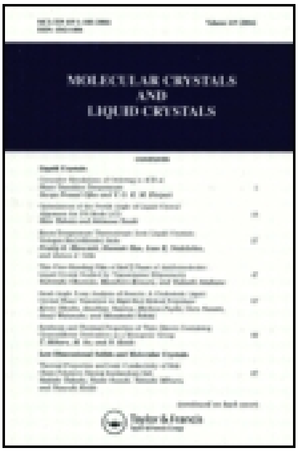

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EFFECTS OF INTERCHAIN INTERACTIONS ON THE LOCALIZATION OF DOPING INDUCED DEFECTS IN QUASI ONE-DIMENSIONAL SYSTEMS.

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Abstract The effects of interchain interactions and chain-dopant interactions in model systems of *trans*-polyacetylene are studied in detail. We find that a singly charged polaron is transverse, i.e., it is delocalized over more than one chain. In lightly doped *trans*-polyacetylene, the electronic wavefunctions associated with solitons are localized to a single soliton center only. At a critical doping concentration, however, the wavefunctions of the solitons become delocalized over several soliton centra as well as over several chains.

INTRODUCTION

Conjugated polymers are characterised as quasi-one-dimensional materials in which the interactions along the chains are considerably stronger than those between chains. Some properties of conjugated polymers are totally dominated by intrachain interactions. Calculations of these properties, e.g. the electronic structure and lattice vibrations, are therefore usually performed on a single-chain system. In particular, single-chain studies of doping induced states such as solitons in *trans*-polyacetylene have shown very good agreement with experimental data on multi-chain systems[1]. However, there are other properties of the polymers that can not be studied without taking the interchain interactions into account. Crystal packing effects and transport properties, for instance, are both dependent on interchain interactions. Experimental studies of the conductivity as a function of temperature in heavily doped *trans*-polyacetylene has shown that in some samples the conductivity approaches a finite, non-zero value as the temperature goes to zero (metallic behaviour) whereas other samples are essentially insulating at very low temperatures.[2] Obviously, the interchain interaction strength is of great importance for these observations and they determine if the electronic wavefuncitons are quantum coherent in three dimensions, which results in metallic conductivity, or if the conductivity is of hopping type between chains.

It is well known that the electron-phonon coupling favours localized excitations instead of ordinary band states in one-dimensional systems. In a quasi-one-dimensional system, such as conjugated polymers, the relation between the intra- and interchain coupling determines whether self-localization and the formation of gap states occurs or if the excitation can be described within the rigid band picture. As mentioned above, the soliton is an examples of such self-localized excitations which is stable enough to overcome the destabilizing interchain interactions. Polarons and bipolarons, however, have considerably smaller intrachain stabilisation energies and are therefore expected to be effected more by the interchain couplings. Emin[3] derived the following condition for stability of polarons: $t_\perp/t_\parallel < 12\xi^2$, where $t_\perp$ and $t_\parallel$ are the hopping integrals perpendicular and parallel to the chain direction, respectively, and ξ is the polaron half width (in units of the C-C spacing). Estimates of the anisotropy of conjugated polymers show that this condition is not fulfilled, i.e., the anisotropy is less than required to create a polaron. This result has been confirmed by explicit calculation on a three-dimensional *trans*-polyacetylene lattice[4] and is also supported by optical and magnetic data that fail to detect the properties of polarons predicted from single-chain calculations. Such properties are instead observed in samples of long polyene chains where matrix isolation techniques have been used in order to reduce the interchain coupling strength.[5] A high concentration of chain defects might also have the effect of reducing the interchain interactions enough to stabilize the intrachain polaron.[6]

Another important factor which strongly influences the properties of doping induced defects is the counterion. These ions are intercalated between polymer chains where they act as bridges that enhance the interchain interactions. Calculations of Cohen and Glick[7] on *trans*-polyacetylene showed that the enhancement is around a factor of 2 in the crystalline material. The heavily doped material, where the concentration of these type of bridges is large, is therefore best characterized as a three-dimensional (anisotropic) solid.[8]

