PHYSICAL REVIEW B VOLUME 52, NUMBER 7 15 AUGUST 1995-I

Excitons, biexcitons, and the band gap in poly(*p*-phenylene vinylene)

Z. G. Yu, R. T. Fu, C. Q. Wu, and X. Sun
*T. D. Lee Laboratory and Department of Physics, Fudan University, Shanghai 200433, China**
and National Laboratory of Infrared Physics, Academia Sinica, Shanghai 200083, China

K. Nasu
Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305, Japan
(Received 21 February 1995)

The excited states of poly(*p*-phenylene vinylene) (PPV) are studied in the Su-Schrieffer-Heeger model appended by a long-range Coulomb interaction. We have calculated the energy levels of singlet and triplet excitons with odd and even parity, the biexciton state, and the onset of the continuum band in PPV; these results can comprehensively interpret relevant experimental data. More significantly, we have constructed the wave function of the biexciton by using the Heitler-London method and calculated the binding energy and radius of the biexciton in conjugated polymers.

I. INTRODUCTION

Since the discovery that poly(*p*-phenylene vinylene) (PPV) and its derivatives can be used as the active luminescent layer in electroluminescent light-emitting diode (LED) devices,[1] many efforts have been devoted to understanding the photoexcitation in order to improve the efficiency of PPV based LED devices.[2–9] From these intensive studies, however, some controversies on the photophysics of PPV also arose. A sharp conflict among them is which one is the primary photoexcitation, the free electron-hole pair or the exciton. This depends on the role of electron-electron (*e*-*e*) interaction.[2–4,6] Nevertheless, there are more and more evidences that the *e*-*e* interaction is significant in PPV, e.g., site-selective fluorescence and transient photoconduction experiments[2,4] showed that the lowest excited state is of excitonic character, photoluminescence and photoinduced absorption indicated that strong photoluminescence in PPV is due to radiative recombination of the singlet exciton,[3] etc. Another important issue in conjugated polymers is the lattice relaxation effect. The small difference observed between emission and absorption edges[10] suggests that little lattice relaxation energy can be gained in the creation of the exciton. Although the vanishing Stokes shift is not incompatible with the pronounced lattice distortion in the excited states,[11] we can study an effective electron-correlated model with no explicit lattice relaxation effect involved,[12] as long as we focus our attention on the electronic states in PPV. Actually, choice of the parameters in this Hamiltonian to fit experimental data does result in the inclusion of the effect of electron-phonon interaction.

Many experimental and theoretical works have been undertaken to investigate the excited states, especially the lowest singlet exciton in PPV and PPV oligomers,[2,7,10–18] but estimates of the exciton binding energy, the energy difference between the onset of the conduction band and the excitonic state, vary widely, ranging from 0.4 (Refs. 2, 10, 11, and 13–15) to 1.1 eV.[7,12] We noticed that the divergence comes from the discrepant location of the threshold of the conduction band obtained in these works. Our calculation shows that the on-site Hubbard repulsion plays a significant role in determining the band gap and should, therefore, be dealt with carefully. Among these experimental works, the measurements of Leng *et al.* presented more information about the excited levels, including excitons, the onset of the continuum band and the biexciton, in PPV.[7] The approximate calculations based on the extended Hubbard model of a short chain also supported their assignments.[7,19] To explain the experiments better and reveal more physical properties of these excited states in PPV, in this paper, we will study the infinite system rather than a short chain and consider the long-range Coulomb interaction, which, we believe, is more appropriate than the short-range Hubbard type model in conjugated polymers.

There have been several works to develop the exciton theory in polymers.[20–23] Abe and co-workers introduced the standard exciton theory[24] to one-dimensional polymers, neglecting the lattice relaxation of the excited state,[23] and also took account of the relaxation effect in subsequent works.[25] But, from their theory, the threshold of the conduction band, as pointed out by Guo *et al.*,[19] is independent on U, the on-site Hubbard repulsion. This unreasonable result is due to their unbalanced treatment to the *e*-*e* interaction, in which the effect of *e*-*e* interaction was merely considered in the Hartree-Fock level for the states in continuum bands, but for the exciton states, the correlation effect was also included. One of the authors (C.Q.W.) has studied the effect of electron correlation on the band gap in polymers[26] by applying the projection technique developed by Becker and Fulde.[27] Making use of the results of Ref. 26, we can give the correct threshold of the conduction band.

