Excitons in quasi-one dimensional organics: Strong correlation approximation

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I. INTRODUCTION

In recent years, the exciton concept of electron-hole bound states has gained popularity in conjugated organic polymers. Experimentally, it has been discovered that poly(phenylene vinylene) (PPV) and its derivatives, e.g., poly[2-methoxy, 5-(2' ethyl-hexoxy)-1,4 phenylene vinylene] (MEH-PPV) can be used as the active luminescent layer in electroluminescent light-emitting diode devices. By using different conjugated polymers, polymer light-emitting diodes (PLED) have been fabricated which emit throughout the visible region of the spectrum. It is believed that radiative recombination of excitons gives rise to luminescence, so a comprehensive understanding of exciton properties in polymer chains is very important to guide improvements in quantum efficiency of these PLED devices. Also, conjugated polymers have shown potential application in photonics for their large optical nonlinearity and ultrafast response time. View of the significant role excitons play in optical properties of a system, a detailed study of the exciton is also an important issue for polymer photonic device design. Theoretically, excitons in conjugated polymers are both attractive and challenging because of the coexistence of low-dimensional confinement and strong electron-electron (e-e) correlation in these systems. These ingredients have in fact led to many controversies during the study of excitons in polymers.

Discussion of excitons in solids can be traced back more than half a century to the pioneering work by Frenkel which even preceded than the band theory in solids. After numerous studies on excitons over several decades, the exciton, as an elementary excitation, has been well established in bulk insulators. This is the reason why in the existing exciton theories for polymers, the standard exciton theory in semiconductors was usually borrowed with limited justification. In these theories, the polymer is regarded as a Peierls insulator which means the gap between the conduction and valence bands arises from the Peierls dimerization, a well-known nesting effect in one-dimensional metals. Then the exciton states are solved considering the e-e interaction as a perturbation as in traditional exciton theory. But the polymer is significantly different from the conventional semiconductor. In a semiconductor, the electron correlation effects can largely be neglected and it is plausible to treat the e-e interaction as a perturbation. However, the polymer is typically a strongly correlated system with a moderate to large on-site Hubbard repulsion, and much of the band gap is due to the electron correlation rather than the dimerization. Thus the foundation of existing exciton theories in conjugated polymers is not so firm, and these theories have already led to some qualitatively incorrect results. For example, from these theories, the $1B_u$ exciton is lower than the $2A_g$, but typically the order

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should be reversed. Again, the threshold of the conduction band is independent of $U$, the on-site Hubbard repulsion. This is unreasonable since, when an electron is excited to the conduction band, double occupation must occur and cause an additional Hubbard repulsion.

Having appreciated the central importance of electron correlation in polymers, several efforts have been undertaken to take account of the strong correlation effect on exciton states. In these works, numerical exact diagonalization and density matrix renormalization group (DMRG) approaches are employed to handle small systems. From those numerical results, some useful information on the electron structure of the polymer can be captured by extrapolating the results to a long chain. However, these works cannot be regarded as constituting an exciton theory, since only some specific states are focused on in the calculations and the exciton is not treated as a quasi-particle. We must seek a more complete exciton theory of conjugated polymers, in which the correlation is stressed and the exciton is an elementary excitation. This kind of theory will then be useful to study the optical and transport properties related to the exciton. In this paper, we will develop a new exciton theory in the limit in which the Hubbard $U$ is the main origin of the band gap (i.e., the polymer is regarded as a Mott insulator). In this regime, the spin has little effect on the exciton states and the energy difference between the singlet and triplet states is negligibly small compared with their binding energies. Using scattering theory, we will analytically calculate the exciton states and find a critical strength of the $e-e$ interaction for the existence of bound exciton states.

Currently, chemically synthesized polymers cannot be free from impurities and the “pristine” samples of polymers contain a non-negligible density of impurities and defects from the cross-linking, complex morphological effects, conjugation length effects, and some extrinsic defects. Such impurities sometimes critically influence the properties of the system, e.g., the transport. For example, the conductivity in trans-polyacetylene can be dramatically enhanced by 13 orders of magnitude by doping. In an impurity-free system, the exciton states with different center-of-mass momenta form exciton bands, and within the band the exciton moves coherently as a composite particle. The disorder tends to produce localized states, and in one-dimensional systems, any nonvanishing impurity potential will lead to a localized electronic state. Thus it is interesting to examine the localization of an exciton, a composite particle, due to the impurities, and furthermore to determine if the exciton ceases to be a composite particle of electron and hole when the impurity is strong enough. In this paper, we will address the interplay of coherent motion of the exciton and different types of impurities in our conjugated polymer model.

