Excitons in two coupled conjugated polymer chains

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Abstract

We have studied the exciton states in two coupled conjugated polymer chains which are modeled individually by the Su-Schrieffer-Heeger Hamiltonian and coupled by an interchain electron-transfer term. Both the intra- and inter-chain long range Coulomb interactions are taken into account. The properties of the lowest symmetric and antisymmetric exciton states are extensively discussed for both the parallel and anti-parallel ordering between these two chains. It is found that, for these two kinds of ordering, the features of excitons are quite different. Possible implications for the experiment of luminescent polymers are also addressed.
I. INTRODUCTION

The significance of excitons in conjugated polymers has been recognized for many years in a class known as polydiacetylene [1]. Recently, the interest in excitons has been heightened by discovering that poly(\(p\)-phenylene vinylene) (PPV) and its derivatives can be used as the active luminescent layer in electroluminescent light-emitting diode devices [2], since it is believed that radiative recombination of singlet excitons gives rise to luminescence. Although a general picture of understanding of photoinduced absorption (PA) and photoconductivity (PC) experiments of PPV and its derivatives remains a subject of intense debate [3–11], the dramatically different PA behavior of dilute solutions and thin films of poly[2-methoxy, 5-(2’ ethyl-hexoxy)-1,4 phenylene vinylene] (MEH-PPV) [12], together with the photoconductivity being observed to start at the absorption edge in PPV [13], clearly indicate the important role the interchain coupling plays. Actually, electron-diffraction experiments indicate that the interchain coherence length of PPV is about 60 Å [14]. However, the properties of excitons in coupled chains, to the best of our knowledge, have never been discussed.

There have been several works to develop the exciton theory in a single polymer chain [15–18]. Abe and co-workers introduced the standard exciton theory [19] to one-dimensional polymers [18]. Within the single configuration interaction (SCI) approximation, the energy levels and wave functions of exciton states in a long chain can be obtained. In this paper, we will extend their approach and explore the features of excitons in two coupled polymer chains. Interestingly enough, we find that, for two kinds of ordering, i.e., the parallel- and anti-parallel-ordering between the two chains, the properties of excitons are quite different. Although this study does not result in quantitative explanations of the PA and PC experiments, it is helpful for understanding the photophysics better in luminescent polymers like PPV, and is also a foundation of further calculations of optical properties of coupled polymers.

In Sec. II, the model is defined and the formulation is derived. In Sec. III, we present numerical results on the lowest symmetric and antisymmetric excitons and
II. FORMALISM

We start with the two coupled chains model introduced by Baeriswyl and Maki [20], in which, each chain is described by the Su-Schrieffer-Heeger Hamiltonian (SSH) [21]

\[ H_j = -t \sum_n [1 - (-1)^n z_j] (c_{jn+1}^d c_{jn} + \text{H.c.}) , \]  

where \( j = 1, 2 \) denotes the chain index, and is coupled by an interchain hopping term

\[ H_\perp = -t_\perp \sum_n (c_{1n}^d c_{2n} + \text{H.c.}) . \]  

Here \( c_{jn} \) is the annihilation operator of the electron at site \( n \) on the \( j \)th chain, the spin indices have been omitted for simplicity. Each chain is assumed to be dimerized in accordance with the Peierls theorem [22], \( z_j \) is the dimerization amplitude of the \( j \)th chain, \( |z_1| = |z_2| = z \), but they may differ in sign. Strictly speaking, the SSH model is directly applicable only to polyacetylene, however, recent works have shown that the primary excitation in luminescent polymers like PPV can also be described within the linear chain model [23,10,11]. In PPV and its derivatives, the lowest excitonic wave function extends over several repeat units [9,13], the properties of exciton are therefore not very sensitive to the delicate structure within the unit. From the viewpoint of renormalization [24], we can map the complex structure of PPV into an effective SSH system with the same significant physical properties by integrating out the freedom of benzene rings and only considering the electrons on the nonbenzene carbon atoms [11]. Thus the features of exciton in SSH model must have some implication to that in luminescent polymers. We have also adopted the rigid lattice approximation, since many experiments and theories had demonstrated that the primary excitation is the exciton and electron-electron interactions are predominant over electron-lattice interactions in luminescent polymers [4,8,10,11,23]. Theoretical works that have taken into account the electron-lattice interaction also show that incorporation of lattice relaxation effect would not
lead to an increase in binding energy of exciton \[23\]. This simplification enables us to handle electron-electron interactions in long chains and arrive at an understanding of electronic states in luminescent polymers without loss of essential physics, although the quantitative explanation of some lattice property like vibronic structure or bond length should, indeed, take into account the lattice relaxation effects \[26\].