Compared with the exciton and band gap, the features of biexciton in the polymer, however, are far from fully explored, especially when the *e*-*e* interaction is of long-

0163-1829/95/52(7)/4849(6)/$06.00

range type. Recently, Shakin and Abe investigated the effect of double-electron-hole pairs excitation on the optical nonlinearity in polymers,[28] but, to our knowledge, the binding energy and radius of biexciton have never been touched.

In this paper, first, we combine the theories of Refs. 23 and 26 to calculated the energy levels of singlet and triplet excitons and the onset of the conduction band in PPV. Then, we use the obtained singlet exciton wave function to construct the biexciton state in the Heitler-London approach[29] and determine its energy and radius. Our results can quantitatively explain the experimental data from Leng *et al.*[7]

Since the model we deal with has the universality for the quasi-one-dimensional polymers, our method and results can also be employed to study the excited states in other polymers. Moreover, these excited states are the "essential states," which dominate the optical nonlinearity in conjugated polymers, so our calculations are helpful for better understanding the nonlinear optical properties of the polymers, too. The paper is organized as follows. In Sec. II, we briefly review the exciton theory of Abe, Yu, and Su (AYS) (Ref. 23) and the band gap theory of Ref. 26. In Sec. III, we develop the biexciton theory in conjugated polymers. We give numerical results to explain experimental data and discuss some properties of the biexciton in Sec. IV. Finally, some conclusions are presented in Sec. V.

II. EXCITONS AND THE BAND GAP

The unit cell of PPV consists of a benzene ring and a vinylene, and the direct calculation involving the benzene ring can only be carried out for a small system.[11–14,30] To extend the computation to an infinite system, we study a simplified model, in which, only the electrons on the nonbenzene carbon atoms are considered, and the benzene ring just affects the electron hopping between those atoms, leading to a large effective bond alternation. So the effective Hamiltonian of PPV also has the Su-Schrieffer-Heeger (SSH) form[31] and previous results of conjugated polymers can be used. In this section, we briefly review the theories of exciton and band gap in polymers of Refs. 23 and 26.

A. Excitons

The π-electron tight-binding Hamiltonian of conjugated polymers discussed in Ref. 23 reads

$$H = H_0 + H_{e-e} \ , \tag{1}$$

$$H_0 = -t_0 \sum_{ls} [1-(-1)^l z_0](c^\dagger_{l+1s} c_{ls} + \text{H.c.}) \ , \tag{2}$$

where $c^\dagger_{ls}$ is a creation operator of electron at site l with spin s. The system is assumed to be dimerized according to the Peierls theorem.[32] The rigid lattice approximation is adopted. This is feasible since, as mentioned in the Introduction, we are mainly interested in the electronic states of PPV. The e-e interaction is described by a long-range form

$$H_{e-e} = \sum_l V_{ll}\rho_{l\uparrow}\rho_{l\downarrow} + \frac{1}{2}\sum_{ll'}{}' V_{ll'}\rho_l\rho_{l'} \ , \tag{3}$$

where $\rho_{ls} = c^\dagger_{ls}c_{ls} - \frac{1}{2}$, $\rho_l = \rho_{l\uparrow} + \rho_{l\downarrow}$, and the parameters of e-e interaction are selected according to

$$V_{ll} = V_0 = U, \quad V_{l,l+i} = V_i = \frac{V}{|i|} \ .$$

The single-particle Hamiltonian H_0 can be diagonalized easily, yielding,

$$H_0 = \sum_{ks} [\epsilon_c(k) a^\dagger_{ks} a_{ks} - \epsilon_v(k) b^\dagger_{ks} b_{ks}] \ , \tag{4}$$

where $a^\dagger_{ks}$ and $b^\dagger_{ks}$ create the electron in the conduction band and the hole in the valence band in momentum space, respectively, and

$$\epsilon_c(k) = -\epsilon_v(k) = 2t_0\sqrt{\cos^2 k + z_0^2 \sin^2 k} \ . \tag{5}$$

The excited state of a single-electron-hole pair from the ground state $|g\rangle$ is written as

$$|k_c, k_v\rangle = \frac{1}{\sqrt{2}}(a^\dagger_{k_c\uparrow} b^\dagger_{-k_v\downarrow} \pm a^\dagger_{k_c\downarrow} b^\dagger_{-k_v\uparrow})|g\rangle \ , \tag{6}$$

where k_c and $-k_v$ are the momenta of electron and hole, + is for the spin singlet and − for one of the triplet. The relative and center-of-mass motions can be separated by introducing the variable k and K so that $k_c = k + K$ and $k_v = k - K$. k and $2K$ are the momenta of the relative motion and center-of-mass motion of the electron-hole pair.

