

Off-diagonal interactions, bond density correlation, and their effects on the excitons in conjugated polymers

Hua Zhao and Rong-tong Fu

T. D. Lee Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, China
and Shanghai Institute of Technical Physics, Academia Sinica, Shanghai 200083, China*

Xin Sun

Department of Physics, Fudan University, Shanghai 200433, China
and Institute for Molecular Science, Okazaki 444, Japan*

Zhi-lin Zhang

*Department of Material Science, Jiading Campus, Shanghai University, Shanghai 201800, China
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The effects of electron-electron interactions with both diagonal and off-diagonal parts on the excitons in conjugated polymers are studied, and it is found that the bond-charge interaction W and the bond-site interaction X affect the excitons oppositely: the former suppresses the excitation energy of excitons whereas the latter increases it except for the $2A_g$ state. We find that the screening (originating from the bond density correlation effect of π electrons), which controls the bond correlation, is a reason that the binding energy of the exciton is reduced. Our calculation shows that the off-diagonal interactions affect the singlet exciton with small binding energy even at normal screening, but for large exciton energy, such effects are negligible. [S0163-1829(97)09240-0]

I. INTRODUCTION

Unlike the transition metals¹ and high- T_c superconducting cuprate oxides,² the π -conjugated polymer has a much wider bandwidth³ due to the delocalization of π electrons. There is, furthermore, not a real antiferromagnetic ground state observed in the polymer chains.⁴ Therefore, the Hubbard interaction U is not the sole effect determining the physical properties of π -conjugated polymers. It is necessary to use the long-range Coulomb interaction (PPP model)⁵ or the extended Hubbard interaction V (Ref. 6) to study the electron-hole excitations⁷ and nonlinear optical behaviors⁸ of π -conjugated polymers, such as polyacetylene (PA), polydiacetylene (PDA), poly(*p*-phenylenevinylene) (PPV), etc. In polymer materials, U and V have been popularly considered, but when the screening effect of the π electrons in conjugated polymers is striking,⁹ the off-diagonal interaction W between the bond charges and X between the bond charge and the site charge should not be omitted in calculation. Actually W or X has been added into the Hamiltonian to investigate ferromagnetism¹⁰ or superconductivity¹¹ in non π -electron systems and organic molecular materials. There have been many papers¹²⁻¹⁷ discussing the roles of the off-diagonal interactions (W , X).

According to theoretical calculation^{9,18} with a screened electron-electron ($e-e$) interaction potential, it is now generally accepted that the influence of the $e-e$ interactions in the π -electronic conjugated systems on the dimerization and energy gap is dependent on the screening strength. When the screening is weak or normal, the $e-e$ interaction increases the dimerization and energy gap; but, when the screening becomes strong, the $e-e$ interaction can decrease the dimer-

ization and energy gap. In the extreme screening limit, even ferromagnetic order in polymers could be set.¹⁹ However, to our knowledge, there has been a lack of systematical discussion about the effects of W and X on the excitons in conjugated polymers. The exciton in conjugated polymers is an important excitation, which is closely related to the nonlinear optical properties and electroluminescence,⁸ and moreover, at present there are sharp disputes^{20,21} about the magnitude of exciton binding energy in conjugated polymers.

The purpose of this paper is to study the excitation spectra and the binding energy of the exciton in conjugated polymers with $e-e$ interactions (U , V , W , and X) under different screening strengths. Standard exciton theory²² and the approach²³ under the single excitation configuration are used in the study.

This paper is organized as follows. In Sec. II we calculate the diagonal and off-diagonal matrix elements of $e-e$ interactions (U , V , W , and X) in A_g and B_u states and the excitonic excitation spectra in π -conjugated polymers. In Sec. III we present a detailed discussion about the excitation energies of $2A_g$ and $1B_u$ states for fixed and screened on-site interaction U , respectively. In Sec. IV we investigate the effective energy gap affected by W and X in the Hartree-Fock (HF) approximation, and calculate the exciton binding energies under different screening strengths. It is found that even around normal screening ($\beta \sim 1$), the off-diagonal interactions (W , X) will bring about a meaningful effect on the exciton binding energy only if the relative values of U , V , W , and X obtained from the screened Coulomb potential are proper. In Sec. V we present a comprehensive discussion of the relationship among off-diagonal interactions, bond density correlation of the π electrons, and

screening factor β . It is seen that the bond correlation (BC) (due to off-diagonal interactions), which is important for π -conjugated systems with broad bandwidth, can shed light on some existing questions, such as the magnitude of the exciton binding energy^{20,21,24} in π -conjugated polymers. Finally, we summarize our results.

II. MODEL HAMILTONIAN AND MATRIX ELEMENTS

We begin our study from the following Hamiltonian:

$$H = H_0 + H_{e-e}, \quad (1)$$

where H_0 is the Su-Schrieffer-Heeger (SSH) Hamiltonian,²⁵

$$H_0 = - \sum_{l\sigma} [t_0 - (-1)^l \delta t_0] (m_{l\sigma} + m_{l\sigma}^\dagger) \quad (2)$$

and H_{e-e} is the $e-e$ interaction Hamiltonian:

$$\begin{aligned} H_{e-e} = & U \sum_l n_{l\uparrow} n_{l\downarrow} + V \sum_{l\sigma\sigma'} n_{l\sigma} n_{l+1\sigma'} + W \sum_{l\sigma\sigma'} (m_{l\sigma} + m_{l\sigma}^\dagger) \\ & \times (m_{l\sigma'} + m_{l\sigma'}^\dagger) + X \sum_{l\sigma\sigma'} (m_{l\sigma} + m_{l\sigma}^\dagger) (n_{l\sigma'} + n_{l+1\sigma'}), \end{aligned} \quad (3)$$

where $C_{l\sigma}^\dagger$ ($C_{l\sigma}$) is the creation (annihilation) operator of an electron with spin σ at site l . $n_{l\sigma} = C_{l\sigma}^\dagger C_{l\sigma}$, the electron density. $m_{l\sigma} = C_{l\sigma}^\dagger C_{l+1\sigma}$, the bond-charge density of an electron with spin σ lying between the sites l and $l+1$. t_0 is the hopping integral and δt_0 is the bond alternation. In H_{e-e} , the first term is the Hubbard interaction, the second term is the nearest-neighbor Coulomb repulsive interaction, the third term describes the bond-charge Coulomb repulsive interaction between the adjacent sites l and $l+1$, and the final term represents the interaction of the bond charge and the site charges. The final term, the bond-site interaction term, breaks the charge-conjugate symmetry (CCS) of the system. In the HF approximation of the $e-e$ interaction Hamiltonian H_{e-e} , the X term is equivalent to a single-particle term and just renormalizes the hopping term from the bare hopping t_0 to $t_0 - 2X$ [see Eq. (23) in Sec. IV and Ref. 19]. The off-diagonal matrix element contributed by the X term is zero at $K=0$. Here the Peierls distortion of the lattice (without $e-e$

