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Singlet and triplet excitons in conjugated polymers

Shuji Abe
*Electrotechnical Laboratory, Umezono, Tsukuba 305, Japan**
and Institut für Physikalische Chemie, Johannes-Gutenberg-Universität, 6500 Mainz, Federal Republic of Germany

J. Yu and W. P. Su
Department of Physics, University of Houston, Houston, Texas 77204-5504

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Exciton states in conjugated polymers are theoretically studied in the Su-Schrieffer-Heeger model supplemented by long-range Coulomb interactions. The relationship between exciton energies and basic interaction parameters is clarified, demonstrating the special nature of one-dimensional excitons. The binding energies of the lowest singlet and triplet excitons depend sensitively upon the on-site Coulomb energy. Relevant experiments in polydiacetylene can be explained by the present model using moderate interaction strength.

I. INTRODUCTION

Much effort has been devoted to the understanding of the electronic structure of conjugated polymers,[1] which are a type of one-dimensional semiconductor. In the last decade, the role of Coulomb interactions between electrons has been a subject of discussions concerning the nature of the ground state[2] as well as excited states.[3] Although most of the discussions have focused upon electron correlation originating from the Hubbard on-site Coulomb energy, the long-range part of Coulomb interactions can also play an important role in excited states through the formation of excitons—a well-known effect in semiconductors and insulators. The purpose of this paper is to discuss theoretically the exciton effect in conjugated polymers.

Experimentally, the significance of excitons in conjugated polymers has been recognized for some time in a class of materials known as polydiacetylene.[4-6] The optical absorption spectrum[7] of polydiacetylene is characterized by a strong peak at about 2 eV (the exact energy depends on the detailed structure of the backbone chain as well as on the kind of side chains). Initially, there were discussions about whether the absorption peak is either due to excitons or due to the van Hove singularity of the one-dimensional band-to-band absorption spectrum.[7] The clear observation of phonon side bands[7] and resonance Raman scattering[8] in single crystals led Bloor *et al.*[7] to suggest that the absorption is due to excitons. Since then, many optical experiments have been carried out which have supported the exciton interpretation. The redshift of the absorption peak under electric field—a Stark effect well known for excitons—has been observed.[9,10] More recently, the intensity dependence of the refractive index has been measured and successfully explained by the phase-space filling model originally developed for excitons confined to quantum wells.[11] Thus, the exciton picture in polydiacetylene has been rather well established at least from the experimental point of view.

A few calculations on excitons in conjugated polymers exist in the literature.[12-17] They commonly indicate that the exciton has an intermediate character between Frenkel and Wannier exciton, which can be understood as a characteristic feature of one-dimensional Wannier excitons in Peierls semiconductors.[18] Besides this qualitative agreement, there are discrepancies in the exciton energies between the calculations. Obviously the exciton energies depend on the interaction potential used in the calculation. In the present paper we report a systematic study of exciton states in conjugated polymers by examining the dependences of the exciton energies on relevant interaction parameters. This study also provides a foundation for further calculations on the nonlinear optical properties of conjugated polymers.[19]

II. MODEL

We start with the tight-binding Hamiltonian of the Su-Schrieffer-Heeger model,[20] which is a standard model for conjugated polymers:

$$H_0 = -\sum_{n,s} t_{n+1,n}(C^\dagger_{n+1,s}C_{n,s} + C^\dagger_{n,s}C_{n+1,s}) , \tag{1}$$

where $C^\dagger_{n,s}$ are creation operators for electrons at site n with spin s. The nearest-neighbor transfer energies $t_{n+1,n}$ (>0) depend on the bond lengths. Since we do not consider electron-phonon coupling in the present paper, we assume that the system is already Peierls distorted so that the transfer energy $t_{n+1,n}$ is modulated as

$$t_{n+1,n} = t - (-1)^n \delta t . \tag{2}$$

This modulation induces a Peierls gap $4|\delta t|$ in the one-electron spectrum. A part of the modulation δt can also be considered as the symmetry-breaking term for systems with nondegenerate ground states. In polydiacetylene, there is also an additional modulation with the period of four atoms.[21] Although it is straightforward to take this into account, we consider here the simpler dimerized system, so that the model has as few as possible parameters yet contains the essential physics. This is permissible because we are primarily interested in the states near the semiconducting gap whose nature is mostly determined by the modulation of Eq. (2).[22]