The symmetry of system, with respect to the spatial inversion at a bond center, indicates the states can be divided into two subspaces, A_g (symmetric) and B_u (antisymmetric). The B_u state is written as

$$|k;+,K\rangle = (|k,K\rangle + |-k,K\rangle)/\sqrt{2} \ , \tag{7a}$$

and the A_g state is

$$|k;-,K\rangle = (|k,K\rangle - |-k,K\rangle)/\sqrt{2} \ . \tag{7b}$$

The energy spectrum and wave functions can be obtained by diagonalizing the matrix[23]

$$\begin{aligned}\langle k';\pm,K|(H-E_0)|k;\pm,K\rangle &= \delta_{k'k}[\tilde{\epsilon}_c(k+K) - \tilde{\epsilon}_v(k-K)] + 2\delta_S W_X(k',k;\pm,K) \\ &\quad - W_C(k',k;\pm,K) \ ,\end{aligned} \tag{8}$$

where $E_0 = \langle g|H|g\rangle$, $\delta_S = 1$ and $\delta_S = 0$ correspond to the spin singlet and triplet, respectively. $\tilde{\epsilon}_c$ and $\tilde{\epsilon}_v$ are the renormalized value of ϵ_c and ϵ_v by taking account of the

e-e interaction in the Hartree-Fock level, the expressions of $\tilde{\epsilon}_c$ and $\tilde{\epsilon}_v$ as well as W_X and W_C can be found in Ref. 23.

From the expressions of $\tilde{\epsilon}_c$ and $\tilde{\epsilon}_v$, we can see that the band gap is independent on the Hubbard U. This is an artifact of their treatment, in which the effect of e-e correlation on the states in continuum bands is neglected. One of the authors (C.Q.W.) applied the projection technique developed by Becker and Fulde[27] to discuss the effect of correlation on the band gap.[26]

B. The band gap

The unperturbed Hamiltonian in Ref. 26 is an effective single-particle one,

$$\tilde{H}_0 = -t\sum_{ls}[1-(-1)^l z](c^\dagger_{l+1s}c_{ls} + \text{H.c.}) \ , \tag{9}$$

which has taken account of the e-e interaction in the Hartree-Fock level in the ground state. For the extended Hubbard model, Hamiltonians (2) and (9) are connected by the relations

$$t = t_0 + V\bar{m} \ , \tag{10}$$

$$z = \frac{z_0 t_0 + V\delta m}{t_0 + V\bar{m}} \ , \tag{11}$$

where $\langle c^\dagger_{l+1s}c_{ls}\rangle = \bar{m} - (-1)^l\delta m$. Thus, the residual e-e interaction is the two-particle part,[21]

$$H_1 = H - \tilde{H}_0 = \sum_m \tilde{V}_m O_m \ , \tag{12}$$

$$O_m = O^{(1)}_m + (O^{(2)}_m + \text{H.c.}) + (O^{(3)}_m + \text{H.c.}) \ , \tag{13}$$

$$\begin{aligned} O^{(1)}_m = \sum_{lss'}\{ & (a^\dagger_{ls}a^\dagger_{l+ms'}a_{l+ms'}a_{ls} + b^\dagger_{ls}b^\dagger_{l+ms'}b_{l+ms'}b_{ls}) \\ & -(a^\dagger_{ls}b^\dagger_{l+ms'}b_{l+ms'}a_{ls} + a^\dagger_{l+ms}b^\dagger_{ls'}b_{ls'}a_{l+ms}) \\ & +(a^\dagger_{ls}b^\dagger_{l\bar{s}}b_{l+m\bar{s}'}a_{l+ms'} + a^\dagger_{l+ms}b^\dagger_{l+m\bar{s}}b_{l\bar{s}'}a_{ls'})\} \end{aligned} \tag{14}$$