interaction) induces an energy gap $E_g^0 = 4\delta t_0$ at the Fermi surface k_F , that is, the system is in the bond order wave (BOW) phase. When the $e-e$ interaction is switched on, the energy gap will become

$$E_g = E_g^0 + E_g^{e-e}, \quad (4)$$

where E_g^{e-e} is a gap contributed by the $e-e$ interactions. E_g^{e-e} can be approximately written as a sum of two parts: E_g^{HF} and E_g^C , where E_g^{HF} is the energy gap under the HF approximation and E_g^C is the correlation gap induced by the residual $e-e$ interactions. For a detailed discussion of the correlation energy gap see Refs. 26 and 27; in this paper we do not consider it (see Sec. V for the reason).

As usual, according to standard exciton theory,²² we choose one-electron states of H_0 as the basis and constitute a set of single electron-hole pair excitation states (we only consider single excitation configuration) from the ground state $|g\rangle$:

$$|k_c, k_v\rangle = \frac{1}{\sqrt{2}} (C_{k_c\uparrow}^\dagger C_{k_v\uparrow} \pm C_{k_c\downarrow}^\dagger C_{k_v\downarrow}) |g\rangle, \quad (5)$$

where “+” denotes the spin singlet and “-” the spin triplet. Then we calculate the diagonal matrix elements and the off-diagonal matrix elements of the total Hamiltonian H relative to the ground-state energy E_0 . We introduce the relation $k_c = k + K$ and $k_v = k - K$, where k is the relative momentum of the electron-hole pair and K is the momentum of the center of mass of the electron-hole pair. Thus the state $|k_c, k_v\rangle$ is represented by the state $|k, K\rangle$. In the electron-hole pair excitation states $|k, K\rangle$, the matrix elements of the excitation Hamiltonian H are written as

$$\begin{aligned} \langle k', K' | (H - E_0) | k, K \rangle = & \delta_{K'K} \{ \delta_{k'k} [\tilde{\epsilon}_c(k+K) - \tilde{\epsilon}_v(k-K)] \\ & + \langle k', K | H_U | k, K \rangle + \langle k', K | H_V | k, K \rangle \\ & + \langle k', K | H_W | k, K \rangle \\ & + \langle k', K | H_X | k, K \rangle \}, \end{aligned} \quad (6)$$

where $E_0 = \langle H \rangle$, representing the expectation value of H in the ground state $|g\rangle = \prod_{k_v} C_{k_v\uparrow}^\dagger C_{k_v\downarrow}^\dagger |0\rangle$, $|0\rangle$ is the vacuum state without electrons. The off-diagonal matrix elements are as follows:

$$\langle k', K | H_U | k, K \rangle = (2\delta_S - 1) \frac{U}{M} (\xi_{k'-K} \xi_{k'+K}^* + \xi_{k-K}^* \xi_{k+K} + \text{c.c.}), \quad (7)$$

$$\langle k', K | H_V | k, K \rangle = 2(2\delta_S \langle k', K | H_V | k, K \rangle_X - \langle k', K | H_V | k, K \rangle_C), \quad (8)$$

$$\langle k', K | H_V | k, K \rangle_C = \frac{V}{M} \{ \xi_{k'+K} \xi_{k+K}^* \xi_{k'-K} \xi_{k-K}^* \exp[-2i(k'-k)a] + \xi_{k'+K}^* \xi_{k+K} \xi_{k'-K}^* \xi_{k-K} \}, \quad (9)$$

$$\langle k', K | H_V | k, K \rangle_X = - \frac{V}{M} \{ \xi_{k'+K}^* \xi_{k+K} \xi_{k'-K} \xi_{k-K} \exp[2i(2K)a] + \xi_{k'+K} \xi_{k+K}^* \xi_{k'-K}^* \xi_{k-K} \}, \quad (10)$$

$$\begin{aligned} \langle k', K | H_W | k, K \rangle = & \frac{2W}{M} \{ [\xi_{k'+K} \xi_{k+K} \xi_{k'-K}^* \xi_{k-K}^* \{ 1 + \exp[-2i(2K)a] \} + \text{c.c.}] + 2\delta_S [\xi_{k'+K} \xi_{k+K}^* \xi_{k'-K}^* \xi_{k-K} \\ & \times \{ 1 + \exp[2i(k+k')a] \} + \text{c.c.}] + (1-2\delta_S) [\xi_{k'-K}^* \xi_{k'+K} \xi_{k-K}^* \xi_{k+K} \{ 1 + \exp[2i(k+k')a] \} + \text{c.c.}] \}, \end{aligned} \quad (11)$$

$$\langle k', K | H_X | k, K \rangle = 0 \quad (\text{when } K=0), \quad (12)$$

where $\xi_k = (-z_k^*/2|z_k|)^{1/2}$ and $|z_k| = 2\sqrt{t_0^2 \cos^2(ka) + \delta t_0^2 \sin^2(ka)}$; c.c. denotes complex conjugate. C and X in Eq. (8) mean the Coulomb part and the exchange part, respectively, as in Ref. 23. Due to the spatial inversion symmetries at a bond center, the exciton space can be divided into two subspaces: symmetric A_g states $|k; -, K\rangle [\equiv (|k, K\rangle - |-k, K\rangle)/\sqrt{2}]$ and antisymmetric B_u states $|k; +, K\rangle [\equiv (|k, K\rangle + |-k, K\rangle)/\sqrt{2}]$. By some steps, the matrix elements of the excitation Hamiltonian can be transformed to the matrix elements in the A_g and B_u subspaces:

$$\langle k'; \pm, K | (H - E_0) | k; \pm, K \rangle = \delta_{k',k} [\tilde{\epsilon}_c(k+K) - \tilde{\epsilon}_v(k-K)] + \langle k'; \pm, K | H_{e-e} | k; \pm, K \rangle, \quad (13)$$

where

$$\begin{aligned} \langle k'; \pm, K | H_{e-e} | k; \pm, K \rangle &= (2\delta_S - 1) \left(\frac{1 \pm 1}{2} \right) \langle k'; \pm, K | H_U | k; \pm, K \rangle + 2[2\delta_S \langle k'; \pm, K | H_V | k; \pm, K \rangle_X - \langle k'; \pm, K | H_V | k; \pm, K \rangle_C] \\ &+ (1 - 4\delta_S)^{(1 \mp 1)/2} \langle k'; \pm, K | H_W | k; \pm, K \rangle, \end{aligned} \quad (14)$$

where $\delta_S = +1$ represents the spin singlet and $\delta_S = 0$ the spin triplet; the upper sign corresponds to the B_u state and the lower sign to the A_g state.