We perturb the Hamiltonian H_0 with electron-electron Coulomb interactions:

$$H = H_0 + H_{e\text{-}e} \; , \tag{3}$$

$$H_{e\text{-}e} = \sum_{n} V_{n,n}\rho_{n\uparrow}\rho_{n\downarrow} + \tfrac{1}{2}\sum_{n}\;\sum_{n'\,(\neq n)}\;\sum_{s,s'} V_{n,n'}\rho_{n,s}\rho_{n',s'} \; , \tag{4}$$

where $\rho_{n,s} \equiv C^{\dagger}_{n,s}C_{n,s} - \frac{1}{2}$, where $-\frac{1}{2}$ ensures charge neutrality. We assume that the interaction potential $V_{n,n'}$ in Eq. (4) is translationally invariant, i.e., $V_{n,n+i} \equiv V_i$. Although the formulation presented in the next section allows any form of V_i, we use a simple model in the actual calculations:

$$V_{n,n+i} \equiv V_i = \frac{V}{|i|} \quad (\text{with } i \neq 0) \; , \tag{5a}$$

$$V_{n,n} \equiv V_0 = U \; . \tag{5b}$$

Here U is the usual on-site Coulomb (Hubbard) energy, while V is the nearest-neighbor Coulomb energy and represents the strength of the Coulomb-type long-range potential. The distance dependence of dielectric screening has not been taken into account in Eq. (5a). We can write $V = e^2/\epsilon a$, with e being the electron charge, ϵ the static dielectric constant, and a the average intersite spacing. The dielectric constant ϵ here is for electrons on a single chain surrounded by other chains and may be different from the bulk dielectric constant. In the present paper we treat V and U as model parameters. In polydiacetylene, a is about 1.4 Å, hence, for example, $\epsilon \approx 5$ corresponds to $V \approx 2$ eV.

III. ELECTRON-HOLE INTERACTION

We implement a standard exciton theory[23] on the tight-binding Hamiltonian given above. The calculation procedure is as follows. We first obtain the one-electron states of H_0 and construct the ground state $|g\rangle$ and the excited states of a single electron-hole pair. Then the matrix of the Hamiltonian $H = H_0 + H_{e\text{-}e}$ within the single-excitation subspace is calculated and diagonalized. Actually, this diagonalization has to be carried out numerically for a finite chain. Calculations are much simplified by adopting the periodic boundary condition, which assures that the total momentum of a single excitation is a good quantum number. Then, the diagonalization can be performed for each total momentum independently. In the following we give expressions for the matrix elements, the derivations of which are presented in Appendix.

Consider a single electron-hole pair excitation in which an electron in a state of wave number k_v in the valence band is promoted to a state of wave number k_c in the conduction band. Note that the wave numbers are quantized as $k_{c(v)} = j\pi/Ma$ (j = integers, $-M/2 \leq j < M/2$), where M is the number of unit cells in the chain (the number of sites is $N = 2M$). We introduce new variables k and K so that

$$\begin{aligned} k_c &= k + K \; , \\ k_v &= k - K \; , \end{aligned} \tag{6}$$

and denote the excited state as $|k,K\rangle$. Here k and $2K$ are the wave numbers of the relative motion and the center-of-mass motion, respectively, of the electron-hole pair. The matrix elements of the excitation Hamiltonian in this representation are written as

$$\langle k',K'|(H - E_0)|k,K\rangle = \delta_{K',K}\{\delta_{k',k}[\tilde{\varepsilon}_c(k+K) - \tilde{\varepsilon}_v(k-K)] + 2\delta_S W_X(k',k;K) - W_C(k',k;K)\} \tag{7}$$

for spin singlet ($\delta_S = 1$) and triplet ($\delta_S = 0$) states, with $E_0 \equiv \langle g|H|g\rangle$ being the ground-state energy. The quantities $\tilde{\varepsilon}_c$ and $\tilde{\varepsilon}_v$ in Eq. (7) are the energies of one-electron states in the conduction and the valence bands, respectively, including the first-order energy corrections with respect to the interaction, their explicit forms being given in the Appendix. The Coulomb part W_C and the exchange part W_X in Eq. (7) can be written as

$$W_C(k',k;K) = (\zeta_{k'+K}\zeta^*_{k'-K}\zeta^*_{k+K}\zeta_{k-K} + \text{c.c.})V_{2,k-k'} + \{\zeta^*_{k'+K}\zeta^*_{k'-K}\zeta_{k+K}\zeta_{k-K}\exp[-i(k-k')] + \text{c.c.}\}V_{1,k-k'} \; , \tag{8}$$

$$W_X(k',k;K) = (\zeta_{k'+K}\zeta^*_{k'-K}\zeta^*_{k+K}\zeta_{k-K} + \text{c.c.})V_{2,2K} - [\zeta_{k'+K}\zeta^*_{k'-K}\zeta_{k+K}\zeta^*_{k-K}\exp(-i2K) + \text{c.c.}]V_{1,2K} \; , \tag{9}$$

where c.c. denotes complex conjugate,

$$\zeta_k = (z_k/2|z_k|)^{1/2} \; , \tag{10a}$$

$$z_k = t + \delta t + (t - \delta t)\exp(2ika) \; , \tag{10b}$$

and $V_{1,q}$ and $V_{2,q}$ are the Fourier transforms of the potential V_i for i = odd and for i = even, respectively:

$$\begin{aligned} V_{1,q} &= \frac{1}{M}\sum_{j} V_{2j-1}\exp[iq(2j-1)a] \; , \\ V_{2,q} &= \frac{1}{M}\sum_{j} V_{2j}\exp(iq2ja) \; . \end{aligned} \tag{11}$$