Recently, Bussac and Zuppiroli[9] pointed out the importance of dopants in the context of interchain delocalization of polarons and bipolarons. They showed that for certain relations between the attraction strength of the counterion and the electron-electron repulsion, polarons and bipolarons are spread over several chains but remain localized in the vicinity of the dopant. The present work is closely related to this study, but instead of using a parametrized Hamiltonian we present results of *ab initio* calculations at the local spin density (LSD) level. Interchain and chain-dopant interactions are accounted for in a model system consisting of two polyene chains together with a sodium atom as the dopant agent. Because of the large computational efforts in solving the LSD equations, these studies involve a single doping induced polaron only. To treat the effects of counterions and interchain interactions in a more extended system we have used a semi-empirical method of calculation. These calculations are focused on the delocalization of soliton wave functions both along the individual polymer chains and between chains.

METHODOLOGY

Calculations on different two-chain system with a maximum total number of carbon atoms of 16 were performed using the local spin density (LSD) approximation with the Vosko-Wilk-Nusair analytic expressions for the exchange-correlation potential[10]. A Gaussian type basis set of split valence quality, optimized for density functional purposes, and including d-type polarization functions for the heavy atoms was used. The calculations were performed using the DGauss programme[11] and include full geometry optimizations as well as determination of the charge and spin densities.

Calculations on larger systems than those that are possible to study at the *ab initio* level have been performed by employing the semi-empirical PM3 method[12] contained in the MOPAC programme package[13]. These calculations involve studies of intra- and interchain interactions between two sodium doped *trans*-polyacetylene chains. Full geometry optimizations are performed in order to determine the ground state geometrical and electronic structure of these extended systems .

RESULTS AND DISCUSSION

A system of two polyene chains, $C_{10}H_{12}$ and C_6H_8, is studied in three different situations: a) with a sodium atom intercalated between the chains, b) with a sodium atom placed in close contact with the $C_{10}H_{12}$ chain only, and c) negatively charged but without the sodium atom present. The calculated spin densities for these three cases, as obtained from LSD calculations including full geometry optimizations, are shown in Fig. 1. The differences between case a and b are clear, when the sodium atom is placed between the chains, the spin density is spread over both polyenes. No spin density is observed on the sodium ion in this case, i.e., the electron spin has been completely transferred from the sodium atom to both the polyene chains. In the terminology introduced by Bussac and Zuppiroli[9], this corresponds to a transverse polaron. If, instead, the sodium atom is placed in such a way that it interacts exclusively with the $C_{10}H_{12}$ chain, the spin density is localized to this chain only with some minor contribution also on the sodium ion (Fig. 1b). In the last case where a single electron is added to the system, without the presence of a counterion, the spin is spread over both chains even though the major part resides on the longer polyene. This shows that the counterion alone is not responsible for the creation of the transverse polaron, the interaction between the two polyene chains is strong enough to destabilize the single-chain defect. The optimized distance between the chains is slightly shorter in the absence of the sodium ion, which leads to stronger interchain interactions in that case. The intercalated counterion therefore introduces two competing effects; one is to separate the chains which decreases the interchain interaction,