is the interaction between electron-electron, hole-hole, and electron-hole, $a^\dagger_{ls}$ and $b^\dagger_{ls}$ are the creation operators of the electron and hole in real space, respectively,

$$O^{(2)}_m = \sum_{lss'} a^\dagger_{ls}a^\dagger_{l+ms'}b^\dagger_{l+m\bar{s}'}b^\dagger_{l\bar{s}} \tag{15}$$

is the spontaneous creation of two-electron-hole pairs and

$$\begin{aligned} O^{(3)}_m = \sum_{lss'} & (a^\dagger_{ls}a^\dagger_{l+ms'}b^\dagger_{l+m\bar{s}'}a_{ls} + a^\dagger_{l+ms}a^\dagger_{ls'}b^\dagger_{l\bar{s}'}a_{l+ms} \\ & +b^\dagger_{ls}b^\dagger_{l+ms'}a^\dagger_{l+m\bar{s}'}b_{ls} + b^\dagger_{l+ms}b^\dagger_{ls'}a^\dagger_{l\bar{s}'}b_{l+ms}) \end{aligned} \tag{16}$$

is the creation of an electron hole through the scattering of an electron or a hole. Where

$$\tilde{V}_0 = \frac{V_0}{2} = \frac{U}{2}, \ \ \tilde{V}_m = V_m \ .$$

The band gap can be determined by calculating the excitation energy when an electron or a hole is added to the half-filled system,

$$\varepsilon(k) = E_1(k) - E_0 \ . \tag{17}$$

The excitation energy can be written as

$$\varepsilon(k) = 2t\sqrt{\cos^2 k + z^2\sin^2 k} + \varepsilon^{\text{corr}}(k) \ , \tag{18}$$

including two parts: mean field energy spectrum and the correlation contribution.

From the physical picture, the correlation contribution mostly comes from two parts: one is the blocking of spontaneous excitation of electron-hole pairs if those excitations are associated with the extra particle, the other is the excitation of electron-hole pairs through the scattering of the extra particle. The former gives rise to a *loss* of the correlation energy in the ground state and the latter gives rise to a *gain* of the polarization energy. Thus, the correlation contribution

$$\varepsilon^{\text{corr}}(k) = \varepsilon^{\pi}(k) + \varepsilon^{\eta}(k) \ . \tag{19}$$

The *gain* of the polarization energy $\varepsilon^\pi(k)$ and the *loss* of the correlation energy $\varepsilon^\eta(k)$ can be calculated by projecting the operators into the relevant space R_0, which embodies these two essential processes. The explicit expressions were given in Ref. 26. So the band gap is combined by two parts, the mean field band gap $4tz$ and the correlation gap $E_{\text{CG}} = 2\varepsilon^{\text{corr}}(k_0 = \pi/2)$.

III. THE BIEXCITON

To construct the biexciton wave function in conjugated polymers, it is necessary to know the wave function of exciton in real space. For the singlet 1 ^1B_u state $|\psi\rangle$, its wave function can be written as

$$\psi(i,I) = \sum_{k=0}^{\pi/2}\langle i\uparrow, I\downarrow|k;+,0\rangle\langle k;+,0|\psi\rangle \ , \tag{20}$$

i and I denote the positions of the electron and hole. We also fix $K=0$, since we are only concerned with the relative motion of the electron and hole in the exciton. $\langle k;+,0|\psi\rangle$ can be obtained by diagonalizing the matrix (8), and

$$\langle i\uparrow, I\downarrow|k;+,0\rangle = \begin{cases} \frac{1}{2M}[e^{ik(i-I)}\xi_k\xi^*_k + e^{-ik(i-I)}\xi_{-k}\xi^*_{-k}], & i \text{ and } I \text{ are even} \\ \frac{1}{2M}[e^{ik(i+1-I)}\xi^*_k\xi^*_k + e^{-ik(i+1-I)}\xi^*_{-k}\xi^*_{-k}], & i \text{ is odd and } I \text{ is even} \\ -\frac{1}{2M}[e^{ik(i-I-1)}\xi_k\xi_k + e^{-ik(i-I-1)}\xi_{-k}\xi_{-k}], & i \text{ is even and } I \text{ is odd} \\ -\frac{1}{2M}[e^{ik(i-I)}\xi^*_k\xi_k + e^{-ik(i-I)}\xi^*_{-k}\xi_{-k}], & i \text{ and } I \text{ are odd} \ , \end{cases} \tag{21}$$