We note that W_C and W_X satisfy the following relationships for each K:

$$W_C(-k',-k;K)=W_C(k',k;K)\ , \tag{12a}$$

$$W_X(-k',-k;K)=W_X(k',k;K)\ , \tag{12b}$$

$$W_X(k',-k;K)=W_X(k',k;K)\ . \tag{12c}$$

Considering the symmetry of the system with respect to the spatial inversion at a bond center, we introduce a new basis set by the transformation

$$\begin{aligned} |k;+,K\rangle &\equiv (|k,K\rangle + |-k,K\rangle)/\sqrt{2}\ , \\ |k;-,K\rangle &\equiv (|k,K\rangle - |-k,K\rangle)/\sqrt{2}\ , \end{aligned} \tag{13}$$

for $0<k<\pi/2a$. (We do not need to reorganize the states with respect to the center-of-mass motion K, which is already a good quantum number. The states with K and $-K$ are degenerate.) It can be easily shown (see the Appendix) that the spatial inversion transforms the state $|k,K\rangle$ into $-|k,-K\rangle$, hence, the states $|k;\pm,K\rangle$ into $\mp|k;\pm,-K\rangle$. Therefore, $|k;+,K\rangle$ and $|k;-,K\rangle$ are antisymmetric (B_u) and symmetric (A_g), respectively, with respect to the spatial inversion, concerning the relative motion of electron and hole. For $k=0$ and $k=\pi/2a$, the state $|k,K\rangle$ $(=|-k,K\rangle)$ is already a B_u-symmetry state, i.e., $|k;+,K\rangle \equiv |k,K\rangle$.

One can easily see from Eqs. (12) and (13) that the matrix elements between B_u and A_g states vanish. That is, the matrix is now decoupled into the B_u and the A_g subspaces. The matrix elements in each of the subspaces are written in a similar form as Eq. (7):

$$\langle k';\pm,K|(H-E_0)|k;\pm,K\rangle = \delta_{k',k}[\tilde{\varepsilon}_c(k+K)-\tilde{\varepsilon}_v(k-K)] + 2\delta_S W_X(k',k;\pm,K) - W_C(k',k;\pm,K)\ , \tag{14}$$

W_C and W_X in this representation being obtained from those in Eqs. (8) and (9) by

$$W_C(k',k;+,K)=W_C(k',k;K)+W_C(k',-k;K)\ , \tag{15a}$$

$$W_X(k',k;+,K)=2W_X(k',k;K)\ , \tag{15b}$$

$$W_C(k',k;-,K)=W_C(k',k;K)-W_C(k',-k;K)\ , \tag{16a}$$

$$W_X(k',k;-,K)=0\ , \tag{16b}$$

where we have used Eq. (12). Equation (16b) implies that the exchange part vanishes in the A_g subspace, hence, all the A_g states have degenerate singlet and triplet states.

IV. EXCITON STATES

An example of calculated excitation energies at $K=0$ for a chain of $N=400$ is shown in Fig. 1. The parameters used here are $\delta t=0.2t$, $V=t$, $U=2t$, which turn out to give approximately correct exciton energies in polydiacetylene (see Sec. V). The left two columns are singlet B_u and A_g states, and the right two are triplet B_u and A_g states. Actually, the energy levels of the ${}^3A_g$ states are the same as those of the ${}^1A_g$ states, as mentioned above. E_c denotes the gap of the electron-hole (quasi)continuum,[24] defined as

$$E_c=\tilde{\varepsilon}_c\left[\frac{\pi}{2a}\right]-\tilde{\varepsilon}_v\left[\frac{\pi}{2a}\right]\ , \tag{17}$$

which is the minimum of the renormalized one-electron excitation energy $\tilde{\varepsilon}_c(k+K)-\tilde{\varepsilon}_v(k-K)$ in Eq. (7). Formally, the states below and above E_c can be viewed as exciton states and unbound electron-hole states, respectively, although the distinction cannot be strict especially near E_c because of the finiteness of the system (see below).