Strictly speaking, the polymer is only a quasi-one dimensional system, in which interchain couplings always exist, and sometimes their effects are striking. Many calculations have shown that nonlinear excitations like solitons and polarons may be unstable by taking the interchain coupling into account. Recently, great attention has been paid to the interchain effects in luminescent polymers, since many experiments demonstrated that a large fraction of primary photoexcitations are interchain excitons or polaron pairs. Also, some theoretical calculations have been carried out to explore the interchain coupling effects on exciton properties. Although the terminology of interchain exciton and intrachain exciton are widely used in current literature, these concepts are not so clearly delineated. From the principles of quantum mechanics, the wavefunction of every eigenstate in the coupled system must be distributed over the whole system, so it is difficult to distinguish from the wavefunction which one corresponds to the interchain and which one to the intrachain exciton. We will clarify what the interchain and intrachain exciton states are, and calculate their energies and wavefunctions.

Photoconductivity in conjugated polymers can sometimes be greatly enhanced by intercalating or doping the polymer with a particular species of molecule. Interesting examples of this phenomenon occur when MEH-PPV is doped by fullerene $C_{60}$ molecules. This is because the exciton, the bound electron and hole state in the polymer, will decay when the dopant molecule is introduced. The electron (or hole) in the exciton will transfer from the polymer chain to the doped molecule, giving rise to a free carrier. Rice and Gartstein recently proposed a theory to explain the ultrafast time scale for this charge transfer. From a quantum mechanics perspective, assuming we have an exciton state in the polymer chain due to photoexcitation, when the coupling between the chain and the molecule is switched on, the electron will move in the whole system (including the chain and the molecule), and this state must have a lower energy than the initial state. So another point of view from which to study the charge transfer is to ask what percentage of the electron (hole) has transferred from the polymer chain to the dopant. This percentage should depend on the acceptor level and the coupling between the chain and the molecule, as well as the initial exciton wavefunction in the polymer chain. We will discuss this issue here.

The paper is organized as follows. First, we develop an exciton theory for conjugated polymers in the strong correlation (large Hubbard $U$) approximation in Sec. II. In Sec. II.A we simplify a Peierls-extended Hubbard model to a model represented by spinless fermions with short-range $e-e$ interactions in real space. Then we use $t$ matrix scattering theory to determine the wavefunction and binding energy of exciton states analytically and derive a criterion for the existence of the $B_u$ exciton in Sec. II.B. This criterion is further proved according to the Levinson’s theorem in scattering theory in Sec. II.C. In Sec. II.D a more formal and compact formalism for optical absorption in conjugated polymers is presented based on our exciton theory in the large-$U$ limit. Sec. III is devoted to the impurity effects on the coherent motion of the exciton. Using a suitably defined electron-hole correlation function, we study
different types of impurity. In Sec. IV, we investigate interchain coupling effects by considering a two-chain system supplemented by nearest-neighbor interchain hopping $t_{\perp}$ and interchain $e$-$e$ interaction $V_{\perp}$. Using $t$ matrix formalism, we analytically determine the poles corresponding to intrachain and interchain excitons, respectively. We also show the wavefunction of the interchain exciton. In Sec. V, the static $A_g$ and $B_u$ excitons are used to study the charge transfer in a molecularly-doped polymer. By constructing a variational wavefunction for the whole system, the energy of this variational state, and accordingly the probability of charge transfer, can be obtained. Finally, we summarize our results in Sec. VI.

II. A NEW EXCITON THEORY IN CONJUGATED POLYMERS

In existing theories, the polymer is regarded as a Peierls insulator, and then the exciton state is determined by treating the $e$-$e$ interaction (including the on-site Hubbard interaction) as a perturbation. In this picture, the single particles (electron and hole) are defined based on a non-interacting Su-Schrieffer-Heeger model, so the band gap, from these theories, is independent of the $e$-$e$ interaction. In a strongly correlated system, the electronic states are quite different from the non-interacting model. Since the ground state is half-filled, an electron excited to the conduction band must cost the additional Hubbard repulsion energy caused by the double occupation. In conjugated polymers and related organic conductors, it is now accepted that the origin of the band gap comes typically from the Hubbard repulsion rather than the Peierls dimerization. So the Hubbard term should be given priority when one develops an exciton theory. In this section, we will regard the polymer as a Mott insulator and develop the exciton theory in large-$U$ limit. In this energy regime, double and higher order electron-hole excitations can be neglected because of their high energies ($\geq 2U$), and a single configuration interaction approximation is reasonable in determining exciton states. Before carrying out the calculation, let us recall how large the Hubbard $U$ (in units of electronic hopping energy) is in real systems: $U/t \sim 3-4$ in conjugated polymers and $U/t \sim 8-10$ in segregated stack charge transfer salts.\[47\] Strictly, this strong correlation limit is applicable only when $U \gg t$, thus real conjugated polymers only marginally satisfy this approximation.