$2M$ is the number of the lattice sites,

$$\xi_k = \left(-\frac{z_k}{2|z_k|}\right)^{1/2} , \tag{22a}$$

$$z_k = t_0(1+z_0) + t_0(1-z_0)e^{i2k} . \tag{22b}$$

The space of two-electron-hole pairs excitations in a long chain is too large to carry out any meaningful calculations. However, when we consider the biexciton, the bound state of two-electron-hole pairs, we can confine ourselves in its subspace spanned by the basis,

$$|e,h;e,h\rangle = a^\dagger_{i\uparrow} b^\dagger_{I\downarrow} a^\dagger_{j\downarrow} b^\dagger_{J\uparrow}|g\rangle \equiv |i\uparrow, I\downarrow; j\downarrow, J\uparrow\rangle . \tag{23}$$

This selection relies on two factors: one is from the experiment, which indicated that the biexciton is composed by two 1 ^1B_u excitons,[7] the other is from the consideration that two electrons (holes) with reverse spins favor to be bound together and reduce energy, otherwise there is repulsion due to the Pauli exclusion principle. Since the holes in this subspace have opposite spins, the spatial wave function is symmetric by exchanging these two holes. We construct the symmetric wave function of biexciton in real space by the Heitler-London method,[29]

$$\Psi(i\uparrow, I\downarrow; j\downarrow, J\uparrow) \simeq \psi(i,I)\psi(j,J) + \psi(j,I)\psi(i,J) . \tag{24}$$

Here, we drew an analogy between the biexciton and hydrogen molecule. The holes in the biexciton are regarded as the protons in hydrogen molecule and $\psi(i,I)$ is similar to the $1s$ hydrogen orbital wave function. The spin effect of the holes, as that of the protons in hydrogen molecule, was neglected.

In PPV, since the effective masses of electron and hole are close to each other,[15] it is different from hydrogen molecule, where the mass of proton is far larger than that of electron. As in the case of positronium molecule,[33] the polarization effect should be considered to improve our results in polymers. However, our calculation shows that the simple Heitler-London wave function can also give a considerable binding of the excitons in polymers.

The energy of the biexciton is computed by

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} . \tag{25}$$

A straightforward calculation gives

$$E = \frac{1}{A^2+S^2}[2(A^2+S^2)E_e + J + K] , \tag{26}$$

where,

$$A = \sum_i |\psi(i,I)|^2 , \tag{27}$$

$$S^2 = \sum_{ij} \psi^*(i,I)\psi^*(j,J)\psi(j,I)\psi(i,J) , \tag{28}$$

$$J = \sum_{ij} \psi^*(i,I)\psi^*(j,J)(V_{|i-j|} + V_{|I-J|} - V_{|i-J|} - V_{|j-I|})\psi(i,I)\psi(j,J) , \tag{29}$$

$$K = \sum_{ij} \psi^*(i,I)\psi^*(j,J)(V_{|i-j|} + V_{|I-J|} - V_{|i-I|} - V_{|j-J|})\psi(j,I)\psi(i,J) , \tag{30}$$

and E_e is the energy of 1 ^1B_u exciton, so the binding energy is

$$E_B = \frac{1}{A^2+S^2}(J+K) . \tag{31}$$

To improve our calculation, we also try to construct the wave function of biexciton in another way,[34]

$$\Psi(i\uparrow, I\downarrow; j\downarrow, J\uparrow) = [\psi(i,I) + \lambda\psi(i,J)][\psi(j,J) + \lambda\psi(j,I)] , \tag{32}$$

where a variational parameter λ is introduced to adjust the relative weight of "ionic" and "covalent" parts in the biexciton.

IV. NUMERICAL RESULTS

In PPV, the benzene ring causes a relatively large effective bond alternation.[35] Since the existing works show little difference on the energy levels of excitons, the parameters in Hamiltonian (1) are chosen by fitting the energy spectrum of singlet and triplet excitons with the experimental data. If we choose $z_0 = 0.19$, $U = 3t_0$, $V = t_0$, and t_0 is set to be 2.0 eV, the energies of 1 ^1B_u, m^1A_g, 1 ^3B_u, and 2 ^3A_g, achieved by diagonalizing the matrix (8) with $K = 0$, are 2.42, 2.78, 1.41, and 2.78 eV, respectively, which are very close to the experimental values, 2.4, 2.9, 1.4, and 2.85 eV, from Ref. 7. Then we use these determined parameters to calculate the band gap and the energy of biexciton in PPV.