In Fig. 2, we display the envelope of the wave functions $\Psi(x_e,x_h)$ of the five lowest singlet states whose energies are below E_c in the example of Fig. 1, x_e and x_h being the coordinates of the electron and the hole. The actual wave functions contain rapid staggered oscillations with a period of $4a$. To make the symmetry of the wave functions more manifest, we have plotted $\Psi(x_e,x_h)/f(x_e)f(x_h)$ with

$$f(na)=\sqrt{2}\cos\left[\frac{\pi}{2}\left[n+\frac{1}{2}\right]\right]\ .$$

This does not alter the symmetry of the wave function since the product $f(x_e)f(x_h)$ is invariant under the spa-

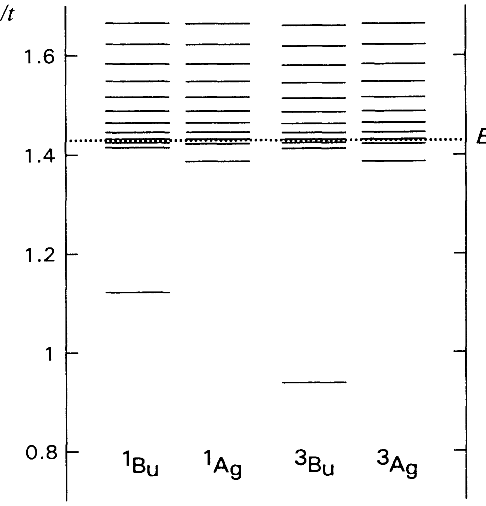

FIG. 1. Example of calculated excitation levels (in a low-energy region) for a ring of $N=400$ sites. The used parameters are $\delta t=0.2t$, $V=t$, and $U=2t$. E_c is the gap of the electron-hole continuum.

tial inversion at a bond center. Each wave function is illustrated by four curves corresponding to the four possibilities of electron (e) and hole (h) being at odd (1) or even (2) sites. The spatial inversion at a bond center involves the inversion of the coordinate $x_e - x_h$ as well as the interchange of the even and the odd sites, i.e., of the indices 1 and 2. With this rule it is easy to see that the wave functions in Figs. 2(a), 2(c), and 2(e) change sign upon inversion, corresponding to the B_u symmetry, while those in Figs. 2(b) and 2(d) do not, corresponding to the A_g symmetry.

The formation of an exciton is evident for the three lowest states (a)–(c) in Fig. 2, the exciton size $d \equiv \sqrt{\langle (x_e - x_h)^2 \rangle}$ being obtained as (a) $d \cong 6.0a$, (b) $d \cong 21.8a$, and (c) $d \cong 55.8a$. The fourth state (d) has an intermediate character between an exciton and an unbound electron-hole pair, its size d being comparable to the system size. The fifth state (e) can be looked upon as an unbound electron-hole pair for the present system size, even if its energy is slightly below E_c.

The lowest triplet state, the wave function of which is shown in Fig. 3, lies below the corresponding singlet state (see Fig. 1) and accordingly has a smaller exciton size $d \cong 4.5a$. The wave functions of the higher states are similar to their singlet counterpart in Fig. 2. (Actually, those of the ${}^3A_g$ states are the same as those of the corresponding ${}^1A_g$ states because of the exact degeneracy mentioned above.)

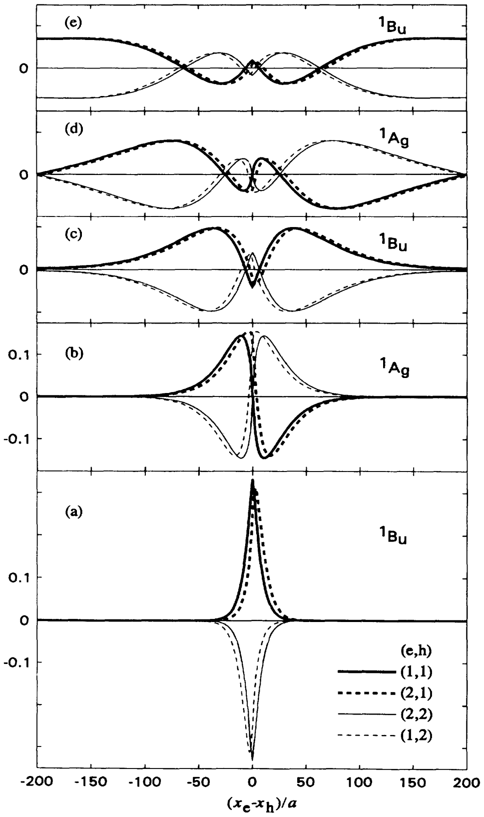

FIG. 2. Envelope $\Psi(x_e,x_h)/f(x_e)f(x_h)$ of the wave functions of the five lowest singlet excitations in the example of Fig. 1, with $f(na) \equiv \sqrt{2}\cos[(\pi/2)(n+1/2)]$, from (a) to (e) in the order of increasing energy. For each wave function four curves are diplayed distinguishing whether the electron (e) and the hole (h) are at odd (1) or even (2) sites.

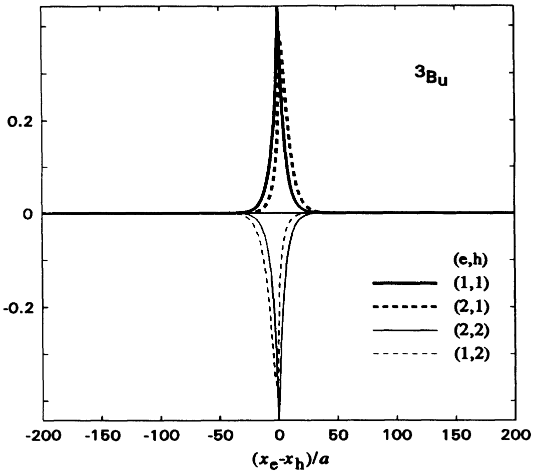

FIG. 3. Same as Fig. 2 for the lowest triplet excitation.