When $K=0$, we have the following relations with respect to the off-diagonal matrix elements:

$$\langle k'; -, K | H_U | k; -, K \rangle = 0, \quad (15)$$

$$\langle k'; -, K | H_V | k; -, K \rangle_X = 0, \quad (16)$$

$$\langle k'; \pm, K | H_X | k; \pm, K \rangle = 0, \quad (17)$$

and

$$\langle k'; +, K | H_W | k; +, K \rangle_{1B_u} = \langle k'; +, K | H_W | k; +, K \rangle_{3B_u}, \quad (18)$$

$$\langle k'; -, K | H_W | k; -, K \rangle_{1A_g} = (-3) \langle k'; -, K | H_W | k; -, K \rangle_{3A_g}, \quad (19)$$

$$\langle k'; \pm, K | H_V | k; \pm, K \rangle_X = 2 \langle k', K | H_V | k, K \rangle_X, \quad (20)$$

where H_U , H_V , H_W , and H_X are the first, second, third, and fourth terms, respectively, in Eq. (3). Note that $\langle k'; \pm, K | H_X | k; \pm, K \rangle \neq 0$ when $K \neq 0$. The diagonal matrix elements $[\tilde{\epsilon}_c(k) - \tilde{\epsilon}_v(k)]$ in Eq. (13) are equal to

$$\epsilon_c(k) - \epsilon_v(k) + \Delta\epsilon_c(k) - \Delta\epsilon_v(k), \quad (21)$$

where $\Delta\epsilon_c(k)$ and $\Delta\epsilon_v(k)$ are related to V , W , and X , but not to U . Equation (17) tells us that at $K=0$, X does not contribute to the off-diagonal matrix elements, and Eqs. (18) and (19) mean that W gives the same contributions for the off-diagonal matrix elements of singlet $1B_u$ and triplet $3B_u$ states but different contributions for the off-diagonal matrix elements of singlet $1A_g$ and triplet $3A_g$ states. We can see below that despite relation (19), the degeneration of the 2^1A_g and 2^3A_g states is still not lifted for all screening strengths.

III. EXCITATION SPECTRA OF EXCITON

In order to study the influences of the $e-e$ interactions (U , V , W , and X) upon the excitons under different screen-

ing strength, we need direct relationships of U , V , W , and X with the screening factor β . In our calculation we set $t_0 = 2.0$ eV, $\delta t_0 = 0.2t_0$ for the SSH Hamiltonian (2). Our system is a ring with $N = 400$ sites as in Ref. 23. We assume in Sec. III A that the on-site $e-e$ interaction U stays unchanged in all screening strengths. The value of U is set to 6.0 eV. In Sec. III B we study the situations in which U is changeable with the screening strength. In order to make clear what roles the off-diagonal $e-e$ interactions (W , X) play in the excitation energies of the exciton when the screening changes, below we study four cases: $W=X=0$; $X \neq 0$; $W \neq 0$; both $W \neq 0$ and $X \neq 0$. We must realize that the correlation effects between the π electrons always exist in π -conjugated systems since the $e-e$ interactions always exist in it. When $\beta \neq 0$, the case $W=X=0$ is similar to Ref. 28, in which the PPP Hamiltonian was employed to investigate the effect of correlation on the π -electron spectrum of polyenes by using an exponentially decaying repulsive potential: $V_{ij} = U \exp(-r_{ij}/D_0)$, where D_0 was the decay constant. However, V and U were not connected through the integrals over the π -electron wave functions. This is a salient difference from our study. Thus the case $W=X=0$ (when $\beta \neq 0$) reflects the effect of the bond density correlation of π electrons, and is used to make comparisons with the case $W \neq 0$, $X \neq 0$, and both $W \neq 0$ and $X \neq 0$. In our study, the factor β is mainly used to represent the screening effect induced by a complicated bond density correlation from the delocalized π electrons on a single chain and the surrounding chains. Then, it is seen that, through such comparisons, the case $W=X=0$ can be used as a reference to judge whether the off-diagonal interactions (W , X) are important or indispensable in describing the physical properties of the π -conjugated polymers. For detailed explanations of the relationships among the π -electron bond density correlation effect, β and the off-diagonal interactions (W , X), see Sec. V.

In the analyses below, the unit of all numbers is t_0 .

A. Excitation energies in the fixed on-site interaction

According to Ref. 18, we can find the quantitative relations of V , W , and X , relative to U , corresponding to the different screening strengths. Through the numerical diagonalization of the matrix of Eq. (13) we obtain the excitation energies of A_g and B_u states under different screening and

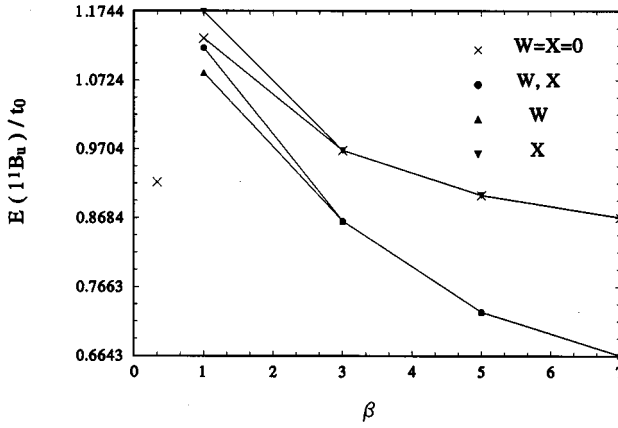


FIG. 1. The variation of the excitation energies of 1^1B_u with β under fixed U . The \times is an estimate of excitation energy at $\beta=1/3$ for the case $W=X=0$.

find the following results. To see the changes of excitation energies of $2A_g$ and $1B_u$ states at $\beta < 1$, we estimate the excitation energies of these states at $\beta=1/3$, where $U < 2V$. The energies of $2A_g$, 1^1B_u , and 1^3B_u excitons are approximately 1.5925, 0.9209, and 0.9444, respectively. When $U=2V$ and $W=X=0$, the excitation energies of 1^1B_u and 1^3B_u are degenerate, as in Ref. 29. When $\beta < 3$, the excitation energy spectra of A_g and B_u states are clearly composed of two parts: discrete and continuous branches, that is, four discrete excitonic states, 2^1A_g , 2^3A_g , 1^1B_u , and 1^3B_u , plus the electron-hole pair continuum of higher excitation energies starting from $\tilde{\epsilon}_c(\pi/2a) - \tilde{\epsilon}_v(\pi/2a)$.