By introducing operators $a_{jk}$ and $b_{jk}$ through the relation (we take the lattice constant $a = 1$ in this section) \[20\]

$$c_{jn} = \frac{1}{\sqrt{N}} \sum_k e^{ikn} [(-1)^n a_{jk} + i b_{jk}] , \quad (3)$$

here $N$ is the number of sites per chain, and by using the Bogoliubov transformation

$$\begin{pmatrix} a_{jk} \\ b_{jk} \end{pmatrix} = \begin{pmatrix} \cos \theta_{jk} & \sin \theta_{jk} \\ -\sin \theta_{jk} & \cos \theta_{jk} \end{pmatrix} \begin{pmatrix} \alpha_{jk} \\ \beta_{jk} \end{pmatrix} , \quad (4)$$

$H_j$ is diagonalized when $\tan 2\theta_{jk} = z_j \tan k$,

$$H_j = \sum_k E_k (\alpha_{jk} \alpha_{jk} - \beta_{jk} \beta_{jk}) , \quad (5)$$

with

$$E_k = 2t \sqrt{\cos^2 k + z_j^2 \sin^2 k} . \quad (6)$$

The interchain hopping term then becomes

$$H_\perp = -t_\perp \sum_k [\cos(\theta_{1k} - \theta_{2k})(\alpha_{1k}^\dagger \alpha_{2k} + \beta_{1k}^\dagger \beta_{2k}) + \sin(\theta_{1k} - \theta_{2k})(\beta_{1k}^\dagger \alpha_{2k} - \alpha_{1k}^\dagger \beta_{2k}) + \text{H.c.}] . \quad (7)$$

There are two kinds of orderings between the two chains, the parallel ordering ($\theta_{1k} = \theta_{2k}$) and anti-parallel one ($\theta_{1k} = -\theta_{2k}$) \[20\]. For the case of $\theta_{1k} = \theta_{2k}$,

$$H_\perp = -t_\perp \sum_k (\alpha_{1k}^\dagger \alpha_{2k} + \beta_{1k}^\dagger \beta_{2k} + \text{H.c.}) , \quad (8)$$

the full Hamiltonian $H = H_1 + H_2 + H_\perp$ can be written as
\[ H = \sum_k (\alpha_{1k}^\dagger \alpha_{2k}^\dagger) \begin{pmatrix} E_k & -t_\perp \\ -t_\perp & E_k \end{pmatrix} \begin{pmatrix} \alpha_{1k} \\ \alpha_{2k} \end{pmatrix} + \sum_k (\beta_{1k}^\dagger \beta_{2k}^\dagger) \begin{pmatrix} -E_k & -t_\perp \\ -t_\perp & -E_k \end{pmatrix} \begin{pmatrix} \beta_{1k} \\ \beta_{2k} \end{pmatrix}, \]  

and is readily diagonalized by the orthogonal transformation

\[ (A_{1k} A_{2k} B_{1k} B_{2k})^T = O(\alpha_{1k} \alpha_{2k} \beta_{1k} \beta_{2k})^T, \]

\[ H = \sum_k [(E_k - t_\perp)(A_{1k}^\dagger A_{1k} - B_{1k}^\dagger B_{1k}) + (E_k + t_\perp)(A_{2k}^\dagger A_{2k} - B_{2k}^\dagger B_{2k})] \],

where, \( A_{ik}^\dagger \) and \( B_{ik}^\dagger \) (\( i = 1, 2 \)) create an electron in the \( i \)th conduction and valence band respectively.