In Fig. 4 we show how these exciton states split off from the electron-hole continuum with increasing the interaction strength V. Here the on-site Coulomb energy U is assumed to scale as $U = 2V$. The gap E_c of the electron-hole continuum grows linearly with V from the value $4\delta t = 0.8t$ at $V=0$, due to the first-order energy correction of the one-electron states with respect to the interaction. The lowest (singlet or triplet) exciton with B_u symmetry has a fairly large binding energy even for small V. The next exciton state with A_g symmetry (singlet and triplet degenerate) is well identifiable in the region $V \gtrsim 0.5t$ for the system size used here ($N = 400$).

Figure 5 shows the dependences of the states on the ratio U/V for a fixed V. The energies of the lowest singlet and triplet B_u excitons strongly depend on U, while the other states and the continuum gap E_c are insensitive to U. Physically, we expect that $U/V \gtrsim 1$. The triplet state

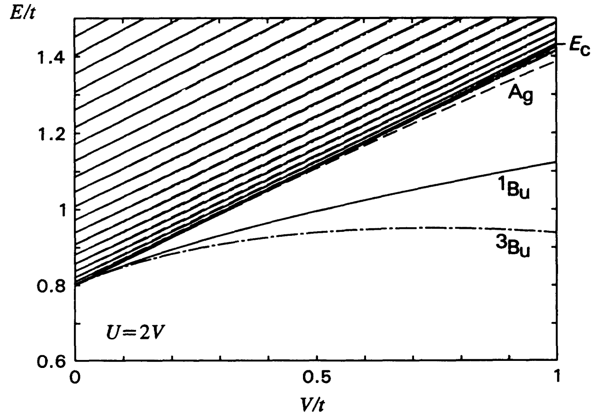

FIG. 4. Excitation energies vs the interaction strength V for $U = 2V$, $\delta t = 0.2t$, and $N = 400$. Solid, dashed, and dot-dashed curves are ${}^1B_u$, A_g (singlet and triplet degenerate), and ${}^3B_u$ states, respectively. E_c indicates the edge of the electron-hole continuum at $V = t$.

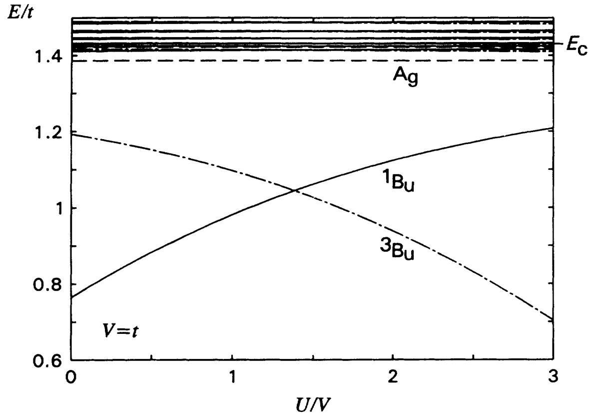

FIG. 5. Excitation energies vs the ratio U/V for $V=t$, $\delta t=0.2t$, and $N=400$ with the same notations as in Fig. 4.

is higher than the singlet state for $U\approx V$, while the order is reversed for much larger U. The crossing occurs at $U/V\cong 1.39$.

Actually, the singlet-triplet ordering is determined solely by the ratio U/V, independent of the other parameters t and δt. This can be shown as follows. By putting $K=0$ in Eq. (9) and using Eqs. (10) and (11), we immediately get

$$W_X(k,k';K=0)=\tfrac{1}{2}(V_{2,K=0}-V_{1,K=0})$$
$$=\frac{1}{N}\left[\sum_{i\ \mathrm{even}} V_i-\sum_{i\ \mathrm{odd}} V_i\right]. \qquad (18)$$

This implies that W_X is constant for all k and k'. Therefore, if the constant W_X is positive, i.e., $\sum_{i\ \mathrm{even}} V_i > \sum_{i\ \mathrm{odd}} V_i$, then the singlet energy is higher than the triplet energy for any eigenstate of the matrix of Eq. (7) for $K=0$ in the B_u subspace. (The singlet and the triplet states are degenerate in the A_g subspace.) The condition corresponds to $U/V>2\ln 2\cong 1.386$ for the potential of Eq. (5) (for N infinite), in accordance with Fig. 5. The singlet-triplet crossing, in fact, occurs at the same U/V for all the B_u states, although this can hardly be seen in the energy scale of Fig. 5.