A. Hamiltonians

The theoretical model we consider is the Peierls-extended Hubbard model, i.e., the Su-Schrieffer-Heeger model augmented by an extended Hubbard interaction. For a one-dimensional chain, this model Hamiltonian is

$$H = -t \sum_{l,\sigma} [1 - (-1)^l \delta] (c_{l\sigma}^\dagger c_{l+1\sigma} + \text{H.c.}) + U \sum_l n_{l\uparrow} n_{l\downarrow} + V \sum_l (p_l - 1)(p_{l+1} - 1). \quad (2.1)$$

Here $c_{l\sigma}^\dagger$ creates an electron of spin $\sigma$ on site $l$, $t$ is the one-electron hopping integral, $\delta$ is a bond-alternation parameter, $U$ and $V$ are respectively the on-site and nearest-neighbor Coulomb interaction, $n_{l\sigma} = c_{l\sigma}^\dagger c_{l\sigma}$ is the number operator, and $p_l = n_{l\uparrow} + n_{l\downarrow}$. Since we will be concerned only with electronic excitations in this work, we consider a rigid dimerized ground state as a starting point, and do not specify its explicit origin (e.g., $e$-$e$ interactions, electron-phonon couplings, or crystal structure). Strictly speaking, this Peierls-extended Hubbard model is directly applicable only to trans-polyacetylene. However, recent calculations have shown that the primary excitation in luminescent polymers like PPV can also be described within an effective linear chain model. In these luminescent polymers, the lowest excursive wave function extends over several repeat units. The properties of exciton are therefore not very sensitive to the detailed structure within the unit cell. From the viewpoint of renormalization, we can map the complex structure of a luminescent polymer into an effective Peierls-extended Hubbard system with the same significant physical properties by integrating out the superfluous degrees of freedom caused by the complicated unit cell structure. We have also neglected lattice relaxation, since many experiments and theories have demonstrated that $e$-$e$ interactions dominate electron-lattice interactions in many luminescent polymers. This simplification enables us to handle $e$-$e$ interactions in long chains and arrive at an understanding of electronic states in conjugated 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 lattice relaxation effects.

To emphasize the electron correlation, we begin with the Hubbard model

$$H_0 = -t \sum_{l,\sigma} (c_{l\sigma}^\dagger c_{l+1\sigma} + \text{H.c.}) + U \sum_l n_{l\uparrow} n_{l\downarrow}. \quad (2.2)$$

Although the exact wave function and the ground-state energy of this Hamiltonian have been obtained by Lieb and Wu, the Green’s function and correlation functions are difficult to calculate directly by using the exact wave function,
and it is also difficult to use their solution to study the exciton. As a practical alternative, here we make the strong correlation (large-$U$) approximation. In this approximation, as we will see later, the band gap is essentially $U$, which is not the same as the exact solution for the Hubbard model by Lieb and Wu, where the charge excitation gap is $U - 4t + \sum_{n=1}^{\infty} (\frac{1}{2} n U - t^2 + \frac{1}{4} n^2 U^2)^{1/2}$. However, for the strong correlation limit $U \gg 4t$, this difference is not important, and does not affect the exciton trends we wish to establish.

The density product $n_{l\uparrow} n_{l\downarrow}$ can be expressed by the on-site electron number and spin operator, and the Hubbard model is rewritten as

$$H_0 = -t \sum_{l\sigma} (c_{l\sigma}^\dagger c_{l+1\sigma} + \text{H.c.}) + U \sum_{l} \frac{1}{2} (n_l - (-1)^l \mathbf{S}_l \cdot \mathbf{n}_l),$$

where $S_l$ is the electron spin operator at site $l$,

$$S_l = \frac{1}{2} \sum_{\sigma} c_{l\sigma}^\dagger \sigma \sigma' c_{l\sigma'},$$

and $n_l$ is a unit vector along the spin polarization axis of the electron.