For the case of \( \theta_{1k} = -\theta_{2k} = \theta_k \),

\[ H_\perp = -t_\perp \sum_k [\cos 2\theta_k (\alpha_{1k}^\dagger \alpha_{2k} + \beta_{1k}^\dagger \beta_{2k}) + \sin 2\theta_k (\beta_{1k}^\dagger \alpha_{2k} - \alpha_{1k}^\dagger \beta_{2k}) + \mathrm{H.c.}] \],

the total Hamiltonian reads

\[ H = \sum_k (\alpha_{1k}^\dagger \alpha_{2k}^\dagger \beta_{1k}^\dagger \beta_{2k}^\dagger) \begin{pmatrix} E_k & -t_\perp \cos 2\theta_k & 0 & t_\perp \sin 2\theta_k \\ -t_\perp \cos 2\theta_k & E_k & -t_\perp \sin 2\theta_k & 0 \\ 0 & -t_\perp \sin 2\theta_k & -E_k & -t_\perp \cos 2\theta_k \\ t_\perp \sin 2\theta_k & 0 & -t_\perp \cos 2\theta_k & -E_k \end{pmatrix} \begin{pmatrix} \alpha_{1k} \\ \alpha_{2k} \\ \beta_{1k} \\ \beta_{2k} \end{pmatrix}. \]

Making the orthogonal transformation \( O \), we obtain the diagonalized Hamiltonian,

\[ H = \sum_k [\varepsilon_{1k}(A_{1k}^\dagger A_{1k} - B_{1k}^\dagger B_{1k}) + \varepsilon_{2k}(A_{2k}^\dagger A_{2k} - B_{2k}^\dagger B_{2k})] \],

with

\[ \varepsilon_{1k} = \sqrt{E_k^2 + t_\perp^2 + 4tt_\perp \cos k}, \]

\[ \varepsilon_{2k} = \sqrt{E_k^2 + t_\perp^2 - 4tt_\perp \cos k}, \]

and, meanwhile, the transformation matrix \( O \).
We add the long range Coulomb interaction \( H_{e-e} \) to \( H \) and study the exciton state,

\[
H_{e-e} = \frac{1}{2} \sum_{I,J} \sum_{ss'} V_{II'}^{IJ} \rho_{IIa} \rho_{JJa'} ,
\]

(17)

where \( \rho_{IIa} = c_{IIa}^\dagger c_{IIa} - 1/2 \), \( I \) and \( J \) are the chain indices, and the interaction potential

\[
V_{II'}^{IJ} = \begin{cases} 
V_{II'}, & I = J \\
\tilde{V}_{II'}, & I \neq J .
\end{cases}
\]

The intrachain Coulomb interaction is the commonly used form [18]

\[
V_{II} = U, \quad V_{II'} = V \vert l - l' \vert (l \neq l') .
\]

Here \( U \) is the on-site Hubbard repulsion, \( V \) the nearest-neighbor Coulomb interaction. We assume that the interaction potential between the two chains has a relatively simple form,

\[
\tilde{V}_{II'} = \frac{\tilde{U}}{\sqrt{R_0^2 + (l - l')^2}} ,
\]

\( R_0 \) will be set to be 1 in following calculations.

The procedure to determine the exciton state is a standard one. First, we use the single particle state of \( H \) to construct the ground state \(|g\rangle\),

\[
|g\rangle = \prod_{jk} B_{jk}^\dagger c_{jk}^\uparrow B_{jk}^\dagger c_{jk}^\downarrow |0\rangle .
\]

Within the SCI approximation, the exciton state can be achieved by diagonalizing the Hamiltonian \( H + H_{e-e} \) in the subspace of the single electron-hole excitation

\[
|i, k_c; j, k_v\rangle \equiv \frac{1}{\sqrt{2}} \left( A_{ik_v}^\dagger B_{jk_v}^\dagger \pm A_{ik_v}^\dagger B_{jk_v}^\dagger \right) |g\rangle ,
\]

(18)

where + is for the spin singlet, − for one of the triplet. \( k_c \) and \( -k_v \) are momenta of the electron in conduction band and the hole in valence band, respectively. \( i \) and \( j \) \((= 1, 2)\) are the band indices.