To determine the onset of the continuum band, at first, by solving Eq. (11), in which $\bar{m}$ and δm can be explicitly expressed by

$$\delta m = \frac{z}{\pi(1-z^2)}[K(\sqrt{1-z^2}) - E(\sqrt{1-z^2})] , \tag{33}$$

$$\bar{m} = \frac{1}{\pi(1-z^2)}[E(\sqrt{1-z^2}) - z^2K(\sqrt{1-z^2})] , \tag{34}$$

where $K(x)$ and $E(x)$ are the complete elliptic functions of the first and second kinds, respectively, we obtained the parameters in the effective Hamiltonian (9), $t = 1.3t_0$ and $z = 0.26$.

If only the Hubbard model is considered, the exact result by Lieb and Wu indicates the correlation gap is[36]

$$E_{\rm CG} = U - 4t + 8\sum_{n=1}^{\infty}(-1)^n[\tfrac{1}{2}nU - (t^2 + \tfrac{1}{4}n^2U^2)^{1/2}] . \tag{35}$$

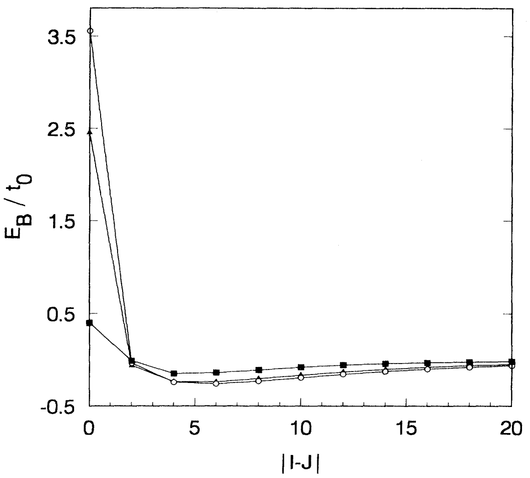

FIG. 1. Binding energy of the biexciton as a function of the distance between two holes for different Hubbard parameter U, with $V = t_0$ and $z_0 = 0.19$. The open circle, solid triangle, and solid box correspond to $U = 4t_0$, $U = 3t_0$, and $U = t_0$, respectively.

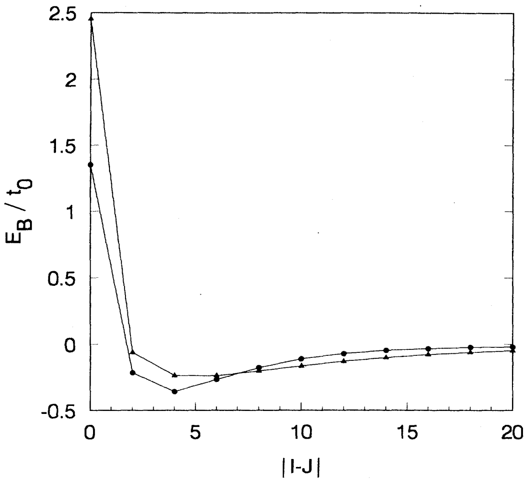

FIG. 2. Binding energy of the biexciton as a function of the distance between two holes for different Coulomb interaction parameter V, with $U = 3t_0$, $z_0 = 0.19$. The circle and triangle correspond to $V = 2t_0$ and $V = t_0$, respectively.

In the present case, $E_{\rm CG} = 0.37t_0$, thus the band gap should be

$$E_g = 4tz + E_{\rm CG} = (1.35 + 0.37)t_0 = 3.44 \text{ eV}. \quad (36)$$

If we consider the long-range Coulomb interaction Eq. (12) and neglect the fine distinction between the Coulomb interaction and Ohno's[37] empirical formula, from Fig. 3(a) of Ref. 26, $E_{\rm CG} \sim 0.064U^2/t$. We obtain the band gap

$$E_g = 4zt + E_{\rm CG} = (1.35 + 0.44)t_0 = 3.58 \text{ eV}, \quad (37)$$

which agrees with the experimental value $E_g = 3.5$ eV in Ref. 7, thus supporting that the exciton binding energy in PPV is large, ~ 1.0 eV rather than 0.4 eV.