When $U \gg t$, the ground state is expected to have Néel order. We make an approximation by assuming that $n_l$ always coincides with the $z$ axis, which implies that the spin excitations have been ignored. Thus, in this approximation, the singlet and triplet excitons have the same energy and are not distinguishable. This is reasonable since for a one-dimensional Hubbard model, the spin and charge excitations are separated when $U \rightarrow \infty$ and by order $U/t$ for $U \gg t$, and the exciton is a charge excitation. This point is also directly justified by comparing energies of the singlet and triplet states obtained from a finite chain exact diagonalization calculation.

This Hamiltonian is readily diagonalized by introducing

$$c_{l\sigma} = \frac{1}{\sqrt{N}} \sum_k' e^{ikl} [(u_k + \sigma p_l v_k) \alpha_{k\sigma} + p_l (u_k - \sigma p_l v_k) \beta_{k\sigma}].$$

Here the prime means that the summation runs over the reduced Brillouin zone $|k| < \pi/2$ and $p_l = (-1)^l$. Then

$$H_0 = -\sum_{k\sigma} \left[ (E_k - \frac{U}{2}) \alpha_{k\sigma}^\dagger \alpha_{k\sigma} + (E_k + \frac{U}{2}) \beta_{k\sigma}^\dagger \beta_{k\sigma} \right],$$

with

$$E_k = \sqrt{\frac{U^2}{4} + \varepsilon_k^2},$$

$$\varepsilon_k = -2t \cos k.$$

The functions $u_k$ and $v_k$ are

$$u_k = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{\varepsilon_k}{E_k}} \simeq \frac{1}{\sqrt{2}} \left( 1 + \frac{\varepsilon_k}{U} \right),$$

$$v_k = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{\varepsilon_k}{E_k}} \simeq \frac{1}{\sqrt{2}} \left( 1 - \frac{\varepsilon_k}{U} \right).$$

In the case of $U \gg t$, a localized picture is more convenient. Two spinless fermions can be defined in the lattice representation as follows:

$$\alpha_l = \sum_{\sigma} \theta(p_l \sigma) \sqrt{2/N} \sum_k' e^{-ikl} \alpha_{k\sigma},$$

$$\beta_l = \sum_{\sigma} \theta(p_l \sigma) \sqrt{2/N} \sum_k' e^{ikl} \beta_{k\sigma},$$

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where \( \theta(x) \) is the step function. Expanded in powers of \( t/U \), \( c_{l\sigma} \) can be expressed by \( \alpha_l \) and \( \beta_l \):

\[
c_{\sigma} = \theta(p_l \sigma) \alpha_l + \theta(-p_l \sigma) p_l \beta_l + \theta(-p_l \sigma) \frac{t}{U} (\alpha_{l+1} + \alpha_{l-1}) + \theta(p_l \sigma) p_l \frac{t}{U} (\beta_{l+1} + \beta_{l-1}) + O\left(\frac{t^2}{U^2}\right). \tag{2.14}
\]

If we include the bond alternation part in our unperturbed Hamiltonian, then

\[
H'_0 = H_0 + \sum_{l\sigma} (-1)^l \delta t (c^\dagger_{l\sigma} c_{l+1\sigma} + \text{H.c.})
\]

\[
= J \sum_l (h^\dagger_l h_l + \beta^\dagger_l \beta_l) + U \sum_l \beta^\dagger_l \beta_l + \frac{J}{2} \sum_l (h^\dagger_{l+2} h_l + \beta^\dagger_l \beta_{l+2} + \text{H.c.})
\]

\[
+ \delta t \sum_l (-h_l \beta_{l+1} + h_{l+1} \beta_l - \beta^\dagger_{l+1} h^\dagger_l + \beta^\dagger_l h^\dagger_{l+1}). \tag{2.15}
\]

Here we have introduced the hole operator \( h^\dagger_l = \alpha_l \), and \( J = 2t^2/U \).

By introducing the Fourier transformations

\[
h_l = \frac{1}{\sqrt{N}} \sum_k e^{i k l} h_k,
\]

\[
\beta_l = \frac{1}{\sqrt{N}} \sum_k e^{-i k l} \beta_k,
\]

we can rewrite \( H'_0 \) in momentum space as

\[
H'_0 = \sum_k [(J + J \cos 2k) h^\dagger_k h_k + (U + J + J \cos 2k) \beta^\dagger_k \beta_k + 2i \delta t \sin k (h_k \beta_{-k} - \beta^\dagger_{-k} h^\dagger_k)]. \tag{2.18}
\]