For the spin singlet exciton,

\[
\langle i', k_c'; j', k_v' | H + H_{e-e} - E_0 | i, k_c; j, k_v \rangle
\]

\[
= \delta_{k_c', k_c} \delta_{k_v', k_v} \left( \delta_{jj'} (\delta_{ii'} \varepsilon_{ik_v} + \sum_{IJ} V_{II'}^{IJ} \langle c_{Ij'} c_{Ij}^\dagger \rangle \langle c_{Jl'} c_{Jl}^\dagger \rangle \langle c_{HI} A_{ik_v}^\dagger \rangle) + \delta_{ii'} (\delta_{jj'} \varepsilon_{jk_v} - \sum_{IJ} V_{II'}^{IJ} \langle B_{Ij'} c_{Jl} \rangle \langle c_{HI} c_{Ij}^\dagger \rangle \langle c_{HI} B_{Ij}^\dagger \rangle) \right) + 2E_X - E_C ,
\]

(19)
where $E_0 = \langle g | H + H_{e-e} | g \rangle$, and for the triplet,

$$
\langle j', k'; j', k' | H + H_{e-e} - E_0 | i, k_c; j, k_v \rangle
$$

$$
= \delta_{k_c', k_c} \delta_{k_v', k_v} [ \delta_{j,j'} ( \delta_{ii'} \varepsilon_{ik_c} + \sum_{IJll'} V_{II'}^{IJ} \langle A_{ik_c} c^\dagger_{Jk_v} \rangle \langle c_{Jl'} c^\dagger_{II'} \rangle \langle c_{II'} \rangle ) ]
$$

$$
+ \delta_{ii'} ( - \delta_{jj'} \varepsilon_{jk_v} - \sum_{IJll'} V_{II'}^{IJ} \langle B_{jk_v} c_{Jl'} \rangle \langle c_{II'} c^\dagger_{IJ} \rangle \langle c^\dagger_{II'} c_{Jl'} \rangle ) ] - E_C ,
$$

(20)

and

$$
E_X = \sum_{IJll'} V_{II'}^{IJ} \langle A_{ik_c} c^\dagger_{II'} \rangle \langle c_{Jl'} A_{ik_c} \rangle \langle B_{jl'} c_{Jl'} \rangle \langle c^\dagger_{Jl'} B_{jl'} \rangle ,
$$

(21)

$$
E_C = \sum_{IJll'} V_{II'}^{IJ} \langle A_{ik_c} c^\dagger_{II'} \rangle \langle c_{Jl'} A_{ik_c} \rangle \langle B_{jl'} c_{Jl'} \rangle \langle c^\dagger_{Jl'} B_{jl'} \rangle ,
$$

(22)

where $\langle ... \rangle \equiv \langle g | ... | g \rangle$. We show how to evaluate $\langle c^\dagger_{II'} A_{ik_c} \rangle$, $\langle B_{jl'} c_{Jl'} \rangle$, and $\langle c^\dagger_{Jl'} B_{jl'} \rangle$ in the Appendix.

This two-coupled-chain system also has the symmetry with respect to the spatial inversion at a bond center like a single chain. The inversion operator $R$ is defined by

$$
R[c_{jn}] = c_{jN-n+1} ,
$$

(23)

and it is easy to prove

$$
R[\alpha_{jk}^\dagger] = -e^{ik} \alpha_{j-k}^\dagger , \quad R[\beta_{jk}] = e^{-ik} \beta_{j-k} ,
$$

so

$$
\alpha_{ik_c}^\dagger \beta_{jk_v} | g \rangle \xrightarrow{R} -e^{i(k_e-k_v)} \alpha_{-ik_c}^\dagger \beta_{j-k_v} | g \rangle ,
$$

