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INTER-IMPURITY INTERACTION IN DOPED CONJUGATED POLYMERS: TWO IMPURITY PROBLEM AND DEPENDENCE ON IMPURITY-POTENTIAL FORMS

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Abstract Effects of inter-impurity interaction in conjugated polymers are numerically investigated. The Su-Schrieffer-Heeger (SSH) hamiltonian is used for the polymer chain. There are two acceptor-type long-ranged impurities, with anisotropic dielectric constants and a screening factor. Direct inter-impurity repulsion is taken into account. Impurity arrangements as well as lattice and electron configurations are determined so as to minimize the total energy. Impurity clustering occurs when the range of the impurity potential is long enough. Impurities are isolated each other when the range becomes shorter. In order to look at how the clustering would be observed, optical absorption is calculated. There exists only one mid-gap absorption peak. This is the consequence of the strong impurity potential.

INTRODUCTION

Doping of conjugated polymers such as polyacetylene greatly effects on physical properties. An electronic structure changes from an insulator-like one to a metallic one, as the doping proceeds. As the mechanism has not been established yet, it is quite important to know doping effects on lattice and electronic structures.

Data of X-ray analysis[1] seem to have established ordered arrangement of polymer chains and dopant columns, in the perpendicular direction of chains. However, configuration of the dopants in the chain direction has not been well observed: most of the X-ray data lack information. Thus, disordered models might be a good starting point. We have studied electronic states using this concept.[2]

On the other hand, there is another possibility that some correlations may exist in dopant arrangements. Cohen and Glick[3] have first pointed out possible impurity clustering due to inter-impurity interactions. We have studied dopant configura-

tions in detail,[4] by the extended Peierls-Hubbard model. It has been reported that a trapped bipolaron state is stabilized due to soliton-dopant interactions for any values of Coulomb interactions in the chain. However, direct experimental evidence for the clustered configuration is lacking now. Therefore, it is much necessary to investigate theoretically whether the clustering is realistic or not. In particular, impurity-potential forms may affect the result. In this report, we investigate two-impurity problem and calculate impurity arrangements for various parameters of the impurity potential.

MODEL AND FORMULATION

The SSH model,[5]

$$H_{\rm SSH} = -\sum_{n,s}(t_0 - \alpha y_n)(c^{\dagger}_{n+1,s}c_{n,s} + \text{h.c.}) + \frac{K}{2}\sum_n y_n^2, \tag{1}$$

is studied with impurity terms,

$$H_{\rm imp} = \frac{e^2}{\varepsilon|n_1 - n_2|a} + \sum_{n,s} V_n c^{\dagger}_{n,s}c_{n,s}, \qquad V_n = \sum_{i=1,2}\frac{e^2 e^{-\beta|n-n_i|}}{\varepsilon[(n-n_i)^2a^2 + \gamma d^2]^{1/2}}. \tag{2}$$

In Eq. (1), t_0 is the hopping integral of the undimerized system; α is the electron-phonon coupling; y_n is the bond variable; $c_{n,s}$ is an annihilation operator of a π-electron; K is the spring constant. There are two acceptor-type impurities. In Eq. (2), the first term represents the repulsive interaction between impurities and the second term is the impurity-potential acting on π-electrons. The quantities e is the unit charge; ε is the dielectric constant measured over the sample; a is the lattice constant; d is the perpendicular distance between the impurity center and the chain; n_1 and n_2 are coordinates of impurity centers, assumed to be integers for numerical simplicity. The potential used in Ref. 4 is generalized to include two arbitrary parameters, β and γ. The factor β indicates the possible screening effect by π-electrons; the similar quantity has been introduced in the screened-Ohno potential.[6] The quantity γ is the dielectric constant parallel to the chain divided by the perpendicular one ε. The dielectric constant in the chain direction is not well known; the value used in Ref. 4 is only a theoretical estimation. Therefore, we change it arbitrary.

The system size is $N = 100$, which is a typical chain length. The electron number is $N_{\rm el} = N - 2 = 98$ due to two acceptors. Periodic boundary conditions are assumed. For given impurity positions, bond variables and electronic wave functions are determined by the method used in previous papers.[2] For parameters, we use $t_0 = 2.5$eV, $\alpha = 4.1$eV/Å, $K = 21$eV/Å^2, $e^2 = 14.3$eV/Å^2, $\varepsilon = 2.5$, $a = 1.22$Å, and $d = 2.4$Å.