When $W=X=0$, the model is the extended Hubbard model. However, U and V here have been connected by the screening factor β , that is to say, the bond density correlation effect has been considered here through β . This point is different from Ref. 29. In Figs. 1, 2, and 3 we can see that the excitation energies of the 1^1B_u exciton decrease from 1.1346 at $\beta=1$ to 0.8686 at $\beta=7$ (very strong screening) and those of the $2A_g$ (1^3B_u) states monotonically decrease from 1.5925(0.9444), 1.4100(0.8168) at $\beta=1/3, 1$ to 0.8782(0.4446) at $\beta=7$. But the excitation energy of the 1^1B_u exciton is about 0.9209 at $\beta=1/3$. When β increases

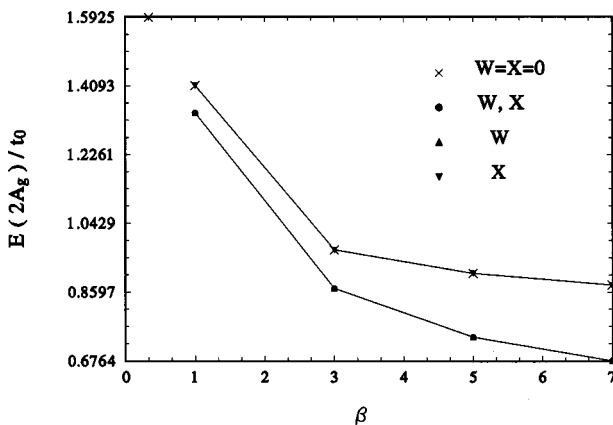


FIG. 2. The variation of the excitation energies of $2A_g$ with β under fixed U . The \times is an estimate of excitation energy at $\beta=1/3$ for the case $W=X=0$.

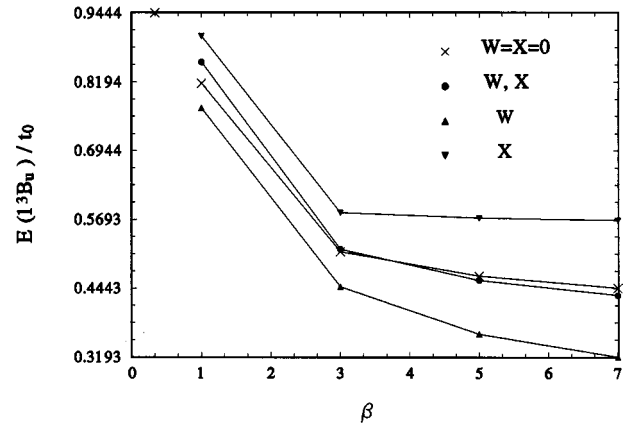


FIG. 3. The variation of the excitation energies of 1^3B_u with β under fixed U . The \times is an estimate of excitation energy at $\beta=1/3$ for the case $W=X=0$.

from $1/3, 1$ to 7 , the nearest-neighbor Coulomb interaction V decreases correspondingly from 3.07, to 2.34, to 0.30 eV.

When $W=0$ and $X \neq 0$, X causes the excitation energy of 1^1B_u to increase by an increment 0.0398 at $\beta=1$. The excitation energies of 1^1B_u at $\beta=3, 5, 7$ are almost the same as those when $W=X=0$. See Fig. 1. The excitation energies of $2A_g$ at all β values are the same as those when $W=X=0$, which means X does not affect the excitation energies of $2A_g$. See Fig. 2. The changes of excitation energies of the 1^1B_u (1^3B_u) exciton relative to the case of $W=X=0$ are $-0.0398(-0.0852)$, $-0.0002(-0.0712)$, $-0.0003(-0.1054)$ and $-0.0004(-0.1234)$ when $\beta=1, 3, 5$, and 7 , respectively. The minus sign in front of the numbers shows that X enhances the excitation energies of 1^1B_u and 1^3B_u excitons. The effect of X on the 1^3B_u exciton is larger than on the 1^1B_u exciton. See Figs. 1 and 3.

When $W \neq 0$ and $X=0$, all the excitation energies of 1^1B_u , 1^3B_u , and $2A_g$ states are lowered with increasing β and these reductions become greater with β , as shown in Figs. 1, 2, and 3. In comparison with the case $W=X=0$, the changes of excitation energies of 1^1B_u (1^3B_u , $2A_g$) are 0.0514(0.0450, 0.0732), 0.1045(0.0638, 0.1033), 0.1730(0.1059, 0.1708), and 0.2043(0.1253, 0.2018) when $\beta=1, 3, 5$, and 7 , respectively.

When $W \neq 0$ and $X \neq 0$, the excitation energy of 1^1B_u at $\beta=1$ is increased by 0.0374 as compared with the case $W \neq 0$ but $X=0$. Those of 1^1B_u at $\beta=3, 5$, and 7 are almost the same as the case $W \neq 0$ but $X=0$. This is because X only affects the energy of the 1^1B_u exciton at $\beta=1$. See Fig. 1. As for the 1^3B_u exciton, since X enhances its energy but W decreases its energy when β is from 1 to 7, the joint influence of W and X induces the energy of 1^3B_u to increase from $\beta=1$ to 3 and to decrease from $\beta=5$ to 7. See Fig. 3. The excitation energies of $2A_g$ at all β values are almost the same as those of $W \neq 0$ and $X=0$. See Fig. 2.

When $\beta \geq 3$, the excitation energies of the $2A_g$ and 1^1B_u states have become close to each other in the above four cases. See Fig. 4 for this situation where $W \neq 0$ and $X \neq 0$.