(24)

and from the transformation matrix $Q$, which diagonalizes the Hamiltonians (9) and (13), we also have

$$
|i, k_c; j, k_v \rangle \xrightarrow{R} -e^{i(k_e-k_v)} | i, -k_c; j, -k_v \rangle .
$$

(25)

Thus we can construct the symmetric state ($A$) and anti-symmetric one ($B$). The $A$ state is written as
\[ |i, k_c; j, k_v; -\rangle = \frac{1}{\sqrt{2}} \left( |i, k_c; j, k_v\rangle - e^{i(k_c-k_v)} |i, -k_c; j, -k_v\rangle \right), \quad (26) \]

and the \( B \) state is

\[ |i, k_c; j, k_v; +\rangle = \frac{1}{\sqrt{2}} \left( |i, k_c; j, k_v\rangle + e^{i(k_c-k_v)} |i, -k_c; j, -k_v\rangle \right). \quad (27) \]

In the numerical calculation, we may confine ourselves in the \( A \) or \( B \) subspaces to diagonalize the Hamiltonian \( H + H_{e\rightarrow e} \) since the matrix element between \( A \) and \( B \) states vanish. In the exciton state, the relative and center-of-mass motion can also 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. Since we are only interested in the relative motion, we will just consider the case of \( K = 0 \), and now the basis is \( |i, k; j, k; \pm\rangle \).

The wave function of exciton in real space can be determined by

\[ \psi(I, n; J, l; \pm) = \sum_{i,j,k} \langle I, n, \uparrow; J, l, \downarrow | i, k; j, k; \pm \rangle \langle i, k; j, k; \pm | \psi \rangle, \quad (28) \]

the positions of electron and hole are at site \( n \) on the \( I \)th chain and at site \( l \) on the \( J \)th chain, respectively. \( \langle i, k; j, k; \pm | \psi \rangle \) can be obtained by diagonalizing the matrices (19) and (20), and

\[ \langle I, n, \uparrow; J, l, \downarrow | i, k; j, k; \pm \rangle = \frac{1}{\sqrt{2}} \left( \langle c_{I n}^\dagger A_{i k}^\dagger \rangle \langle c_{J l}^\dagger B_{j k} \rangle \pm \langle c_{I n}^\dagger A_{i-k}^\dagger \rangle \langle c_{J l}^\dagger B_{j-k} \rangle \right). \quad (29) \]

III. NUMERICAL RESULTS AND DISCUSSIONS

We have carried out numerical calculations to show the properties of excitons in coupled chains. The intrachain parameters are fixed with realistic values, \( U = 2t \), \( V = t \), and \( z = 0.2 \). The interchain coupling \( t_{\perp} \) can be estimated according to the results of the LDF calculations for PPV by Vogl and Campbell \[27\]. In PPV, the total interchain coupling for a pair of monomers \( t_{\text{mon}} = 0.64 \text{ eV} \[28\]. Naturally, we set the total coupling for a pair of
unit in the SSH model $2t_\perp$ to be $t_{mon}$. Thus $t_\perp$ for PPV ranges from 0.12$t$ to 0.15$t$. In PPV, the nearest interatom distance on adjacent chains is 2.495 Å [28], while the bond lengths are around 1.4 Å, so the Coulomb interaction strength $\bar{U} = 0.5t$ is a reasonable estimate for PPV. We will also vary the interchain hopping $t_\perp$ and interchain Coulomb interaction parameter $\bar{U}$ to make the interchain effects more transparent. The system we study consists of two chains of $N = 200$. The exciton wave functions in the following figures represent the relative distribution of the hole in different positions when the electron is located at site $n = 101$ on the first chain. The 200 + $i$th site in figures means the $i$th site of the second chain.