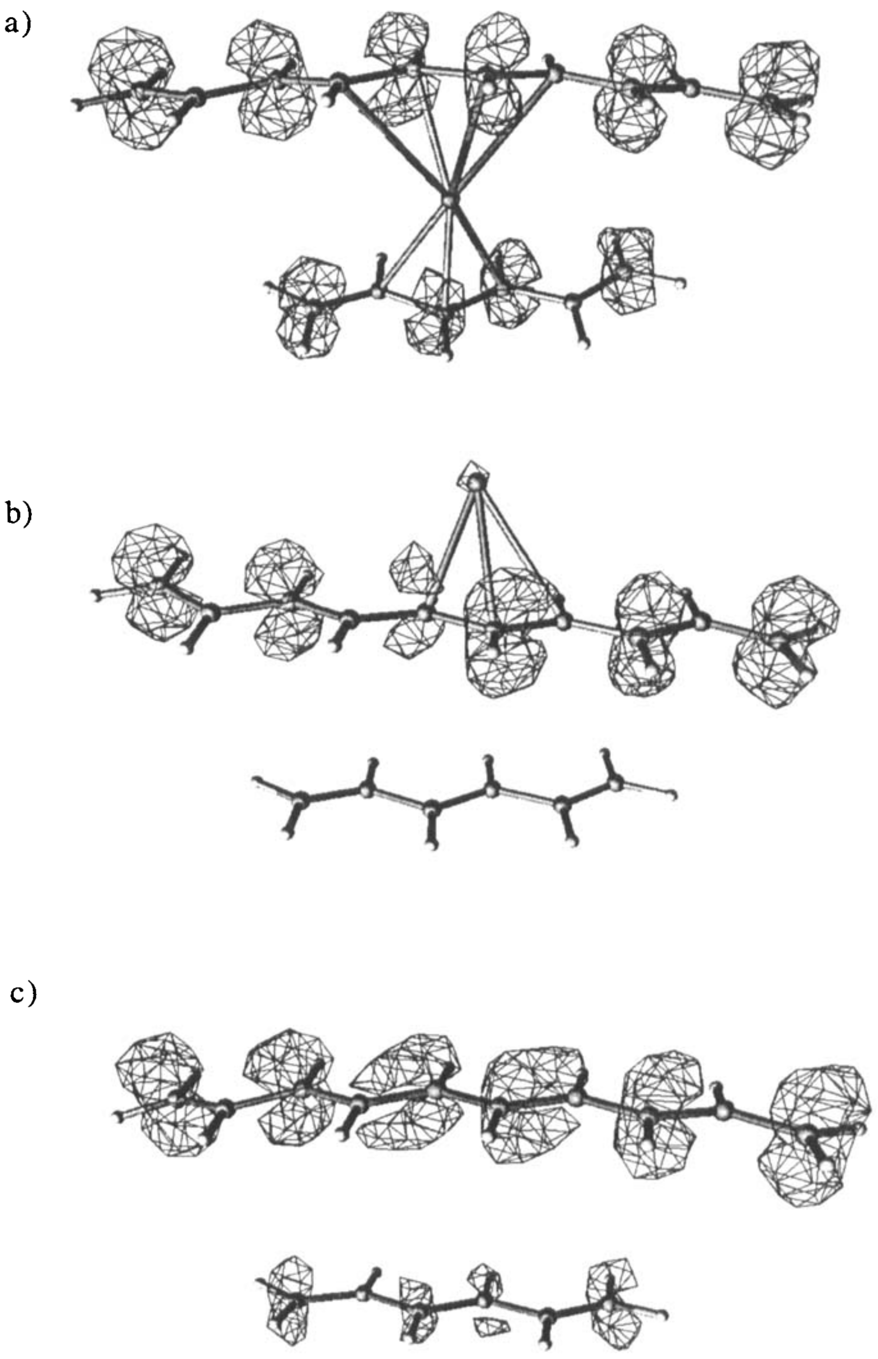

FIGURE 1 Spin density in the $C_{10}H_{12}$, C_6H_8 system a) Na between the chains, b) Na close to $C_{10}H_{12}$ only, and c) singly charge and without Na.

the other is to act as a bridge between the polyene chains and in this role enhance the interaction between these two systems. For the short systems studied here, the net effect of these interactions is an increase in the interchain interactions as indicated by the difference between the spin distributions in Figs. 1a and 1c. For more extended systems, where the delocalization is not limited by the chain length, a difference in the localization length is expected due to the Coulomb attraction between the polaron and the counterion. The result obtained in Fig. 1b shows more clearly the importance of the counterion for the electronic structure. Obviously, in this case the attraction strength from the "external" sodium ion dominates over the interchain interaction strength and creates a single-chain polaron neighboring the counterion.

