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STUDY OF DISORDER IN POLYACETYLENE

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Abstract. In this work, we investigate the effects of disorder on the electronic states of polyacetylene. In effect, due to the impurities and variable environment, we would expect some fluctuations in both the self energies (diagonal disorder) and the hopping integrals (off-diagonal disorder). The consequences of each type of disorder and their relative importance are discussed.

I. INTRODUCTION

In recent years, many theoretical works (1) have been devoted to the study of the electronic properties of polyacetylene.

Polyacetylene, \((\text{CH})_x\), consists of weakly coupled chains of \((\text{CH})\) units forming a quasi one dimensional system. In fact, \((\text{trans})(\text{CH})_x\) shows usually a fibrillar morphology, it is poorly oriented and the doping is often non uniform.

The Hamiltonian of Su, Schrieffer and Heeger (SSH) (2) has been able to provide a successful description of many of its unusual properties. However, such a model is highly idealized and one should expect to have some difficulties when making a detailed comparison between theoretical works and experimental data. It seems thus interesting to study such departures of the real system from the SSH model in order to obtain their influence on the electronic properties of \((\text{CH})_x\). Such theoretical investigations have appeared (3-5), our intent in this work is to study systematically the effects on the electronic density of states of dimerized \((\text{CH})_x\) of two kinds of disorder on an infinite \((\text{CH})_x\) chain. The coherent potential (CPA) will be used as well as its extension to homomorphc clusters (HCPA). We adopt for this study the electronic part of the model SSH Hamiltonian.

\[
H = \sum_n c_n^+ c_n + \sum_{n,n+1} t_{n,n+1} (c_{n+1}^+ c_n + h.c)
\]

where the SSH values for the parameters have been used.

II. DIAGONAL DISORDER

That kind of disorder may be thought to arise due to the presence of impurities lying near the chains. The impurities can be described by a single atomic state hybridizing with the \(\pi\) orbital of the next-nearest carbon. The interaction of these states with the chain can then be modeled by shifting the self energy of the \(\pi\) orbital on the chain near the impurity by an energy \(\epsilon_0\) which depends on the details of the interaction. Because of the random distribution of impurities such shifts actually appear also at random in the diagonal elements of the hamiltonian. In order to obtain quantitative estimations of the consequences of that kind of disorder on the electronic density of states we calculate the averaged density of states:
\[ N(E) = -\frac{1}{\pi} \text{Im} \left( \text{Tr} \langle \langle G \rangle \rangle \right) \]

where \( G \) is the Green's function corresponding to the hamiltonian \( H, G = (\varepsilon - H)^{-1} \), and the double brackets denote an average over all the impurities configurations. The single site CPA has been used to obtain \( N(\varepsilon) \). In this approximation the averaged Green's function is replaced by the Green's function of an effective periodic medium

\[ \langle\langle G(\varepsilon)\rangle\rangle = (\varepsilon - H_{\text{eff}})^{-1} \]

where the effective hamiltonian \( H_{\text{eff}} \) is given as:

\[ H_{\text{eff}} = \sum_n c_n(\varepsilon) C^+_n C_n + \sum_{n,n+1} t_{n,n+1} (C^+_n C_{n+1} + \text{h.c}) \]

Here the self energy \( \sigma(\varepsilon) \) which characterizes the effective medium, is an energy dependent complex function which is determined by requiring that a single site embedded in the effective medium does not produce any scattering. The Green's function needed in the CPA calculation have been obtained by a recursive method specially suited to study one dimensional systems. The results obtained for that kind of disorder are sketched in Fig. 1.

Fig. 1 - CPA Density of states from the simple site impurities compared with the density of states of the perfectly dimerized chain. The two calculations are for \( \varepsilon_0 = 0.1 \). The shift induced by the impurity is \( \varepsilon = 0.1 \) eV (a); \( \varepsilon = 0.5 \) eV (b).

The parameters used in the calculation are the concentration \( c \) of impurities which has been taken equal to 0.1 and the self energy shift \( \varepsilon_0 = 0.1 \) eV (Fig.1a) and \( \varepsilon_0 = 0.5 \) eV (Fig. 1b). The only modifications on the unperturbed (perfectly dimerized chain) density of states afforded by the introduction of that kind of disorder are a shift of the whole density of states corresponding to the mean potential \( c \varepsilon_0 \) and a slight perturbation of the band edges corresponding to the broadening of the single impurity induced level. From these figures it can be said that for realistic values of the parameters corresponding to physically plausible situations, the perturbations introduced by the diagonal disorder on the electronic density of states are very weak.
III. OFF-DIAGONAL DISORDER

A second important consequence of the presence of an impurity or of a perturbed environment in the proximity of the chain should be an imperfect dimerization of that chain.

In the perfect dimerization case the hopping integral along the chain can only have two values $t_{2p,2p+1} = t$ and $t_{2p-1,2p} = t'$.

In the case of imperfect dimerization, we will assume that the hopping integrals are random variables characterized by probability distributions $p(t_{2p,2p+1})$ and $p'(t_{2p-1,2p})$ centered at the value corresponding to the perfectly dimerized chain. A convenient mean investigating the effects of such off-diagonal disorder is to divide the chain into identical (homomorphic) clusters and to apply the CPA formalism to each cluster (b). The self energies terms of the single site CPA theory appear now as matrices whose elements are obtained by a system of non linear coupled equations. As the complexity of these equations grows rapidly when increasing the number $n$ of sites inside the cluster only low $n$ values can be handled efficiently. Specifically $n = 2$ or $3$ is sufficient to study the effect of off-diagonal disorder on the electronic states of the perfectly dimerized chain.

The probability distributions used in the present work to simulate the random distribution of transfer integrals has been taken as:

$$p(t_{2p,2p+1}) = \frac{1}{3} (\delta(t_{2p,2p+1} - t - v) + \delta(t_{2p,2p+1} + t') + \delta(t_{2p,2p+1} - t + v))$$

(with a similar expression holding for $t_{2p-1,2p}$, changing $t$ and $v$ to $t'$ and $v'$): This choice corresponds to an equiprobability of finding three values of $t_{2p,2p+1}$. $t_{2p,2p+1} = t$ or $t + v$ or $t - v$. The homomorphic clusters used to describe the chain are depicted in Fig. 2 and the fluctuations $v$ or $v'$ of the hopping integral have been taken to be 0.1 eV and 0.15 eV.

Fig. 2 - Two examples of homomorphic partitions for a chain.

No correlations between the probability distributions have been included in our calculations.

In Fig. 3, we display the density of states so obtained. As for the precedent study of diagonal disorder it can be observed that the divergence at the band edges in smeared out. However the effect of the off diagonal disorder on the value of the gap is much more pronounced than in the diagonal disorder case. Fig. 3 shows in fact that the reduction of the gap may attain 0.4 eV for realistic values of the involved parameters. This figure shows that a set of three peaks appear at the band edge limiting the gap; this feature is a direct consequence of our choice for the probability distribution energies separating these peaks corresponding to the different values taken by the difference $t_{2p,2p+1} - t_{2p-1,2p}$.

The existence of such sharp structures in the density of states demonstrates the ability of the homomorphic cluster CPA for such studies on non diagonal disorder. It can also be noted that the results obtained here are independent of the model of homomorphic clusters we have chosen (2a or 2b).
Fig. 3 - Density of states vs energy near the gap computed by homomorphic clusters CPA. The values relative to a dimerised chain are those suggested by (SSH). The cluster is shown by Fig. 2a and the width of the probability density is 0.1 (a), and 0.15 (b).

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