First we study the case of parallel ordering. Figure 1 illustrates the wave functions of the lowest $^1B$ and $^1A$ states with $t_\perp = 0.15t$ and $\bar{U} = 0.5t$. Since the actual wave function contains rapid staggered oscillation with a period of $4a$, we have plotted $\psi(I = 1, n = 101; J, l; \pm)/f(l)$ with $f(l) = \sqrt{2}\cos[\frac{\pi}{2}(l + \frac{1}{2})]$ for the odd number $l$ [18]. We give in Tables I and II the exciton energy $E_{ex}$ and the probability $P$ that the hole is at the second chain for several groups of $t_\perp$ and $\bar{U}$. From these tables, we can see that the hole has more probability to stay at the second chain for both $B$ and $A$ states as the interchain hopping $t_\perp$ and interchain Coulomb interaction $\bar{U}$ increase. Since the energies of the $A$ states are close to the continuum band and the wave functions nearly extend over the whole system, the amplitude of wave function in the second chain is comparable to that of the first chain. The energies of $B$ states sit, however, deep in the gap, so that the amplitude of wave function in the second chain is smaller and more sensitively depends on the interchain couplings than the case of $A$ states. The triplet has similar features of the singlet.

Now we divert our attention to the case of anti-parallel ordering, which is more likely to be realized in practical polymers [29]. Meanwhile the features of the exciton in this case are more interesting. We describe the lowest $^1B$ and $^1A$ states for $t_\perp = 0.15t$ and $\bar{U} = 0.5t$ in Fig. 2. We have plotted $\psi(I = 1, n = 101; J, l; \pm)/f(l)$ for the odd number $l$ when $J = 1$ but for the even number $l$ when $J = 2$. The exciton energy $E_{ex}$, the probability $P$ that the hole stays in the second chain, and the separation $d$ between positions of maxima of wave functions...
function amplitude in two chains are listed in Tables III and IV for several groups of the interchain parameters. It is shown that the larger $\tilde{U}$ leads to the more chance to find the hole in the second chain. However, the dependence of probability $P$ on the interchain coupling $t_\perp$ is not so simple as the case of parallel ordering. For the $^1B$ state, $P$ becomes larger when $t_\perp$ increases, while for the $^1A$ state, in contradiction with intuition, $P$ decreases as $t_\perp$ increases. Unlike the parallel ordering, where the profiles of wave functions in two chains are alike and the maxima of wave function amplitude in two chains sit at the same position, in the case of anti-parallel ordering, the wave functions in two chain are well different from each other. For $^1B$ states, when the hole approaches the position of electron $n = 101$ on the first chain, the wave function reaches the maximum; but on the second chain, the wave function goes to zero when the hole is nearest to the electron. While, for $^1A$ states, when the hole and electron overlap on the first chain, the wave function vanishes; but when the hole is on the second chain, the wave function reaches the maximum as the hole approaches the position of electron. The positions with the largest wave function amplitudes in two chains have a separation $\sim 5 – 9a$ for both $B$ and $A$ states. The interchain Coulomb interaction can reduce this separation to a certain extent. This big difference between the two ordering case is understandable. From Eqs. (9) and (13), we can see that, in the case of parallel ordering, there is no mixing between valence and conduction bands of different chains and the system is more like a two-independent-chain system; in the case of anti-parallel ordering, however, the valence- and conduction- band states of these two chains are mixed together and the two chains are really coupled.