It is seen above that the effects of the bond-charge interaction W and the bond-site interaction X are opposite for the 1^1B_u exciton near $\beta=1$ and opposite for the 1^3B_u exciton at all β values. See Figs. 1 and 3. X mainly affects the 1^1B_u

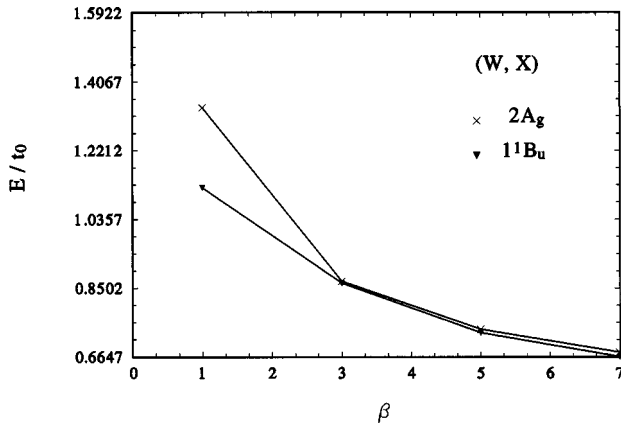


FIG. 4. The excitation energies of $2A_g$ and 1^1B_u come close to one another when $\beta \geq 3$ with W and X under fixed U .

exciton near $\beta=1$ and almost produces no effect on 1^1B_u when $\beta \geq 3$. This effect of X brings energy changes of 0.08, 0.17, and 0 eV to the 1^1B_u , 1^3B_u , and $2A_g$ states, respectively, at $\beta=1$, but these changes become 0, 0.14, and 0 eV, respectively, at $\beta=3$; whereas W (when $X=0$) generates a change of 0.1, 0.09, and 0.15 eV, respectively, on the excitation energies of the 1^1B_u , 1^3B_u , and $2A_g$ states at $\beta=1$ and these changes on the 1^1B_u , 1^3B_u , and $2A_g$ states become about 0.2, 0.12, and 0.2 eV, respectively, at $\beta=3$. At $\beta=1$, the joint effect of W and X leads to excitation energy changes of about 0.028 and 0.076 eV for 1^1B_u and 1^3B_u at $\beta=1$ since the effect of W is opposite to that of X at $\beta=1$.

We observe that in the case $W=X=0$ the excitation energies of the $2A_g$ states, the singlet 1^1B_u , and the triplet 1^3B_u excitons at $\beta=1$, where $U > 2V$, are 1.4100, 1.1346, and 0.8160, respectively, in the present screened potential; their corresponding values in the long-range Coulomb interaction (without W and X) are about 1.37, 1.12, and 0.93, respectively, in Ref. 23 where $U=4$ eV, $V=2$ eV, $t_0=2$ eV, $\delta t_0=0.2t_0$, and the dielectric constant ϵ_σ is set to 5, which is for electrons on a single chain surrounded by the other chains. In Ref. 20 their values are about 1.425, 1.2, and 0.7, respectively, where $U=3t_0$, $V=t_0$, and $\delta t_0=0.2t_0$ for a 16 site linear chain.

B. Excitation energies in the screened on-site interaction

The on-site Coulomb repulsion U in fact decreases with increasing screening strength of π electrons in the screening potential¹⁸ since the ratio U/U_0 decreases with the screening factor β , where U_0 is the on-site Coulomb repulsion with no screening. There is a determined value U at a given screening strength. In addition, the atomic polarization will also cause U_0 to be screened (see Sec. V). For simplicity, here we set the values of U at $\beta=1/3, 1, 3, 5$, and 7 are 8, 6, 4.5, 3, and 1.5 eV, respectively, in order to calculate the excitation energies of excitons under W and X . As in Sec. III A, in all four cases the excitation energies of $2A_g$ and 1^1B_u states become closed still at $\beta \geq 3$ (when $U \leq 4.5$ eV) (the figure is omitted). The 1^3B_u exciton is particularly sensitive to U . When U is 3–6 eV, the energies of the 1^1B_u and 1^3B_u states are more separated; when $U < 3$ eV, they have come close to each other, which is different from the situation in which U is unchanged. See Figs. 4, 5, and 6.

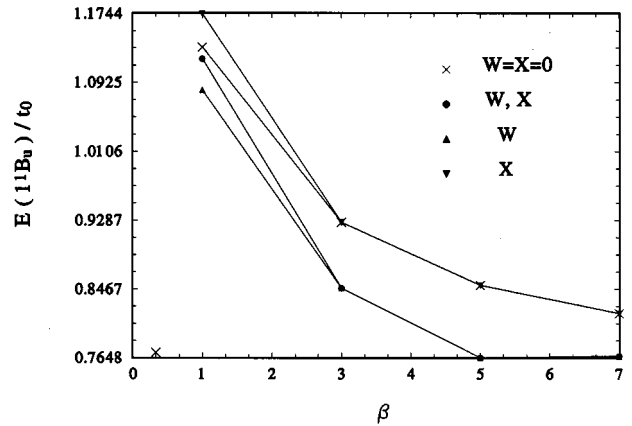


FIG. 5. The variation of the excitation energies of 1^1B_u with β under changeable U . The \times is an estimate at $\beta=1/3$ for the case $W=X=0$.

When $W=X=0$, the energies of the $2A_g$ and 1^1B_u states become smaller (except $\beta=1$) as compared with those of the $2A_g$ and 1^1B_u states in fixed U , because when U is small, V is small also and when V becomes smaller the excitation energies of the $2A_g$ and 1^1B_u excitons will dwindle. The energy of 1^1B_u at $\beta=1/3$ is 0.7708, which is lower than that of 1^1B_u at the same β value in Sec. III A. As for the 1^3B_u exciton, it is more sensitive to U than $2A_g$ and 1^1B_u . Therefore, when U and V become smaller, the excitation energies of 1^3B_u become higher with increasing β . See Fig. 6.

When $W=0$ and $X \neq 0$, only the energy of 1^1B_u at $\beta=1$ is greatly changed by X , and the energies of 1^1B_u at $\beta=3, 5$, and 7 , respectively, are almost unaltered. See Fig. 5. X does not change the energies of $2A_g$, as in Sec. III A (see Fig. 2). The effect of X enhances the energies of 1^3B_u and this increase becomes less with increasing β : -0.085 , -0.0341 , -0.0159 , and -0.0023 when $\beta=1, 3, 5$, and 7 , respectively. This differs from that in Sec. III A. See Figs. 3 and 5.

When $W \neq 0$ and $X=0$, the effect of W is to lower the excitation energies of $2A_g$, 1^1B_u , and 1^3B_u with β from 1 to 7. However, as U becomes smaller, the effect of W at the strong screening ($\beta=7$) is reduced, so that the changes of

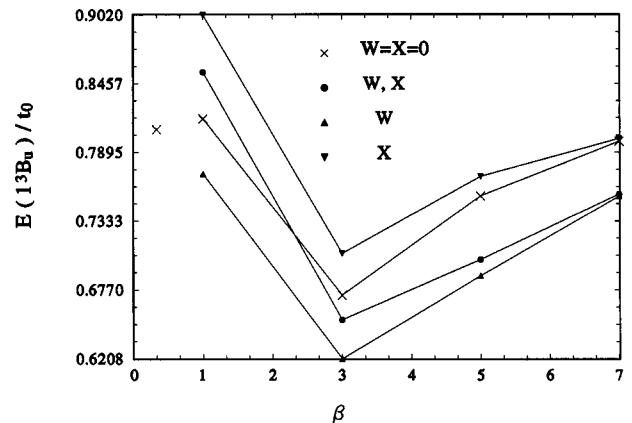


FIG. 6. The variation of the excitation energies of 1^3B_u with β under changeable U . The estimate \times at $\beta=1/3$ is smaller than that in Fig. 3.

the excitation energies of 1^1B_u ($2A_g$) are 0.0514(0.0732), 0.0784(0.0774), 0.0864(0.0854), and 0.0511(0.0505) when β is from 1 to 7, which differs from that in Sec. III A. As for the 1^3B_u exciton, the changes of its excitation energies are 0.0450, 0.0519, 0.0655, and 0.0448 when β is 1–7 as compared with the case $W=X=0$. Thus, the effect of W can well show up only when U has a certain strength.