Making the Bogoliubov transformation

\[
\eta_k = \cos \theta_k h_k + i \sin \theta_k \beta^\dagger_{-k},
\]

\[
\gamma^\dagger_{-k} = -i \sin \theta_k h_k + \cos \theta_k \beta^\dagger_{-k},
\]

Hamiltonian (2.18) can be diagonalized if the relation

\[
\sin 2\theta_k = \frac{-4\delta t \sin k}{U}
\]

is satisfied, yielding

\[
H'_0 = \sum_k (\epsilon_k \eta^\dagger_k \eta_k + \tilde{\epsilon}_k \gamma^\dagger_k \gamma_k), \tag{2.22}
\]

with

\[
\epsilon_k = J(1 + \delta^2) + J(1 - \delta^2) \cos 2k, \tag{2.23}
\]

\[
\tilde{\epsilon}_k = U + J(1 - 3\delta^2) + J(1 + 3\delta^2) \cos 2k. \tag{2.24}
\]

Operators \( \eta^\dagger_k \) and \( \gamma^\dagger_k \) create the hole and electron in the new valence and conduction band, respectively. Their lattice representations are

\[
\eta_l = \frac{1}{\sqrt{N}} \sum_k e^{i k l} \eta_k,
\]

\[
\gamma_l = \frac{1}{\sqrt{N}} \sum_k e^{-i k l} \gamma_{-k},
\]

which can be expressed by \( h_l \) and \( \beta_l \) to order \( 1/U \):
\[ \eta_l \simeq h_l - \frac{\delta t}{U} (\beta_{l+1}^\dagger - \beta_{l-1}^\dagger), \quad (2.27) \]
\[ \gamma_l^\dagger \simeq \beta_l^\dagger + \frac{\delta t}{U} (h_{l+1} - h_{l-1}). \quad (2.28) \]

The inter-site Coulomb interaction is necessary to bind the electron and hole. We consider the \( V \)-term in the Peierls-extended Hubbard model as a scattering potential, which has the local representation
\[ H_{\text{int}} = V \sum_l (\rho_l - 1)(\rho_{l+1} - 1) = V \sum_l (h_{l+1} h_l + \beta_{l+1}^\dagger \beta_l - h_{l+1} \beta_{l+1}^\dagger \beta_l - \beta_{l+1}^\dagger h_l \beta_{l+1}). \quad (2.29) \]

Since the main interest here is an exciton, only the interaction between the electron and hole is relevant. To order \( 1/U \), we have
\[ H_{\text{int}}^{e-h} = -V \sum_l (\eta_{l+1}^\dagger \gamma_l \eta_{l+1} + \gamma_{l+1}^\dagger \eta_{l} \eta_{l+1}). \quad (2.30) \]

**B. Exciton states: \( t \) matrix theory**

Since the Hamiltonian is invariant with respect to translation, the exciton states can be classified according to the total quasimomentum \( K \). We can write the exciton wave function as
\[ |\Psi_K\rangle = \sum_s B_{s,K} |\psi_{s,K}\rangle, \quad (2.31) \]
where \( K \) is the center-of-mass momentum. The basis is chosen as
\[ |\psi_{s,K}\rangle = \frac{1}{\sqrt{N}} \sum_l e^{ik_l (r - s)} \gamma_l^\dagger \eta_l |g\rangle, \quad (2.32) \]
representing a created electron-hole pair from the ground state \( |g\rangle \) with a separation \( s \) in real space. We will determine the exciton state by using \( t \) matrix scattering theory. According to \( t \) matrix theory\(^5\)
\[ T(z) = U + U G(z) T(z), \quad (2.33) \]
where \( T(z) \) is the \( t \) matrix, \( G(z) \) the notation for resolvent \( 1/(z - H_0') \), and \( U \) the potential operator. Equation (2.33) has the formal solution
\[ T(z) = U/[1 - G(z) U]. \quad (2.34) \]

Using the basis of Eq. (2.32), we obtain the Green’s function
\[ (r| G(z)| s) \equiv G(r - s; z) = (\psi_{r,K} | (z - H_0')^{-1} | \psi_{s,K}) = \frac{1}{N} \sum_k \frac{e^{ik(r - s)}}{z - (\epsilon_k + \epsilon_{-k+K})}. \quad (2.35) \]

Here \( z = E_K + i0^+ \) and the potential matrix is
\[ (s| U| s') \equiv (\psi_{s,K} | H_{\text{int}}^{e-h} | \psi_{s',K}) \]
\[ = -V \delta_{ss'} (\delta_{s,-1} + \delta_{s,1}). \quad (2.36) \]