IMPURITY ARRANGEMENTS

Fig. 1 shows the total energy of the system as a function of $\Delta n \equiv |n_1 - n_2|$. We specially take $\gamma = 5.0$ and $n_1 = 40$, here. When $\beta = 0.1$, there is a minimum at $\Delta n = 5$. The energy increases as Δn further grows. When $\beta = 0.2$, there are two minima. One minimum at $\Delta n = 6$ is stable, and the other at $\Delta n = 50$ is metastable. When $\beta = 0.3$, there is one minimum at $\Delta n = 50$. The data indicate that impurities cluster as far as β is small enough. They separate each other when β becomes larger. This variation is due to the decrease of the impurity-potential range with increasing β. The inter-impurity separation of the solution with the clustering is the order of the coherence length.[4] This is the consequence of the fact that the attraction between soliton-impurity pairs is effective only when Δn is the order of the coherence length.

Fig. 2 is a phase diagram on a β-γ plane, which shows whether impurities cluster or not. The filled circles indicate parameters for which impurities cluster. They only exist in the region of small β and γ. This comes from the fact that the impurity range is so long that the attraction between soliton-impurity pairs overcomes the repulsions between solitons and between impurities.

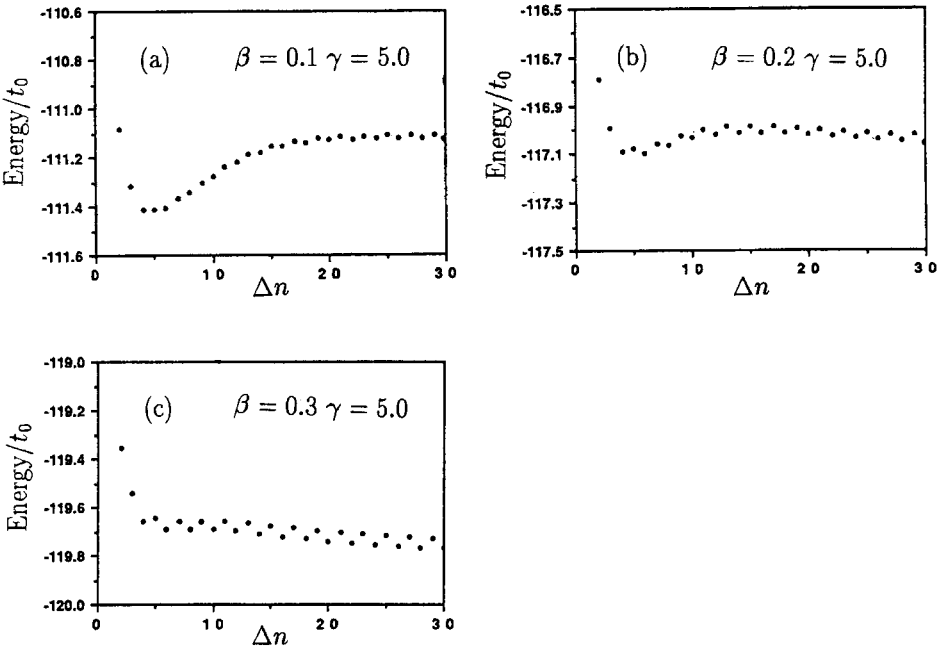

FIGURE 1 Total energy of the system for $\gamma = 5.0$ with (a) $\beta = 0.1$, (b) $\beta = 0.2$, and (c) $\beta = 0.3$. The abscissa is Δn.

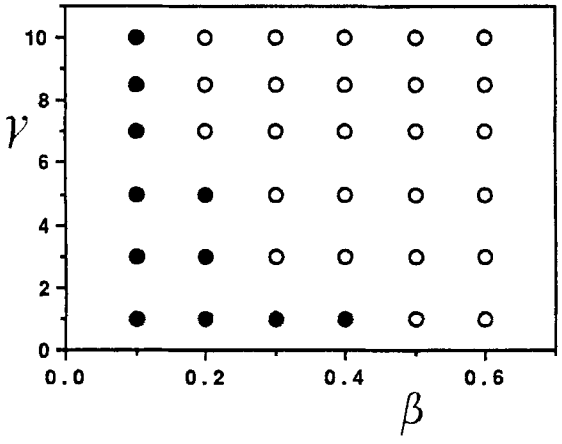

FIGURE 2 The phase diagram of the impurity arrangements. The filled and open circles are for the clustered and isolated impurities, respectively.

