Stabilization of bipolarons in *trans*-polyacetylene by interchain coupling*

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Bipolarons are unstable on single chains of a degenerate polymer dissociating into free solitons and anti-solitons. Stabilization will occur as a result of electronic coupling between π orbitals on neighbouring chains, however. Numerical calculations are reported which estimate the spatial extent of a bipolaron which has been stabilized by interchain coupling.

(Keywords: *trans*-polyacetylene; bipolarons; SSH; interchain coupling)

INTRODUCTION

Considerable advances in the understanding of the electronic properties of conducting polymers have been made using one-dimensional models, the one due to Su, Schrieffer and Heeger (SSH)[1,2] being that most widely used. As more detailed experimental results on crystalline samples appear however, increasing attention is being paid to the effect of coupling between the chains.

Early studies[3,4] of three-dimensional effects in *trans*-polyacetylene considered a pair of chains described by the SSH Hamiltonian with the addition of a simple electronic hopping term between the π orbitals on the two chains. The authors found that an antiparallel bond arrangement (double bonds on one chain adjacent to single bonds on the other) was energetically favoured over the parallel configuration (like bonds together). Non-linear excitations were also considered and it was shown that, for two solitons on different chains, there is confinement in order to minimize the length of the parallel configuration. The result is essentially independent of the charge state of the soliton because the electronic gap state remained unsplit independent of the soliton separation.

A later extension of this work by Baeriswyl and Maki[5] demonstrated that a parallel bond arrangement can be favoured if the hopping term alternates in sign along the chain. Further aspects of interchain hopping within a SSH type of model have been considered in other papers[6–9].

In the work cited, the binding energy of solitons located one on each chain has been calculated. For a soliton and anti-soliton on the same chain the gap state is split and the behaviour depends on the charge state of the pair. For a single chain, only polarons (bound soliton anti-soliton pairs with a single electron or hole) are stable. Doubly charged excitations (bipolarons) are unstable and dissociate into free charged solitons. Of course, in polymers with non-degenerate ground states, bipolarons are stable.

In a three-dimensional environment one would expect bipolarons to be stable even in degenerate polymers. The tendency to dissociate in a single chain is opposed by an energy cost that increases with the separation of the soliton/anti-soliton pair. This arises from the resulting unfavourable bond configuration. The balance will determine the size of the bipolaron.

In this paper we report some results of numerical calculations on bipolarons in a chain which is coupled to another containing no non-linear excitation. We use the SSH model with a simple inter-chain hopping and perform static energy minimizations for long chains. Chains of length greater than about 100 units are sufficient for approximating the behaviour of an infinite system.

MODEL AND CALCULATIONS

The calculations are based on the static part of the SSH Hamiltonian for a pair of chains with a simple interaction term between them

$$H=-\sum_{j,n}[t_0+\alpha(u_{j,n}-u_{j,n+1})]a^{\dagger}_{j,n+1}a_{j,n}-t_1\sum_{n}a^{\dagger}_{1,n}a_{2,n}+\text{h.c.}$$
$$+(K/2)\sum_{j,n}(u_{j,n+1}-u_{j,n})^2 \qquad (1)$$

where $u_{j,n}$ is the displacement of the unit at site n on chain j ($j=1,2$) and $a^{\dagger}_{j,n}$ and $a_{j,n}$ are the corresponding electron creation and annihilation operators.

For a particular configuration $\{u_{j,n}\}$ the eigenvalues for finite chains are found by matrix diagonalization. We used chains with an even number of sites (N per chain) and periodic boundary conditions to eliminate end effects. We wish to study bipolarons so total energies E are calculated for systems with $2N+2$ electrons. The symmetric energy spectrum implies that the total energies for $2N-2$ systems (relevant to hole bipolarons) are identical.

The minimum energy configuration is obtained iteratively by calculating the set of $\{\partial E/\partial u_{j,n}\}$ via $2N+1$ matrix diagonalizations and then improving the configuration $\{u_{j,n}\}$ with the trivial algorithm $u_{j,n}\rightarrow u_{j,n}+\delta\,\partial E/\partial u_{j,n}$ with an empirically chosen δ.