The utility of Eq. (2.34) rests on the possibility of actually constructing the inverse operator \( 1/(1 - G U) \). This can be achieved exactly in our case since, conveniently, the potential is of short range in the local representation. Actually, the portion of the potential \( U \) containing nonzero elements forms a \( 2 \times 2 \) submatrix under the basis Eq. (2.32),
\[
\begin{pmatrix}
U_{11} & U_{11} \\
U_{11} & U_{11}
\end{pmatrix}
= -V \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}.
\] (2.37)

Denoting \( D \) as the determinant of \( 1 - GU \), we have
\[
D(E_K) = \begin{vmatrix}
1 + G(0; E_K)V & G(-2; E_K)V \\
G(2; E_K)V & 1 + G(0; E_K)V
\end{vmatrix}.
\] (2.38)

The determinant will vanish for some specific values of the energy, which are the energies of the localized states. Consequently, to find the energy \( E_K \) of the bound exciton state we look for the root of
\[
D(E_K) = 0.
\] (2.39)

Subsequently, the wave function is calculated by solving the equation
\[
B_{r,K} = \sum_{st} (r|G(E_K)|s)(s|t)B_{t,K}.
\] (2.40)

First, let us focus on the static exciton, i.e., \( K = 0 \). In this case, the system is symmetric with respect to spatial inversion. Introducing the transformation
\[
B_l^+ = \frac{1}{\sqrt{2}}(B_l + B_{-l}) ,
\] (2.41)
\[
B_l^- = \frac{1}{\sqrt{2}}(B_l - B_{-l}) ,
\] (2.42)
where \( B_l = B_{l,K=0} \), and noticing
\[
G(s-t; E_0) = G(t-s; E_0) ,
\] (2.43)
we can write the determinant \( D \) as the product of two parts:
\[
D(E_0) = D_-(E_0)D_+(E_0).
\] (2.44)

Here
\[
D_-(E_0) = 1 + |G(0; E_0) - G(2; E_0)|V
\] (2.45)
is for the \( A_g \) state with the wave function
\[
B_l^- = -V[G(l - 1; E_0) - G(l + 1; E_0)]B_l^- ;
\] (2.46)
and
\[
D_+(E_0) = 1 + |G(0; E_0) + G(2; E_0)|V
\] (2.47)
is for the \( B_u \) state with the wave function
\[
B_l^+ = -V[G(l - 1; E_0) + G(l + 1; E_0)]B_l^+ .
\] (2.48)

We denote \( x \) as the exciton binding energy:
\[
x = E_G - E_0 ,
\] (2.49)
where \( E_G \) is the band gap:
\[
E_G = (\epsilon_k + \epsilon_k)|_{k=\pi/2} = U - 4\delta^2J .
\] (2.50)

When \( \delta = 0 \), \( E_G \) does not equal the exact result by Lieb and Wu\[47.\] However, this is not a problem for estimating correct binding energies of the exciton states, since we will directly calculate the binding energy rather than first calculating the energy of the exciton. The Green’s functions are readily calculated; for \( x > 0 \)
\[
G(2l + 1; E_0) \equiv 0 ,
\] (2.51)
\[ G(2l; E_0) = \frac{(-1)^{l+1}}{\sqrt{x^2 + 4J(1 + \delta^2)x}}\left(1 - \frac{1 - u^2}{u}\right)^{2l}, \]  
(2.52)

with

\[ u^2 = \frac{4J(1 + \delta^2)}{x + 4J(1 + \delta^2)} < 1. \]  
(2.53)

Then, by requiring \( D_- (E_0) = 0 \), we obtain the binding energy of the \( A_g \) exciton as

\[ x_+ = \frac{V^2}{V + J(1 + \delta^2)}, \]  
(2.54)

with corresponding wave function

\[ B_{2l-1}^- = -\frac{G(2l; E_0) - G(2l - 2; E_0)}{\sqrt{-2[G'(0; E_0) - G'(2; E_0)]}}, \]  
(2.55)

\[ B_{2l}^- = 0. \]  
(2.56)

Here \( G'(n; E) \equiv \frac{d}{dE} G(n; E) \).