When $W \neq 0$ and $X \neq 0$, the situation is like that of $W \neq 0$ and $X=0$, because X does not have an effect on the energies of 1^1B_u ($2A_g$) from $\beta=3(1)$ to $\beta=7$. The energy changes of 1^3B_u caused by the joint effect of W and X are -0.0383 , 0.0199 , 0.0521 , and 0.0430 when $\beta=1, 3, 5$, and 7 , respectively, which is different from that in Sec. III A.

It is seen again from the above that the effects of W and X on the excitation energies of $1B_u$ excitons are opposite. See Figs. 5 and 6. X seems an ‘‘active agent,’’ which makes the excitation energies of excitons higher; that is, it causes the number of higher excited states to increase relative to the case without X . However, W suppresses the excitation energies of excitons; that is, it causes the number of lower excited states to increase relative to the case without W , as in Sec. III A. The most striking distinction between Secs. III A and III B lies in the changes of the triplet 1^3B_u exciton with increasing β and decreasing U value. See Figs. 3 and 6. At $\beta=3$, W produces an energy change of 0.16 eV for both 1^1B_u and $2A_g$ states, which is lower than their energy changes (0.2 eV) in Sec. III A, because here U is small (4.5 eV), which leads to small W .

IV. THE EFFECTIVE ENERGY GAP UNDER THE OFF-DIAGONAL INTERACTIONS

A. The effective energy gap

To obtain the binding energy of an exciton we need the values of the energy gap E_g^{e-e} under W and X . With regard to the calculation of the electronic energy gap of conjugated polymers, this problem is not completely solved because of the complexity of the correlation property induced by the residual $e-e$ interactions (which are not considered in the HF approximation) and also by the broad band character of conjugated polymers. In the present work we do not intend to consider the energy gap contributed by the correlations. As this is a preliminary investigation, the HF approximation is used in our consideration. Then the effective one-particle Hamiltonian reads

$$H_{\text{eff}} = - \sum_{l\sigma} [t - (-1)^l \delta t] (m_{l\sigma} + m_{l\sigma}^\dagger), \quad (22)$$

where t is the effective hopping corrected by the $e-e$ interactions:

$$t = t_0 - 2X + (V - 6W)\bar{m} \quad (23)$$

and δt is the effective modulation of lattice by the $e-e$ interactions:

$$\delta t = \delta t_0 + (V - 6W)\delta m, \quad (24)$$

TABLE I. The effective energy gap and the binding energy of the $1B_u$ state in the fixed on-site interaction (in units of t_0). $E_g^{\text{eff}}(z_0)$ and $E_g^{\text{eff}}(z)$ represent the values from z_0 and z , respectively.

	β	1/3	1	3	5	7
$E_g^{\text{eff}}(z_0)$	($W=X=0$)	1.5925	1.4100	0.9721	0.9095	0.8782
	(W,X)		1.3368	0.8688	0.7387	0.6764
	(W)		1.3368	0.8688	0.7387	0.6764
	(X)		1.4100	0.9721	0.9095	0.8782
$E_g^{\text{eff}}(z)$	($W=X=0$)	1.7876	1.5306	0.9825	0.9138	0.8804
	(W,X)		1.3904	0.8663	0.7456	0.6951
	(W)		1.4317	0.8705	0.7401	0.6820
	(X)		1.4837	0.9716	0.9033	0.8715
$E_b(1^1B_u)$	($W=X=0$)	0.6717	0.2755	0.0053	0.0078	0.0096
	(W,X)		0.2163	0.0054	0.0097	0.0118
	(W)		0.2537	0.0056	0.0100	0.0122
	(X)		0.2357	0.0052	0.0075	0.0092
$E_b(1^3B_u)$	($W=X=0$)	0.6481	0.5832	0.4617	0.4430	0.4336
	(W,X)		0.4818	0.3538	0.2804	0.2453
	(W)		0.5651	0.4223	0.3781	0.3571
	(X)		0.5180	0.3915	0.3386	0.3102

where \bar{m} represents the average bond charge density and δm is the fluctuation around this average bond charge density and they are defined by $\langle m_{l\sigma} \rangle = \bar{m}_\sigma \pm \delta m_\sigma$.²⁹ Our study is only in the phase BOW, so the \bar{m}_σ and δm_σ are independent of spin σ . The effective energy gap under the HF approximation at $\pi/2a$ is then

$$E_g^{\text{eff}} = 4[\delta t_0 + (V - 6W)\delta m]. \quad (25)$$

The \bar{m} and δm is determined by the first and second elliptic integrals as follows:

$$\delta m = \frac{z}{\pi(1-z^2)} [K(\sqrt{1-z^2}) - E(\sqrt{1-z^2})], \quad (26)$$

$$\bar{m} = \frac{1}{\pi(1-z^2)} [E(\sqrt{1-z^2}) - z^2 K(\sqrt{1-z^2})], \quad (27)$$

where $z \equiv \delta t/t$. Here one should pay attention to two cases where we determine the effective $e-e$ energy gap E_g^{eff} : in one, the amplitude δm of the bond charge density around its average is changeable with the values of the $e-e$ interactions, and in the other it is not changeable with the $e-e$ interactions. In the first case, by using the initial parameters t_0 and z_0 ($\equiv \delta t_0/t_0$), through solving Eqs. (23)–(27) simultaneously we get the effective parameter z and then get the values of δm and \bar{m} from Eqs. (26) and (27). In the second case, the δm and \bar{m} are directly determined by Eqs. (26) and (27) by using the initial parameters t_0 and z_0 , as has been done in Ref. 23. Our calculations in this paper belong to the latter. See the values of $E_g^{\text{eff}}(z_0)$ in Table I.