Given a suitable initial configuration of displacements, the convergence is fairly rapid. A convenient initial form

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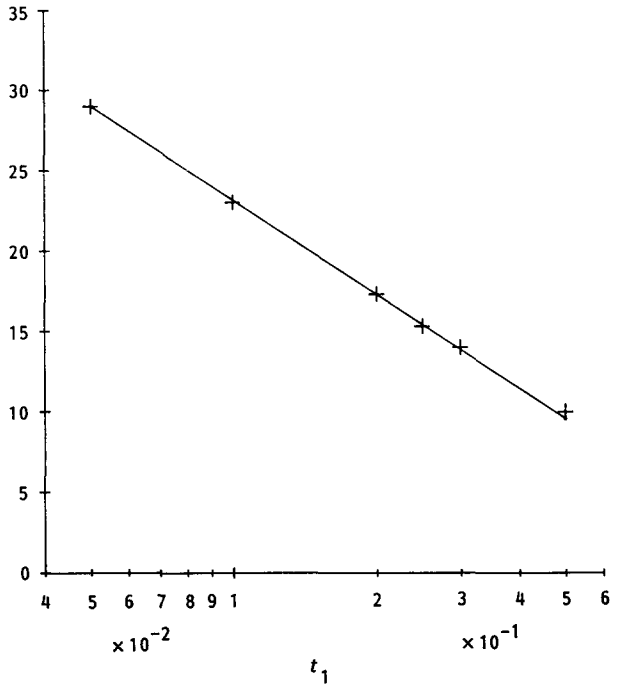

Figure 1 Measure of spatial extent l (lattice spacings) of bipolaron for a range of values of interchain coupling t_1 (eV)

from which to start iterating was found to be

$$u_{1,n}=(-1)^n u_0\begin{cases}-\tanh[(n-n_1)/\xi] & n<n_0\\ \tanh[(n-n_2)/\xi] & n\geqslant n_0\end{cases} \quad (2a)$$

$$u_{2,n}=-(-1)^n u_0 \quad (2b)$$

where $n_0=(n_1+n_2)/2$. Optimum values of n_1 and n_2 were found by inspection and (n_2-n_1) represents the starting approximation to the size l of the bipolaron. Calculations were performed on chains of various lengths. It was found that $N=128$ was of sufficient size to simulate an infinite system.

RESULTS

The following frequently quoted values for the parameters were used: $t_0=2.5$ eV, $\alpha=5.6$ eV Å^{-1}, $K=40$ eV Å^{-2}. In equation (2), $u_0=0.04$ Åand $\xi=8$ Å provided good initial values for the iteration. The size l of the bipolaron for several values of t_1 was calculated. The size is defined as the number of lattice spacings between the two points on the chain where $(-1)^n u_{1,n}$ changes sign after convergence to the energy minimum is attained. A plot of l as a function of $\ln t_1$ is shown in *Figure 1*. As expected the bipolaron is stabilized by the interchain coupling and the confinement increases with increasing t_1.

The behaviour can be understood simply as follows. The total energy can be written approximately in the form

$$E=E_0+A\exp(-l/\rho)+Bt_1^2 l \quad (3)$$

The second term arises from the overlap effects of the soliton/anti-soliton pair and is what causes the dissociation on the single chain. The third term comes from interchain coupling in second order perturbation theory and a soliton/anti-soliton separation of length l represents an energetically unfavourable parallel bond arrangement of that length. The value of l for energy minimization is given by

$$l=\rho[\ln(A/B\rho)-2\ln t_1] \quad (4)$$

It can be seen that *Figure 1* follows equation (4) very well.

From the slope and intercept of *Figure 1* we obtain a value of ρ of 4.5 (lattice spacings) and, for the ratio A/B, a value of 8.8 eV^2. B was obtained by examining the energy of the system when the soliton/anti-soliton pair was held fixed at large l. The second contribution to equation (3) is negligible and equation (2) is an accurate representation of the displacements in this limit. We obtain the following values of B and hence A of 0.125 eV^{-1} and 1.1 eV, respectively.

The calculations[3,4] for single solitons in each chain would lead us to infer that B is equal to $(\pi t_0)^{-1}$, which agrees with our estimate to within numerical accuracy.

CONCLUSIONS

We have demonstrated quantitatively the stabilization of bipolarons that results from interchain coupling. Note that polarons are stable anyway and the interchain coupling will produce little modification in their case. In the earlier literature values of t_1 of 0.1 eV were quoted which, from our calculations, would produce a bipolaron size of about 23 lattice spacings. In a full three-dimensional environment with four neighbouring chains instead of one, the energy in equation (3) would have B replaced by $4B$, which would produce an additional confinement in equation (4) of $-\rho\ln 4$. For $t_1=0.1$ eV, this reduces 23 to 17.

Recent experiments[10] have cast doubt on the assertion that the antiparallel bond arrangement is the ground state. Baeriswyl and Maki[5] have demonstrated how this observation can be reconciled with an extended SSH picture. The numerical procedure described here is easily extended to encompass this more complex model and work is underway to investigate this. However complex the details, the description of bipolaron confinement in terms of the competing effects as formulated in the asymptotic limit by equation (4) should be adequate.

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