For the \( B_u \) state, when \( V > 2J(1 + \delta^2) \), the binding energy of the exciton is

\[ x_+ = \frac{[V - 2J(1 + \delta^2)]^2}{V - J(1 + \delta^2)}, \]  
(2.57)

and the wave function is

\[ B_{2l-1}^+ = -\frac{G(2l; E_0) + G(2l - 2; E_0)}{\sqrt{-2[G'(0; E_0) + G'(2; E_0)]}}, \]  
(2.58)

\[ B_{2l}^+ = 0. \]  
(2.59)

When \( V < 2J(1 + \delta^2) \), a solution \( E_0 < E_G \) satisfying equation \( D_+(E_0) = 0 \) cannot be found, i.e., there is no bound state. This result gives a criterion for the existence of a \( B_u \) exciton. Finite chain numerical DMRG and exact diagonalization calculations show that the binding energy of the \( B_u \) state is near zero when \( V \) is not large, but are not conclusive as to whether the state is strictly bound or free. Our analytical results clearly indicate that the stable \( 1B_u \) exciton does not exist when \( V \) is less than \( 2J(1 + \delta^2) \). Since this critical value is half of the width of the continuum band, \( 4J(1 + \delta^2) \), and the bandwidth describes the kinetic energy of a free particle, this criterion is a reflection of the competition between the kinetic energy and the attraction of the electron and hole.

C. Proof of the criterion: Levinson’s theorem

The criterion derived above can be proven by Levinson’s theorem. Namely, the number of bound states in representation \( s \) lying either above or below the continuum band can be determined by using

\[ \delta_s(E_i) - \delta_s(E_f) = \pi n_s. \]  
(2.60)

Here \( E_i \) is the lowest energy in the band and \( E_f \) the highest. \( n_s \) is number of states in any row of representation \( s \) separated from the band. \( \delta_s \) is the phase shift that appears in the usual partial wave expansion for the scattering amplitude, which can also be extracted from the subdeterminants of \( \det(1 - GU) \),

\[ \tan \delta_s = -\Im D_s/\Re D_s. \]  
(2.61)

In the exciton case,

\[ E_i = E_G, \]  
(2.62)

\[ E_f = (\epsilon_k + \bar{\epsilon}_k)_{k=0} = E_G + 4J(1 + \delta^2). \]  
(2.63)

It should be noted that in a one-dimensional system the density of states at the edge of the continuum band will diverge, so the form of Eq. (2.60) in our case is
\[\delta_s(E_i - 0^+) - \delta_s(E_f + 0^+) = \pi n_s. \quad (2.64)\]

The Green’s functions in different energy regions can be calculated according to the definition Eq. (2.35). We give the explicit expressions in Appendix A. Then the subdeterminants \(D_-\) and \(D_+\) are obtained by straightforward calculations.

For \(E_0 = E_i - 0^+\), i.e., the energy is just below the onset of the continuum band,

\[D_- = -\infty - i0^+, \quad (2.65)\]
\[D_+ = 1 - \frac{V}{2J(1 + \delta^2)} - i0^+, \quad (2.66)\]

and the phase shifts are

\[\delta_- (E_i - 0^+) = \pi, \quad (2.67)\]

\[\delta_+ (E_i - 0^+) = \left\{ \begin{array}{ll} 0 & V < 2J(1 + \delta^2) \\ \pi & V > 2J(1 + \delta^2) \end{array} \right. , \quad (2.68)\]

For \(E_0 = E_f + 0^+\), i.e., the energy is just above the top of the continuum band,

\[D_- = 1 + \frac{V}{2J(1 + \delta^2)} - i\infty, \quad (2.69)\]
\[D_+ = +\infty - i0^+, \quad (2.70)\]

and the corresponding phase shifts are

\[\delta_- (E_f + 0^+) = 0, \quad (2.71)\]
\[\delta_+ (E_f + 0^+) = 0. \quad (2.72)\]

Thus we have

\[\delta_- (E_i - 0^+) - \delta_- (E_f + 0^+) = \pi, \quad (2.73)\]

showing that there is always an \(A_g\) bound exciton for a nonvanishing \(V\). However, when \(V < 2J(1 + \delta^2)\),

\[\delta_+ (E_i - 0^+) - \delta_+ (E_f + 0^+) = 0, \quad (2.74)\]

indicating that there is no \(B_u\) bound exciton. The bound exciton will appear only when \(V > 2J(1 + \delta^2)\), since then

\[\delta_+ (E_i - 0^+) - \delta_+ (E_f + 0^+) = \pi. \quad (2.75)\]