For PPV, there are two kinds of ordering between adjacent chains, namely, in-phase and out-of-phase ordering [30–32]. When the practical structure of PPV is mapped into the simplified SSH model as stated before, each type of ordering is neither parallel nor anti-parallel and the wave function of exciton in PPV should therefore be the composition of that in parallel and anti-parallel ordering. For the $^1B$ state, from Figs. 1(a) and 2(a), the maximum of the composed wave function in the first chain should sit at the position of the electron, since the profiles of wave function in parallel and anti-parallel ordering are same;
while, in the second chain, the position of maximum for the composed wave function must be situated between the site facing the electron and the site where the maximum in the second chain occurs for anti-parallel ordering. For the $^1A$ state, from Figs. 1(b) and 2(b), the composed wave function in the first chain will vanish at the position of the electron, and reach the maximum at the site which lies between the position of the electron and that of the maximum for parallel ordering. The shape of composed wave function, which shows that the position of maximum in the second chain deviates from the location of the electron in the first chain, implies that if the interchain exciton is produced, the electron and hole tend to be separated with several lattice constant. This is similar as the concept of “spatially indirect exciton” proposed by Yan and co-workers to interpret the PA spectrum in PPV [6,7]. We emphasize that it is the exchange effect which prevents the electron and hole in different chains from approaching each other in the presence of the interchain electron-electron interaction, and previous treatments to the interchain Coulomb interaction, in which, only the electrostatic energy is included [33], cannot predict this feature. Another interesting property is that, for the $A$ state, the interchain exciton is even more likely to be created than the intrachain exciton. Recently, it was documented that 80% – 90% photoexcitations in PPV are interchain excitations [4], since in practical materials, defects, interfaces, and thermal fluctuation can lead to the charge transfer and the mixing between the $A$ and $B$ states, the $A$ states with large possibilities of interchain excitons seem to have contributions to the great quantity of the interchain excitations in PPV. Obviously, these interchain excitations are also important to the PC, which is thought an interchain process in PPV.

In summary, we have studied the excitons in two coupled polymer chains. The wave functions of the lowest $A$ and $B$ states for both parallel and anti-parallel ordering have been illustrated. We have shown the pronounced difference of the property of exciton between these two kinds of ordering. For the realistic PPV, whose properties should be the combination of that in each ordering, the electron and hole tend to be separated with several lattice constant when they are not in the same chain, and in the $A$ state, the probability that
the electron and hole are in different chains is even larger than that they are in the same
chain. These features are helpful to clarify the controversies of interpreting experiments of
luminescent polymers like PPV.

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APPENDIX:

In this appendix, we show how to calculate $\langle c^\dagger_{II}A_{ik_e} \rangle$, $\langle B^\dagger_{jk_v}c_{II} \rangle$, and $\langle c^\dagger_{Jl'}c_{II} \rangle$. It is noted
that

$$
\langle c_{II}A^\dagger_{ik_e} \rangle = \langle II|A^\dagger_{ik_e}|0 \rangle ,
$$

(A1)

$$
\langle B^\dagger_{jk_v}c_{II} \rangle = \langle II|B^\dagger_{jk_v}|0 \rangle ,
$$

(A2)

and

$$
\langle c^\dagger_{Jl'}c_{II} \rangle = \sum_{ik_v} \langle 0|B_{ik_v}|Jl' \rangle \langle II|B^\dagger_{ik_v}|0 \rangle .
$$

(A3)

Since from Eqs. (3) and (4), we have

$$
\begin{pmatrix}
\langle 2n|\alpha^\dagger_{jk}|0 \rangle & \langle 2n + 1|\alpha^\dagger_{jk}|0 \rangle \\
\langle 2n|\beta^\dagger_{jk}|0 \rangle & \langle 2n + 1|\beta^\dagger_{jk}|0 \rangle 
\end{pmatrix} = \frac{1}{\sqrt{N}} e^{ik2n} \begin{pmatrix}
\exp(-i\theta_{jk}) & \exp(i\theta_{jk} + i) \\
i \exp(-i\theta_{jk}) & i \exp(i\theta_{jk} + i)
\end{pmatrix} ,
$$

(A4)

with
\[
\cos \theta_{jk} = \frac{1}{\sqrt{2}} \left( 1 + \frac{\epsilon_k}{E_k} \right)^{\frac{1}{2}},
\]
(A5)

\[
\sin \theta_{jk} = \frac{z_j \sin k}{|z_j \sin k|} \frac{1}{\sqrt{2}} \left( 1 - \frac{\epsilon_k}{E_k} \right)^{\frac{1}{2}},
\]
(A6)

here \( \epsilon_k = 2t \cos k \), then combining Eq. (A4) with the transformation matrix \( Q \), we can obtain \( \langle c_{il}^\dagger A_{ik} \rangle \), \( \langle B_{jk}^\dagger c_{il} \rangle \), and \( \langle c_{il}^\dagger c_{il} \rangle \).
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FIGURES

FIG. 1. Wave functions of the lowest $^1B$ and $^1A$ exciton states for the interchain hopping $t_\perp = 0.15t$ and interchain Coulomb interaction $\bar{U} = 0.5t$ in the case of parallel ordering between the two chains. (a) is for $^1B$ state and (b) is for $^1A$ one.