We calculated the binding energy of biexciton for different separation of the two holes to find their equilibrium distance. The two holes are all placed on the even sites to preserve the symmetry of wave function.[23] From Fig. 1, for $U = 3t_0$, $V = t_0$, and $z_0 = 0.19$, we find the biexciton is formed by two near excitons in real space with $\sim 4-6$ lattice constant. Comparing the calculated radius of 1 ^1B_u exciton, ~ 8 lattice constant, with the experimental value, ~ 40 Å,[38] we estimate the equilibrium distance between two holes in the biexciton of PPV is about $20 - 30$ Å. The binding energy $|E_B| \sim 0.24t_0 = 0.48$ eV. If the variational wave function (32) is adopted, we always get $\lambda = 1$ by minimizing the energy of biexciton, and the energy is not further reduced. This is similar as the situation in hydrogen molecule.[34]

As predicated in Sec. III, the Heitler-London type wave function does not take account of the polarization effect, so the calculated binding energy $|E_B|$ is smaller than the experimental value. If the polarization effect is included, as shown by Brinkman, Rice, and Bell (see Fig. 1 of Ref. 39), the binding energy $|E_B|$ will further increase more than 10% compared with the Heitler-London approach. So we estimate the binding energy of biexciton is about 0.55 eV in PPV, and the threshold for the two-electron states (denoted BX in Ref. 7) should be placed at $2E_e - 0.55 = 4.25$ eV, close to the experimental value 4.15 eV.

We also studied the binding energy of the biexciton for different strengths of e-e interaction. Figure 1 illustrates the binding energy for different U. It is shown that the equilibrium distance between holes and the binding energy are insensitive to U. This is readily understood since it is the long-range part V_i ($i \neq 0$) of the e-e interaction rather than the on-site U to bind the electrons and holes together. This point is confirmed in Fig. 2, which demonstrates that the stronger V gives the larger binding energy of the biexciton.

V. CONCLUDING REMARKS

We have applied the SSH model added by a long-range e-e interaction to study the excited states in PPV. We combine the AYS's exciton theory[23] and the band gap theory of Ref. 26 to compute the energy levels of singlet and triplet excitons and the threshold of the conduction band, and we construct the bound biexciton wave function in real space by the Heitler-London method to calculate its binding energy and radius. The theoretical results are in good agreement with the experimental data of the energies of these important excited states in PPV.[7] There are still some small differences between our results and experimental values. The calculated band gap and the energy of biexciton are larger than the experimental values by about 0.1 eV. These differences are comparable to the calculated lattice relaxation energies of singlet and triplet states in PPV oligomers ($\sim 0.1 - 0.2$ eV in phenyl-capped trimer),[11] so we attributed them to the rigid lattice approximation, where further reduction of the energy of the excited state due to the lattice relaxation is not included. We have also discussed some features of the biexciton, showing the different roles of the on-site U and the long-range part V_i of the e-e interaction in the biexciton.

By the comparison between our calculations and the experiments, we have obtained the practical parameters in PPV: the strengths of e-e interaction $U = 6$ eV and $V = 2$ eV, the electron hopping $t_0 = 2$ eV, and the effective bond alternation $\delta = 0.19$. We can see that the electron correlation is of major importance in PPV.

Since in the present work, the studied Hamiltonian is popular for conjugated polymers, our method and results can be extended directly to other polymers, such as polydiacetylene. Moreover, these studied excited states are the "essential states"[19] to determine the third-harmonic generation in polymers and our results are helpful to explore the nonlinear optical properties in these materials.

ACKNOWLEDGMENTS

This work was partly supported by the National Natural Science Foundation of China and the Advanced Materials Committee of China.

---

[*] Mailing address.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature **347**, 539 (1990).

[2] U. Rauscher, H. Bässler, D. D. C. Bradley, and M. Hennecke, Phys. Rev. B **42**, 9830 (1990).

[3] N. F. Colaneri, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. B. Holmes, and C. W. Spangler, Phys. Rev. B **42**, 11 670 (1990).