LATTICE AND ELECTRON CONFIGURATIONS, OPTICAL ABSORPTION

Fig. 3 shows typical lattice and electron configurations, where parameters are $\beta = 0.1$, $\gamma = 5.0$, and $\Delta n = 5$. Two solitons are trapped within the distance of the coherence length and form a bipolaron state. A bipolaron is an unstable excitation in the impurity-free system, but it is stabilized due to soliton-impurity interactions. The electron distribution is determined mainly by the impurity-potential form.

In order to see dynamical properties, we calculate optical absorption. Fig. 4 is a typical data of the solution shown in Fig. 3. Note that we use the Lorentzian broadening of the width $4t_0/N$. The main peak in the region $\omega > 0.5t_0$ is due to the charge excitation between the valence and conduction bands. The localized peak around $\omega \sim 0.3t_0$ reflects the presence of one localized level in the Peierls gap. Two

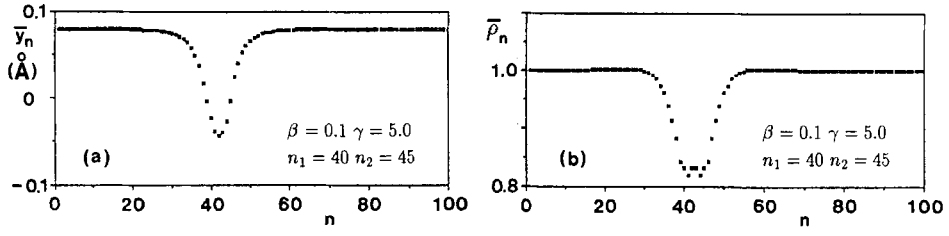

FIGURE 3 A stable solution for $\beta = 0.1$ and $\gamma = 5.0$: (a) the order parameter and (b) the electron density.

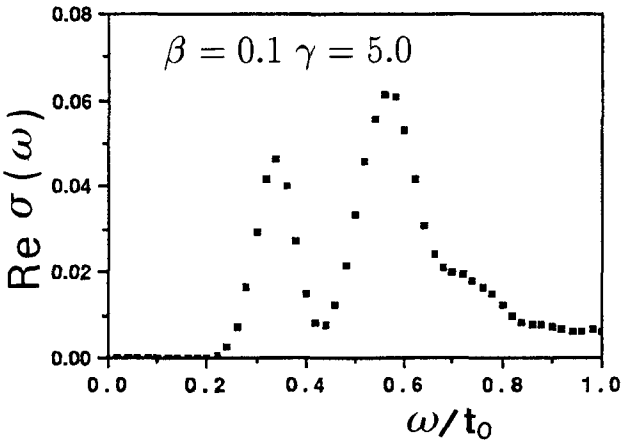

FIGURE 4 Optical absorption for $\beta = 0.1$ and $\gamma = 5.0$.

localized levels of an impurity-free bipolaron move for the higher-energy direction, due to the strong impurity potentials. One is absorbed by the conduction band, and the other remains in the gap. The similar property has been reported in Ref. 7. This property persists even if Coulomb interactions among π-electrons are taken into account.[4]

CONCLUDING REMARKS

Impurity clustering occurs in the small-β-γ region of the phase diagram. In recent articles, Conwell, Mizes, and Jeyadev[8] used $(\beta, \gamma) = (0, 4.6)$, and Takahashi and Fukutome[7] assumed $(\beta, \gamma) = (0.086, 0.286)$. Two sets lie in the region where the clustering is realized. The present calculation corresponds to 2% doping. Even though the clustering would hardly occur when N is larger (impurity concentration is smaller), there would be a good possibility that the impurity-clustering takes place in real samples. Therefore, our data of the optical absorption would be helpful.

The system doped with a divalent ion would be effectively regarded as a two-impurity system. The recent experiment by Kaufman et al.[9] suggests that a pair of charged solitons might be formed around a dopant. Then, the present calculation can be generalized to a system with a divalent dopant.

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