FIG. 2. Wave functions of the lowest $^1B$ and $^1A$ exciton states for $t_\perp = 0.15t$ and $\bar{U} = 0.5t$ in the case of anti-parallel ordering. (a) is for $^1B$ state and (b) is for $^1A$ one.
TABLE I. Interchain parameters ($t_\perp$ and $\tilde{U}$) and resulting exciton properties ($E_{\text{ex}}$ and $P$) of the lowest $^1B$ states for the case of parallel ordering between the two chains.

| $t_\perp$, $\tilde{U}$ (t) | 0.03, 0.5 | 0.03, 1.0 | 0.09, 0.5 | 0.09, 1.0 | 0.15, 0.5 | 0.15, 1.0 |
|-----------------------------|------------|-----------|-----------|-----------|-----------|-----------|
| $E_{\text{ex}}$ (t)         | 1.095      | 1.057     | 1.010     | 0.941     | 0.902     | 0.821     |
| $P$                         | 0.062      | 0.300     | 0.241     | 0.428     | 0.330     | 0.457     |

TABLE II. Interchain parameters ($t_\perp$ and $\tilde{U}$) and resulting exciton properties ($E_{\text{ex}}$ and $P$) of the lowest $^1A$ states for the case of parallel ordering between the two chains.

| $t_\perp$, $\tilde{U}$ (t) | 0.03, 0.5 | 0.03, 1.0 | 0.09, 0.5 | 0.09, 1.0 | 0.15, 0.5 | 0.15, 1.0 |
|-----------------------------|------------|-----------|-----------|-----------|-----------|-----------|
| $E_{\text{ex}}$ (t)         | 1.345      | 1.331     | 1.229     | 1.211     | 1.109     | 1.091     |
| $P$                         | 0.335      | 0.463     | 0.446     | 0.488     | 0.468     | 0.493     |

TABLE III. Interchain parameters ($t_\perp$ and $\tilde{U}$) and resulting exciton properties ($E_{\text{ex}}$, $P$, and $d$) of the lowest $^1B$ states for the case of anti-parallel ordering.

| $t_\perp$, $\tilde{U}$ (t) | 0.03, 0.5 | 0.03, 1.0 | 0.09, 0.5 | 0.09, 1.0 | 0.15, 0.5 | 0.15, 1.0 |
|-----------------------------|------------|-----------|-----------|-----------|-----------|-----------|
| $E_{\text{ex}}$ (t)         | 1.110      | 1.096     | 1.110     | 1.095     | 1.108     | 1.093     |
| $P$                         | 0.005      | 0.007     | 0.045     | 0.059     | 0.111     | 0.139     |
| $d$ (a)                     | 7          | 7         | 7         | 7         | 7         | 7         |

TABLE IV. Interchain parameters ($t_\perp$ and $\tilde{U}$) and resulting exciton properties ($E_{\text{ex}}$, $P$, and $d$) of the lowest $^1A$ states for the case of anti-parallel ordering.

| $t_\perp$, $\tilde{U}$ (t) | 0.03, 0.5 | 0.03, 1.0 | 0.09, 0.5 | 0.09, 1.0 | 0.15, 0.5 | 0.15, 1.0 |
|-----------------------------|------------|-----------|-----------|-----------|-----------|-----------|
| $E_{\text{ex}}$ (t)         | 1.345      | 1.194     | 1.328     | 1.188     | 1.308     | 1.178     |
| $P$                         | 0.913      | 0.987     | 0.701     | 0.903     | 0.609     | 0.798     |
| $d$ (a)                     | 9          | 7         | 9         | 7         | 7         | 5         |