Now we turn to the studies of the interaction between defects, in this case solitons on model systems of *trans*-polyacetylene. In order to study the intrachain interactions we perform (semi-empirical) calculations on a long polyene chains including two sodium-like counterions[13] and two extra electrons. Due to the Coulomb attraction between the negative charge on the polyene chain and the positive counterion, the soliton centra appear next to the counterions. By changing the position of these ions, we are able to study the interaction between the two solitons (soliton and antisoliton) as a function of their separation. The soliton and the antisoliton are located symmetrically around the center of the system. Therefore, we get information about the interaction between these two defects by comparing the coefficients in the LCAO expansion of the next highest occupied molecular orbital (HOMO-1) on the sites left of the center (sites belonging to the soliton) with those to the right (antisoliton). The HOMO-1 corresponds to the bonding orbital formed upon interaction between the wavefunctions of the soliton and the antisoliton. The fractional state density on the soliton (antisoliton) is defined as the sum of the squared amplitudes of the LCAO coefficients left (right) of the center. These two quantities are shown in Fig 2 as a function of the separation between the counter ions (D). In order to avoid degeneracy between the soliton levels, which causes delocalization even at infinite separation between the soliton and the antisoliton, we introduce a difference (disorder) in the strength of the two dopant potentials. This difference results in an energy split (ΔE) of the two soliton levels in the limit of zero overlap. The two sets of data that are shown in Fig. 2 correspond to ΔE=0.1 eV and 0.2 eV, respectively, for a non-interacting soliton-antisoliton pair.

The onset of intrachain soliton-antisoliton interactions occurs at a separation of around 25 sites (ΔE=0.1 eV), which correspond to a doping level of 4%. The delocalization of the soliton wavefunction over both soliton sites becomes important below D≈20, i.e. for doping levels above 5%. This value is very close to the critical doping concentration for which onset of the metallic properties are observed[14]. This point is discussed in more detail below in connection with studies of interchain interaction in the heavily doped system.

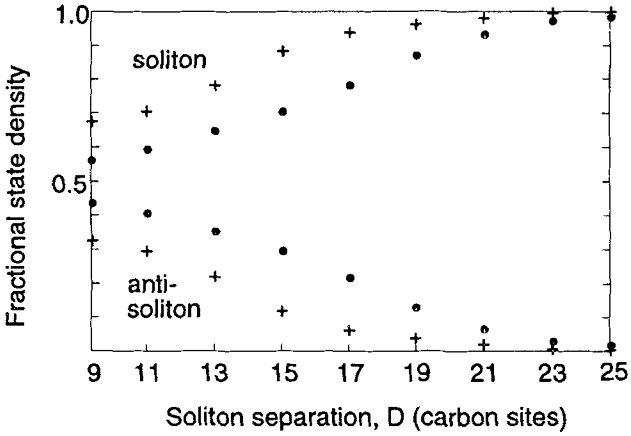

FIGURE 2 Fractional state density (see text) localized to the soliton and the antisoliton as a function of the separation between the soliton and the antisoliton.

When two solitons on neighboring chains are brought close together there is a possibility for interchain delocalization of the soliton wavefunctions.[8] In order to quantify this observation, we study two polyene chains, each containing 29 carbon atoms. The chains are placed 4 Å apart in a similar arrangement as that shown in Fig. 1. Two sodium-like counterions are intercalated between the chains and the polyene chains are charged by two electrons. Optimization of this system results in a structure where each chain contains one soliton, separated in the direction along the chains by a distance controlled by the positions of the counterions. Since there is only one soliton per chain, this system applies to low doping levels only. Similar to the studies of the intrachain localization, we have to break the symmetry in order to avoid degeneracy between the soliton levels.

The state density of the HOMO-1 on each chain separately is calculated as a function of the separation between the counterions (L). At a separation of 8 carbon sites or more along the chain direction, more than 99% of the state density remains on a single soliton center. If the separation is reduced to 4 sites, 88% is still localized to one soliton center. A smaller separation is unrealistic since it results in a high energy state due to electrostatic repulsion between the counterions. Clearly, as compared to the case of intrachain interactions, the solitons have to be very close in order for the wavefunctions to be delocalized over both defects. This result shows that at low doping levels, where the approximation of isolated solitons on each chain is valid, the soliton states are localized to a single soliton center only.