V. POLYDIACETYLENE

From the results shown in Figs. 4 and 5, we see that the ratio of the binding energies of the lowest singlet and triplet excitons is almost uniquely related to the ratio U/V in the present model. Therefore, the latter may be determined from experimental information about the former.

In polydiacetylene crystals, photoinduced absorption at about 1.4 eV has been observed.[25,26] The magnetic-field dependence of its lifetime[27] and the observation of transient ESR (Ref. 28) indicate that it is due to a triplet state. This state shows up as a relaxed state after photoexcitation, being interpreted as an exciton polaron (i.e., neutral bipolaron). The 1.4-eV absorption peak then corresponds to triplet-triplet transitions, most likely the promotion of an electron (or hole) from the lowest triplet exciton to around the edge of the conduction (or valence) band without changing the lattice configuration of the bipolaron. In the absence of Coulomb interactions, this transition energy has previously been calculated as ~0.5 eV.[29] On the other hand, in the presence of the Coulomb interactions and in the absence of electron-phonon coupling, the energy simply corresponds to the bare exciton binding energy. Since the polaron size obtained in Ref. 29, viz., ~$8a$, is not smaller than the exciton size obtained here, viz., ~$4.5a$ (see above), we can safely assume that the exciton wave function is not much altered by the polaron effect and that the triple-triplet transition energy is approximately a simple sum of the two contributions from the polaron effect and the exciton effect. The observed 1.4-eV transition energy and the calculated 0.5-eV polaron transition energy then leads to the conclusion that the pure electronic binding energy of the triplet exciton should be ~0.9 eV.

On the other hand, photoconductivity[30] and electroabsorption[31] measurements have suggested the possible existence of the edge of the electron-hole continuum at ~0.6 eV above the fundamental absorption peak (at ~2 eV) due to the singlet B_u exciton, implying that the binding energy of the exciton is ~0.6 eV. The existence of the continuum edge can be further confirmed[19] by calculating various nonlinear spectra in the present model and comparing the results with experiments.

From the ratio of the two binding energies, namely, ~0.6 eV of the ^1B_u exciton and ~0.9 eV of the ^3B_u exciton, we can conclude that $U/V\sim 2$ (see Fig. 5). By comparing Fig. 4 with the observed excitation energy (~2 eV) and the binding energy (~0.6 eV) of the ^1B_u exciton, we then conclude that $V\sim t\sim 2$ eV. This corresponds to the situation shown in Fig. 1.

The values of U (~4 eV) and V (~2 eV) thus obtained are much smaller than those commonly used in strong-correlation models,[32] namely, $U\sim 11$ eV and $V\sim 8$ eV of the Ohno potential. From a theoretical point of view,[33] this may be a natural consequence of our model which assumes large bond alternation or strong electron-phonon coupling. However, we think that the moderate U and V are realistic in the condensed bulk polymer systems under discussion: $V\sim 2$ eV in the case of polydiacetylene corresponds to the dielectric constant $\epsilon\sim 5$ (as mentioned before), which is fairly reasonable. Also the observation of multiphonon side bands in absorption spectra[7] is a clear indication of strong electron-phonon coupling.

VI. COMPARISON WITH A CONTINUUM MODEL

We compare our results with calculations in a continuum model.[18] In that model, it was necessary to introduce a lower cutoff length of the Coulomb interaction between an electron and a hole. From an intuitive argument, this cutoff length was assumed to be identical to the electronic correlation length ξ associated with the Peierls gap. The assumption was crucial, since the lowest exciton state turned out[18] to depend sensitively on the cutoff because of the special nature of the one-dimensional long-range potential.

We compare Fig. 4 of the present paper with Fig. 1 of

Ref. 18. The B_u and A_g states in the former correspond to the "even" and "odd" states in the latter, where these terms are used for the symmetry of an envelope function (which is different from the one used in the present paper). Singlet and triplet states were not distinguished in the continuum model. The two models agree that the lowest exciton state with B_u symmetry has an extraordinarily large binding energy in contrast to the other exciton states. For a more quantitative comparison, we note that the renormalization of the continuum gap E_c was not taken into account in the continuum model, hence, we should compare the binding energies of the exciton states rather than the exciton energies themselves, with replacing the parameter E_g of the continuum model by the gap $4\delta t$ of our unperturbed system. The parameter V_0 of the continuum model is the value of the Coulomb potential at distance ξ, related to our parameter V as $V_0 = Va/\xi$. Therefore, the dimensionless parameter $u = V_0/E_g$ is related to our V as $u = (Va/\xi)/4\delta t$, where $\xi \equiv a\sqrt{t^2 - \delta t^2}/2\delta t$. In the case of $\delta t = 0.2t$ used in the present calculations, the relationship is $u \cong 0.5V/t$. As an example, we compare the binding energies at $V = t$ in Fig. 1 with those at $u = 0.5$ in Fig. 4 of Ref. 18. The former are $0.31t$ and $0.49t$ for the lowest singlet and triplet B_u states and $0.04t$ for the lowest A_g state, whereas the latter are $0.35E_g = 0.28t$ for the "$n = 0$" state and $0.11E_g = 0.09t$ for the "$n = 1$ (odd)" state. The lowest B_u exciton state is deeper in the present model than in the continuum model, whereas the other exciton states are more shallow. That is, the special character of the lowest exciton state is even more reinforced in the present tight-binding model. The difference is ascribed to the crudeness of the model potential used in the continuum model, while the overall agreement confirms that the basic assumption and the conclusions of the continuum model are qualitatively correct.