[4] M. Gailberger and H. Bässler, Phys. Rev. B **44**, 8643 (1991).

[5] E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman, and H. H. Hörhold, Phys. Rev. B **46**, 9320 (1992).

[6] C. H. Lee, G. Yu, D. Moses, and A. J. Heeger, Phys. Rev. B **49**, 2396 (1994).

[7] J. M. Leng, S. Jeglinski, X. Wei, R. E. Beener, and Z. V. Vardeny, Phys. Rev. Lett. **72**, 156 (1994).

[8] J. W. P. Hsu, M. Yan, T. M. Jedju, and L. J. Rothberg, Phys. Rev. B **49**, 712 (1994).

[9] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **72**, 1104 (1994); **73**, 744 (1994).

[10] K. Picher, D. A. Halliday, D. D. C. Bradley, P. L. Burn, R. H. Friend, and A. B. Holmes, J. Phys. Condens. Matter **5**, 7155 (1993).

[11] D. Beljonne, Z. Shuai, R. H. Friend, and J. L. Brédas, J. Chem. Phys. **102**, 2042 (1995).

[12] M. Chandross, S. Mazumdar, S. Jeglinski, X. Wei, Z. V. Vardeny, E. W. Kwock, and T. M. Miller, Phys. Rev. B **50**, 14 702 (1994).

[13] Z. Shuai, J. L. Brédas, and W. P. Su, Chem. Phys. Lett. **228**, 301 (1994).

[14] R. N. Marks, J. J. M. Halls, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, J. Phys. Condens. Matter **6**, 1379 (1994).

[15] P. Gomes da Costa and E. M. Conwell, Phys. Rev. B **48**, 1993 (1993).

[16] L. S. Swanson, J. Shinar, and K. Yoshino, Phys. Rev. Lett. **65**, 1140 (1990).

[17] L. S. Swanson, P. A. Lane, J. Shinar, and F. Wudl, Phys. Rev. B **44**, 10 617 (1991).

[18] L. S. Swanson, J. Shinar, A. R. Brown, D. D. C. Bradley, R. H. Friend, P. Burn, A. Kraft, and A. B. Holmes, Phys. Rev. B **46**, 15 072 (1992).

[19] D. Guo, S. Mazumdar, S. N. Dixit, F. Kajzar, F. Jarka, Y. Kawabe, and N. Peyghambarian, Phys. Rev. B **48**, 1433 (1993).

[20] S. Suhai, Phys. Rev. B **29**, 4570 (1984).

[21] H. Hayashi and K. Nasu, Phys. Rev. B **32**, 5295 (1985).

[22] H. Tanaka, M. Inoue, and E. Hanamura, Solid State Commun. **63**, 103 (1987).

[23] S. Abe, J. Yu, and W. P. Su, Phys. Rev. B **45**, 8264 (1992).

[24] S. Nakajima, Y. Toyozawa, and R. Abe, *The Physics of Elementary Excitations* (Springer-Verlag, Berlin, 1980).

[25] Y. Shimoi and S. Abe, Phys. Rev. B **49**, 14 113 (1994).

[26] C. Q. Wu, Phys. Rev. B **47**, 4204 (1993).

[27] K. W. Becker and P. Fulde, J. Chem. Phys. **91**, 4223 (1989).

[28] V. A. Shakin and S. Abe, Phys. Rev. B **50**, 4306 (1994).

[29] H. Eyring, J. Walter, and G. E. Kimbal, *Quantum Chemistry* (John Wiley, New York, 1957).

[30] M. C. dos Santos and J. L. Brédas, Synth. Met. **29**, E321 (1989).

[31] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[32] P. E. Peierls, *Quantum Theory of Solid* (Clarendon, Oxford, 1955).

[33] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947); A. Ore, *ibid.* **71**, 913 (1947).

[34] C. A. Coulson and I. Fisher, Philos. Mag. **40**, 386 (1949).

[35] Z. G. Soos, S. Etemad, D. S. Galvao, and S. Ramasesha, Chem. Phys. Lett. **194**, 341 (1992).

[36] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).

[37] K. Ohno, Theor. Chim. Acta **2**, 219 (1964).

[38] S. C. Graham, D. D. C. Bradley, R. H. Friend, and C. Spangler, Synth. Met. **41-43**, 1277 (1991).

[39] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. B **8**, 1570 (1973).