2D Brillouin zone was performed over 1024 points by the use of the special point method(7). The resulting density of states is shown in figure 4 where it can be compared with that of a perfectly dimerized one dimensional $(CH)_x$ chain. The main effect

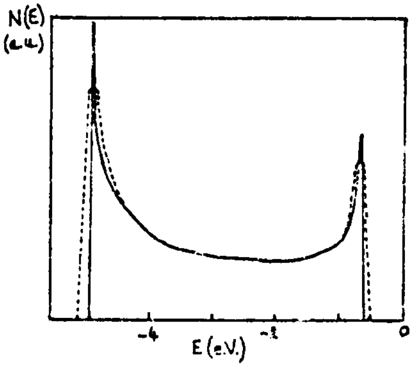

FIGURE 4 Densities of states for a perfectly dimerized chain :
—— : without interchain interactions
---- : with interchain interactions

of the three dimensionality is to broaden the band edges, to smear out the $(E)^{-1/2}$ singularity in the density of states and to reduce the gap.

## CONCLUDING REMARKS

In this work we have shown that a localized interchain coupling between two infinite one dimensional chains of polyacetylene induces four bound states whose energies lie practically at the band-edges. We then studied the influence of a two dimensional distribution of such interactions on the broadening of these edges. It may be of interest to study the influence of such interchain coupling on the semi-conductor-metal transition in $(CH)_x$. In order to get some insight into this effect, we considered a two dimensional infinite network of identical $(CH)_x$ chains where each one of these chains is constitued by a periodic lattice of solitons. The resulting density of states was calculated using equation (7) where $g_{nn}(E)$ is now the Green function for such a soliton lattice[8].

We then found that the closing of the gap between the soliton band and the two neighbouring valence and conduction bands occurs at a concentration of solitons $c \sim 5\%$ which compares rather favourably with the experimentally found value $c \sim 1\%$.

## REFERENCES

1. W.R. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. Lett. 42, 1698, (1979) ; Phys. Rev. B22, 2099 (1980).

2. M.J. Rice, Phys. Lett., 71 A, 152 (1979).

3. D. Vanderbilt and E.J. Mele Phys Rev B 22, 3939, (1980).

4. S.Y. Wu, C.C. Tung and M. Schwartz, J. Math. Phys. 15, 938 (1974).

5. J.P. Albert and C. Jouanin, unpublished results .

6. P.M. Grant and I.P. Batra, Sol. St. Comm. 29, 225, (1979).

7. D.J. Chadi and M.L. Cohen Phys. Rev. B 8, 5747 (1973).

8. J.P. Albert and C. Jouanin, in this issue.