Table I shows us that the values of the energy gap obtained from the effective parameter z are bigger than those calculated directly from the initial parameter z_0 when

$W=X=0$. With increasing β , the effect of W remarkably diminishes the effective energy gap (that is, the effective dimerization δt of π -conjugated systems). The influence of W alone or of both W and X reduces the effective energy gap to values below $E_g^0=4\delta t_0=0.8t_0$ when $\beta\geq 5$. The single effect of X does not change or slightly changes the effective energy gap with increasing β .

Notice that although there is no bond-site interaction X in $E_g^{\text{eff}}=4[\delta t_0+(V-6W)\delta m]$, X can exert its effects on E_g^{eff} through δm and \bar{m} in the first case. See the values of $E_g^{\text{eff}}(z)$ in Table I.

B. The exciton binding energy

The binding energy E_b of an exciton is, by definition, given by the difference (E_g-E) between the energy gap E_g and the exciton energy E . In the HF approximation, we calculate the binding energies of the singlet 1^1B_u and the triplet 1^3B_u excitons under the influence of bond density correlation effect and off-diagonal interactions (W, X) in fixed U . The results are listed in Table I.

It is seen in Table I that the binding energy of the 1^1B_u exciton decreases from finite values at $\beta=1$ to negligible ones at $\beta=5$. At very strong screening ($\beta=7$), the binding energies of 1^1B_u have in reverse a little increase relative to those at $\beta=5$. This is because this strong screening effect causes the excitation energies of 1^1B_u to decrease to their lowest values. The binding energy of the 1^3B_u exciton always keeps a finite value at all screening strengths. This is because the energy level of 1^3B_u always lies in the effective energy gap at all screening strengths.

Only if U also decreases due to the screening (maybe including the screening due to the polarization of σ electrons), the binding energy of the 1^3B_u exciton will be reduced from finite values at the weak or normal screening to negligible ones at the strong screening.

Compared to the case $W=X=0$, the effect of W decreases the binding energy of the 1^1B_u exciton at $\beta=1$ and increases the binding energy of the 1^1B_u exciton from $\beta=3$ to $\beta=7$. The effect of X decreases the binding energy of the 1^1B_u exciton at all screening strengths. As a result, the joint effect of W and X decreases the binding energy of the 1^1B_u exciton at $\beta=1$ and then increases them from $\beta=3$ to 7.

We notice that only when $\beta\leq 1$ are the values of the exciton binding energy (for 1^1B_u) of practical meaning. At $\beta=1$, for the singlet 1^1B_u exciton, the joint effect of W and X creates about a 0.12-eV change relative to the case $W=X=0$; the single effect of W causes only approximately a 0.044-eV change and that of X brings about approximately a 0.08-eV change.

As for the 1^3B_u exciton, the effects of W and X make its binding energy decrease from $\beta=1$ to 7. Thus the joint effect of W and X decreases the 1^3B_u exciton binding energy at all screening strengths.

Thus it seems apparent from the above results that for the conjugated polymer with a small exciton binding energy, such as 0.2 eV for the derivative of PPV, poly [2-methoxy, 5-(2'-ethylhexoxy)-1, 4-phenylenevinylene] (MEH-PPV),²⁴ the off-diagonal interaction W or X will develop its effect, even at the normal screening strength. When the screening strength becomes much stronger ($\beta>1$), W or X produces

no changes on the binding energy of the 1^1B_u exciton, because the bond correlation or the off-diagonal interaction causes the excitation energy of the 1^1B_u exciton to almost approach the bottom of the conduction band (see Secs. III and V), despite the fact that the effect of W increases with increasing screening factor. However, for a large exciton binding energy such as 1.1 eV (Ref. 20) for PPV, the effect of W or X may be omitted because the effects they generate around the normal screening strength on the exciton binding energy are very weak.

V. DISCUSSION AND CONCLUSION

First, the screening from π electrons is different from that from the polarization of σ electrons since the π electrons are delocalized throughout the whole system but the σ electrons are localized in the backbone of π -conjugated systems. The screening by π electrons is a ‘‘dynamical’’ many-body correlation effect, but the screening from σ electrons is an ‘‘electrostatic’’ effect in π -conjugated systems.

The effect of the σ electron polarization leads to the usual static dielectric constant ϵ_σ , which depresses the on-site Coulomb repulsion U and the long-range Coulomb repulsion $V_{ll'}$ of the π electron. Thus the Coulomb interactions or the Ohno potential³⁰ among π electrons are represented by³¹ $V_{ll'}/\epsilon_\sigma$. However, the screening for U is unlike the screening that $V_{ll'}$ feels since U is short ranged and works only within an atomic size. The atomic polarization will cause the atomic value U_0 to be screened, for instance, for 3d transition-metal Cu, $U_0\approx 16$ eV is screened to $U\approx 5$ eV.³² In π -conjugated polymers, the atomic polarization³³ will render U screened from its bare atomic value U_0 to an effective value. For instance, for polyactelene, $U_0=11.13$ eV is screened to about 4.4 eV, where $\epsilon_\sigma=9$ (quite strong) and the nearest-neighbor interaction $V=0.8$ eV.²⁷ For C_{60} , $U_0=3.5$ eV (Ref. 34) is screened to $U\approx 1.5$ eV.³⁵ Therefore, besides the screening factor β , the polarizations of σ electrons and the charges on the neighboring sites³⁴ will cause both U and $V_{ll'}$ to be screened.

Due to the complexity of the dynamical correlation problem, the zero-frequency effect of this problem can be discussed. In this way, the screening effect by the correlation among the π electrons can phenomenologically be represented by a screening factor β , so that the long-range Coulomb interaction is corrected as an exponentially decaying potential: $e^{-\beta r/r}$.^{9,18,19,28} Here we call the many-body effect, which makes the $e-e$ interactions among π electrons effective, the bond density correlation effect and call the many-body correlation due to the off-diagonal interactions (W, X) the bond correlation or the off-diagonal correlation. The correlation effect in π -conjugated systems has been studied carefully in Refs. 28 and 31. However, in Ref. 28 the off-diagonal interactions and the bond correlation effect were not introduced, although the exponentially decaying screened Coulomb potential was applied, so it is somewhat different from ours (see the first paragraph in Sec. III); in Ref. 31, the correlation effect of π electrons was considered mainly from a Hubbard-type interaction. This is also different from ours.