The model system of one single soliton on each of the two chains is not adequate for a heavily doped system in which the intrachain interaction between solitons is strong, i.e., above 5% doping level (see Fig. 2 above). Since in this case, the soliton wave-functions are extended over several soliton centra, there is a formation of a soliton band in the electronic band structure. Therefore, even in the presence of a (weak) disorder in the soliton potential, there is a possibility of near degeneracy between states on different chains, a situation which favours interchain delocalization. In order to study this interplay between intra- and interchain interactions, we have to consider a model system with several solitons on each chain. The system we have chosen consists of two chains, $C_{43}H_{45}$ and $C_{28}H_{30}$. The longer chain is doped by three sodium ions and the shorter by two sodium ions, i.e., the chains contain three and two solitons respectively. The separation between neighboring solitons within the chain is set to 15 CH-units, corresponding to a doping level of 6.67%. This separation is chosen in order to ensure delocalized along the chains (see Fig. 2). The counterions that determine the positions of the solitons on the short chain are placed between the counterions associated with the long chain (see Fig. 3). The separation along the chain axis between solitons on different chains is thus 7-8 CH-units, i.e. well into the regime of localization to a single chain (see above). However, since in this case the soliton wavefunctions are delocalized along the chains, the situation is quite different.

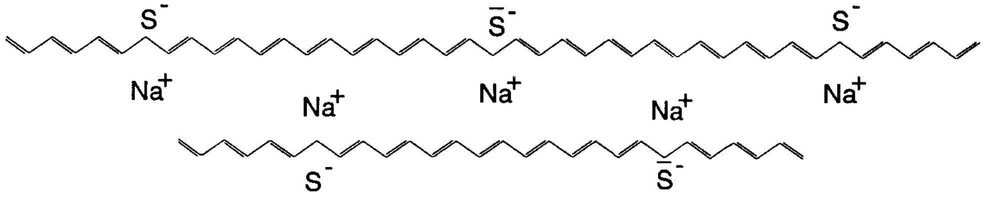

FIGURE 3 Sketch of the $(C_{43}H_{45})^{3-}(Na_3)^{3+}$ $(C_{28}H_{30})^{2-}(Na_2)^{2+}$ system.

In contrast to the case of a single soliton on each chain, we find for the system sketched in Fig. 3 that the soliton wavefunctions are delocalized over both chains. Obviously, when the doping concentration exceeds a critical value which allow for sufficient intrachain delocalization of the soliton wavefunctions, the interchain interaction strength is strong enough to cause delocalization as well. This result is in agreement with the criterion for interchain delocalization proposed by Firsov[15]: $t_{\perp C} \cong \frac{0.3\hbar}{\tau} = \frac{0.3\hbar v_F}{\ell}$. The mean free path of an electron in a soliton state localized to a single defect ($\ell \approx 15$) results in a value of the critical value of the interchain hopping strength ($t_{\perp C}$) which is far above the realistic interchain hopping strength. However, the transition to delocalized states with increasing doping level (or reduced separation between solitons, see Fig. 2) increases the mean free path of the electrons and thus lower $t_{\perp C}$. At some critical doping level, $t_{\perp C}$ becomes equal to the actual interchain hopping strength and interchain delocalization can occur. The implications of this result in connection with the transition into a metallic state of heavily doped *trans*-polyacetylene are obvious. The broadening of the electronic bands due to delocalization of the soliton wavefunctions reduces, or closes, the gap around the Fermi energy. The experimental observation of a first order transition into a metallic state for sodium doped *trans*-polyacetylene[14] is fully consistent with the results of this study.

In summary, the localization properties of doping induced polaron and soliton states in *trans*-polyacetylene are studied in detail. From *ab initio* calculations it is concluded that the counterion is important for the localization properties of polarons. In the case when the counterion is intercalated between two polymer chains, the polaron is spread over both chains. Semi-empirical calcuations on large polymeric systems show that the soliton wavefunctions are localized to a single chain at low doping levels. For the heavily doped sample, however, the states are delocalized over several chains.

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