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APPENDIX: INTERACTION MATRIX ELEMENTS

Consider a chain (actually a ring, because of the cyclic boundary condition) of $N = 2M$ sites. Since our unit cell contains two sites, we write the site index n $(= 1, 2, \ldots, N)$ as $n = 2(m-1) + \mu$, $m = 1, 2, \ldots, M$, with $\mu = 1$ for odd sites or $\mu = 2$ for even sites. The state of an electron at site n is alternatively written as $|n\rangle$ or $|m\mu\rangle$. By introducing the Fourier transform

$$|k\mu\rangle = \frac{1}{\sqrt{M}} \sum_m \exp(2ikma)|m\mu\rangle \quad (\mu = 1, 2) , \tag{A1}$$

with $k = j\pi/M$ (j = integers, $-M/2 \le j < M/2$), the Hamiltonian H_0 can be put into a 2×2 matrix for each k, which can be diagonalized by the transformation

$$\begin{bmatrix} |kc\rangle \\ |kv\rangle \end{bmatrix} = \begin{bmatrix} \zeta_k^* & \zeta_k \\ -\zeta_k^* & \zeta_k \end{bmatrix} \begin{bmatrix} |k1\rangle \\ |k2\rangle \end{bmatrix} , \tag{A2}$$

where Eq. (10) defines ζ_k. Then $|kc\rangle$ and $|kv\rangle$ correspond to the states of wave number k in the conduction band and in the valence band, respectively. The energies ε_{kc} and ε_{kv} of these states are given by

$$\begin{aligned} \varepsilon_{kc} &= -\varepsilon_{kv} \\ &= |z_k| = 2\sqrt{t^2\cos^2(ka) + \delta t^2 \sin^2(ka)} , \end{aligned} \tag{A3}$$

where Eq. (10b) defines z_k. The semiconducting gap is at $k = \pi/2a$, and the gap energy is $4\delta t$. Combining the two transformations (A1) and (A2), we get

$$\begin{aligned} &\begin{bmatrix} \langle m1|kc\rangle & \langle m2|kc\rangle \\ \langle m1|kv\rangle & \langle m2|kv\rangle \end{bmatrix} \\ &\qquad = \frac{1}{\sqrt{M}} \exp(2ikma) \begin{bmatrix} \zeta_k^* & \zeta_k \\ -\zeta_k^* & \zeta_k \end{bmatrix} . \end{aligned} \tag{A4}$$

The ground sate is constructed as $|g\rangle = \prod_k C_{kv\uparrow}^\dagger C_{kv\downarrow}^\dagger |0\rangle$, where the creation operators are defined as usual: $C_{kv}^\dagger |0\rangle = |kv\rangle$. A single electron-hole pair excitation from this ground state is written as

$$|k_c, k_v\rangle = \frac{1}{\sqrt{2}} (C_{k_c\uparrow}^\dagger C_{k_v\uparrow} \pm C_{k_c\downarrow}^\dagger C_{k_v\downarrow})|g\rangle , \tag{A5}$$

where + is for the spin singlet and − for one of the triplets, $C_{k_c\uparrow}^\dagger$ and $C_{k_v\uparrow}$ implying $C_{k_c c\uparrow}^\dagger$ and $C_{k_v v\uparrow}$. The other triplet states are given by $C_{k_c\uparrow}^\dagger C_{k_v\downarrow}|g\rangle$ and $C_{k_c\downarrow}^\dagger C_{k_v\uparrow}|g\rangle$.

To examine the symmetries of the states with respect to the spatial inversion at a bond center, we first note that this operation corresponds to the interchanges $m \to -m$ and $\mu = 1 \leftrightarrow 2$ for the localized states $|m\mu\rangle$. By these interchanges, the states $|k1\rangle$ and $|k2\rangle$ in Eq. (A1) are transformed into $|-k2\rangle$ and $|-k1\rangle$, respectively. Then the states $|kc\rangle$ and $|kv\rangle$ in Eq. (A2) are transformed into $|-kc\rangle$ and $-|-kv\rangle$, hence, the state $|k_c, k_v\rangle$ in Eq. (A5) into $-|-k_c, -k_v\rangle$. Therefore, the spatial inversion at a bond center transforms the state $|k, K\rangle$ into $-|-k, -K\rangle$ with k and K defined by Eq. (6).