Whether β is considered or not, W and X always exist in π -conjugated or other electron systems.¹ When $\beta=0$, the many-center integrals in the bare π -electron Coulomb interaction lead to the diagonal parts (U, V) and off-diagonal parts (W, X) for an isolated benzene:³⁶ $U=16.93$ eV,

$V=9.027$ eV, $X=3.313$ eV, and $W=0.462$ eV. As a comparison, for $3d$ (narrow) band of transition metals,¹ we have $U\approx 20$ eV, $V\approx 6$ eV, $X\approx 1/2$ eV, and $W\approx 1/80$ eV. However, when $\beta\neq 0$, all the values of U , V , W , and X will be changed and are related to one another. Here β is, in fact, a cutoff parameter of the Coulomb interaction. The larger the β , the weaker the Coulomb interaction. Thus the factor β reflects a kind of screening effect on the π electrons in conjugated polymers. But the larger the β , the larger the changes of the relative values among V , W , and X also. This manifests the significance of the screening factor β : the larger β , the stronger the bond density correlations. And only when β reaches a certain strength will the effect of W or X become striking, as seen in Refs. 18,19. Here we emphasize that β is a reflection of the bond density correlation among the π electrons with a large overlap integral in π -conjugated polymers. In this sense, the case $W=X=0$ represents the bond density correlation effect through β , and the case in which $W\neq 0$ or $X\neq 0$ (or both $W\neq 0$ and $X\neq 0$) represents the bond density correlation plus the off-diagonal interactions through β . Moreover, the adoption of the screened Coulomb potential could be regarded as compensating for the shortcomings of the tight-binding approximation.

Second, in the present exciton theory²² used here, the diagonal matrix elements in the momentum representation are, in fact, derived under the HF approximation in which the correlations, except for the correlation between the electrons with parallel spins, are not considered, and the correlations caused by the different interactions (U , V , W , and X) are also not considered in the exciton theory. In addition, we observe that the excitation energy spectra of $1B_u$ and $2A_g$ excitons is mainly controlled by the diagonal matrix elements from our calculations. Therefore we should at the same time add the corresponding corrections to both the energy gap equation and the diagonal matrix elements of the exciton excitation instead of only considering the correction of correlation energy in the energy gap equation. In this way, it would be, we think, more reasonable to study theoretically the exciton binding energy when the residual correlations are to be considered. For example, according to our calculations here we also can see this point. If we utilize the excitation energy value of the 1^1B_u exciton without W but use the energy gap value with W at the same screening factor, say, $\beta=1$, we would get a difference value (exciton binding energy) of $(1.3368t_0-1.1346t_0)$ 0.4 eV. However, if we consider simultaneously the effect of W on the excitation energy calculations and the energy gap equation, we will obtain a difference of 0.5 eV. Thus it can be seen that the results are distinctly different. Notice that this example is just used to indicate that inconsistent treatment would bring about inconsistent results. In fact, whether SCI (single configuration interaction) or DCI (double configuration interaction) is used, as long as the HF approximation is utilized, there exists such a problem. Experimentally, the determination of the binding energy of the singlet exciton 1^1B_u is closely dependent on the measurement of the single-particle energy gap²⁴ or the electron-hole continuum edge (CB threshold²⁰). If this measured value is large, then the singlet exciton binding energy may be large; if this value is small, then the singlet exciton binding energy may be small, since according to calculations²³ or experimental measurement,^{20,24} the excita-

tion energies of the singlet exciton 1^1B_u have no big differences (see the comparison in Sec. IV A). However, it is difficult to accurately determine theoretically the single-particle energy gap and the exciton energy simultaneously if there is no consideration of the contribution of the above-mentioned correlation in the exciton method used here.

In addition, in real conjugated polymer materials there always exists the dielectric constant ϵ_σ . We observe that if ϵ_σ is set to 2 and β to 1 (assuming that β is purely due to the π -electron correlations), we get that the excitation energy of the 1^1B_u exciton is 1.0645 and the HF energy gap value is 1.0683. Thus, the exciton binding energy is found to be 0.0076 eV, which is very small and can be negligible, but if β is taken to be $1/3$, the excitation energy of the 1^1B_u exciton is estimated as 1.1583 and the HF energy gap value is about 1.1998, so the exciton binding energy is approximately 0.08 (~ 0.1) eV. This means that at the given dielectric constant ϵ_σ (say, $\epsilon_\sigma=2$), only the smaller screening factor (say, $\beta=1/3$) will bring forth a positive effect on the exciton binding energy and the large screening factor (say, $\beta=1$) will yield a negligible effect on the exciton binding energy. This implies that the intensity of the bond density correlation determines the magnitude of the exciton binding energy in π -conjugated polymers. If the intensity is big, the exciton binding energy may be small; if the intensity is small, the exciton binding energy may be a non-negligible quantity. On the other hand, if the screening factor β is assumed to contain the effect of σ electrons on the same chain and of π -electron motion on neighboring chains,¹⁹ then W and X together generate about a 0.12-eV change in the binding energy of the 1^1B_u exciton at $\beta=1$, and, when $\beta\geq 3$, the bond density correlation, W and X also produce a negligible effect on the exciton binding energy (see Table I). Thus if the intensity of the bond density correlation is strong, the exciton binding energy is small; if the intensity is small or moderate, the exciton binding energy may be a non-negligible quantity. In the very recent experiment²⁴ for the derivative of PPV, MEH-PPV, the single-electron gap is determined to be 2.45 eV and the exciton absorption peak is measured at 2.25 eV, so the exciton binding energy is determined to be 0.2 eV. Our results of the singlet exciton binding energy above, under the bond density correlation effect, W and X , are comparable with this experimental result.

Therefore these results imply that the π -electronic screening effect (originating from the bond density correlation effect of the π electrons) may be a reason that the exciton binding energy is small in π -conjugated polymers, and W and X will generate their effects on the exciton binding energy even when the screening factor is normal ($\beta\sim 1$). In addition, it is important to make clear how much of the contribution to the exciton is from the π electron screening effect in π -conjugated polymers with a given dielectric constant ϵ_σ . This question needs further study.

In summary, our calculation shows that the effects of the bond-charge interaction W and the bond-site interaction $X(<0)$ on the excitation energies of the 1^1B_u and 1^3B_u states are opposite: W decreases and X increases their excitation energies. W decreases the excitation energies of the $2A_g$ states but X does not change them at all screening strengths, whether the on-site Coulomb repulsion U is screened or unscreened. With increasing β , the effect of W

on 1^1B_u and $2A_g$ goes from weak to strong, and the effect of X on them goes from strong to weak. Under fixed U , the exciton binding energy decreases with increasing β , that is, the stronger the bond density correlation of π electrons, the smaller the exciton binding energy becomes, and, more importantly, we find that the off-diagonal interaction W or X will exert its effect on the small exciton binding energy even

at the normal screening scope. For a large exciton binding energy case, the effects of W and X are negligible.

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*Permanent address.

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