The calculation of the matrix elements $\langle k_c', k_v'|H_{e\text{-}e}|k_c, k_v\rangle$ requires the evaluation of terms like $\langle C_{k_v'}^\dagger C_{k_c'} H_{e\text{-}e} C_{k_c}^\dagger C_{k_v}\rangle$, where $\langle \cdots \rangle \equiv \langle g| \cdots |g\rangle$. This can be carried out by using Wick's theorem and $\langle \rho_n \rangle = 0$, resulting in the form

$$\begin{aligned} \langle k_c', k_v'|H - E_0|k_c, k_v\rangle &= 2\delta_S E_X - E_C \\ &\quad + (\text{diagonal terms}) , \end{aligned} \tag{A6}$$

where $E_0 = \langle H \rangle$, and $\delta_S = 1$ for the singlet and $\delta_S = 0$ for the triplet. The diagonal terms originate from the terms involving the contractions $\langle C_{k_v'}^\dagger C_{k_v}\rangle$ or $\langle C_{k_c'} C_{k_c}^\dagger\rangle$, being explicitly written as

$$\delta_{k_c',k_c}\delta_{k_v',k_v}[\tilde{\varepsilon}_c(k_c)-\tilde{\varepsilon}_v(k_v)] , \tag{A7}$$

where

$$\begin{aligned}\tilde{\varepsilon}_c(k)&=\langle C_{kc}(H-E_0)C_{kc}^{\dagger}\rangle=\varepsilon_{kc}+\Delta\varepsilon_{kc} ,\\ \tilde{\varepsilon}_v(k)&=-\langle C_{kv}^{\dagger}(H-E_0)C_{kv}\rangle=\varepsilon_{kv}+\Delta\varepsilon_{kv} ,\end{aligned} \tag{A8}$$

with

$$\begin{aligned}\Delta\varepsilon_{kc}&=\sum_{n,\,j(\neq 0)}V_j\langle C_{kc}C_{n+j}^{\dagger}\rangle\langle C_{n+j}C_n^{\dagger}\rangle\langle C_nC_{kc}^{\dagger}\rangle ,\\ \Delta\varepsilon_{kv}&=-\sum_{n,j\ (\neq 0)}V_j\langle C_{kv}^{\dagger}C_{n+j}\rangle\langle C_{n+j}^{\dagger}C_n\rangle\langle C_n^{\dagger}C_{kv}\rangle .\end{aligned} \tag{A9}$$

The general terms E_X and E_C in Eq. (A6) are written as

$$E_C=\sum_{n,i}V_i\langle C_{k_c'}C_{n+i}^{\dagger}\rangle\langle C_{n+i}C_{k_c}^{\dagger}\rangle\langle C_{k_v'}^{\dagger}C_n\rangle\langle C_n^{\dagger}C_{k_v}\rangle , \tag{A10}$$

$$E_X=\sum_{n,i}V_i\langle C_{k_c'}C_n^{\dagger}\rangle\langle C_{n+i}C_{k_c}^{\dagger}\rangle\langle C_{k_v'}^{\dagger}C_n\rangle\langle C_{n+i}^{\dagger}C_{k_v}\rangle . \tag{A11}$$

These quantities can be calculated as follows. We first note $\langle C_nC_{k_c}^{\dagger}\rangle=\langle n|kc\rangle$ and $\langle C_{k_v}^{\dagger}C_n\rangle=\langle n|kv\rangle$, for which Eq. (A4) can be used. The summations in Eqs. (A10) and (A11) can be decomposed into four terms, corresponding to whether n and i are even or odd. For example, the summation for $n=$even $(=2m)$ and $i=$even $(=2j)$ in Eq. (A10) yields

$$\frac{1}{M^2}\sum_{m,j}\exp[-i(k_c'-k_c-k_v'+k_v)2m]\exp[-i(k_c'-k_c)2j]V_{2j}\zeta_{k_c'}\zeta_{k_c}^{*}\zeta_{k_v'}^{*}\zeta_{k_v} . \tag{A12}$$

The first exponential factor summed over m in Eq. (A12) yields $\delta_{K',K}$ in Eq. (7), while the rest gives the first term in the right-hand side of Eq. (8). The other terms in Eqs. (8) and (9) can be obtained similarly.

The energy corrections $\Delta\varepsilon_{kc}$ and $\Delta\varepsilon_{kv}$ in Eq. (A9) can be calculated in a similar manner by using

$$\langle C_{n+j}^{\dagger}C_n\rangle=\sum_k\langle kv|n+j\rangle\langle n|kv\rangle \tag{A13}$$

and Eq. (A4). The result is

$$\begin{aligned}\Delta\varepsilon_{kc}&=-\Delta\varepsilon_{kv}\\ &=\sum_q V_{1,q}[(\zeta_k^{*}\zeta_{k+q})^2\exp(-iqa)+\text{c.c.}] ,\end{aligned} \tag{A14}$$

where $V_{1,q}$ is defined by Eq. (11).

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[*] Permanent address.

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