To get an overall picture of the phase shift in this one-dimensional system, we also examine the phase shifts at \(E_i + 0^+\) and \(E_f - 0^+\). For \(E_0 = E_i + 0^+, \) i.e., the energy is just above the onset of the continuum band,

\[D_- = 1 + \frac{V}{2J(1 + \delta^2)} - i\infty, \quad (2.76)\]
\[D_+ = 1 - \frac{V}{2J(1 + \delta^2)} - i0^+, \quad (2.77)\]

and the phase shifts are

\[\delta_- (E_i + 0^+) = \pi/2, \quad (2.78)\]

\[\delta_+ (E_i + 0^+) = \left\{ \begin{array}{ll} 0 & V < 2J(1 + \delta^2) \\ \pi & V > 2J(1 + \delta^2) \end{array} \right. . \quad (2.79)\]

For \(E_0 = E_f - 0^+, \) i.e., the energy is just below the top of the continuum band,
\[ D_- = 1 + \frac{V}{2J(1 + \delta^2)} - i0^+ , \]  
\[ D_+ = 1 - \frac{V}{2J(1 + \delta^2)} - i\infty , \]
and the phase shifts are

\[ \delta_-(E_f - 0^+) = 0 . \]  
\[ \delta_+(E_f - 0^+) = \begin{cases} \pi/2 & V < 2J(1 + \delta^2) \\ \pi/2 & V > 2J(1 + \delta^2) . \end{cases} \]  

Now let us study the behavior of the phase shift as a function of energy. For the \( A_g \) state, when the energy passes through the edge of the band the phase shift falls discontinuously from \( \pi \) to \( \pi/2 \), then gradually approaches zero at the top of the band. So there is always a bound state. For the \( B_u \) exciton, when \( V < 2J(1 + \delta^2) \) the phase shift increases from zero as the energy increases from the bottom of the band, and approaches \( \pi/2 \) just below the top of the band, and then drops to zero again when we pass through the top edge of the band. Thus no bound state exists. When \( V > 2J(1 + \delta^2) \), the phase shift decreases from \( \pi \) to \( \pi/2 \) as the energy increases from the bottom to the top of band, and abruptly falls to zero when we cross the edge of the band. Thus a bound state appears. The discontinuity of the phase shift at the band edges is due to the infinite density of states at the bottom and top of the band.

Figure 1 shows the wave functions of the \( A_g \) and \( B_u \) states with \( U = 10t, V = 0.5t, \) and \( \delta = 0.2 \), corresponding to binding energies \( x_+ = 0.024t \) and \( x_- = 0.353t \), respectively. We can see that the wave function of the \( A_g \) exciton decays more rapidly than that of the \( B_u \) one. For \( x > 0 \), we introduce the parameter \( z \),

\[ z = -\ln\left(\frac{1 - \sqrt{1 - u^2}}{u}\right) > 0 . \]  

Since for large \( l \),

\[ G(2l; E_0) \sim e^{-z^{2l}} , \]
we can define the width \( R \) of the \( K = 0 \) exciton by \( R = 2/z \). From Eq. (2.84), we estimate the width is about 3 lattice constants for the \( A_g \) exciton and about 12 lattice constants for the \( B_u \), as shown in Fig. 1.

We calculate the energy of the exciton for \( K \neq 0 \) from \( D(E_K) = 0 \). A straightforward computation of Eq. (2.35) gives

\[ G(0; E_K) = -\frac{1}{\sqrt{ac - b^2}} , \]

\[ G(2; E_K) = G^*(2; E_K) , \]

\[ = -\frac{1}{4b^2 + (a-c)^2} \left\{ 2(a-c) + \frac{c^2 - a^2}{\sqrt{ac - b^2}} \right\} + i\left[ 4b - \frac{2b(a+c)}{\sqrt{ac - b^2}} \right] , \]

where

\[ a = x + 3J + 5\delta^2J + J(1 - \delta^2)\cos 2K , \]

\[ b = J(1 - \delta^2)\sin 2K , \]

\[ c = x + J(1 - \delta^2) - J(1 - \delta^2)\cos 2K . \]

By solving the equations

\[ 1 + G(0; E_K)V + |G(2; E_K)|V = 0 , \]

\[ 1 + G(0; E_K)V - |G(2; E_K)|V = 0 , \]

we can compute the energy of the moving excitons. In Fig. 2, we have described the energy of the excitons as a function of the center-of-mass momentum \( K \). There are two branches in the energy spectra. The energy difference
between these two branches becomes smaller when $K$ increases, and reaches a minimum at $K = \pi/2$. The bandwidths of these two branches are approximately $J$.

When $V \gg J$, our results show that both $A_g$ and $B_u$ excitons have binding energy $V$, which is consistent with physical intuition. In the strong coupling limit $U \gg V \gg t$, Guo et al. used a local (zero hopping limit) picture and argued, since the ground state has all sites singly occupied and the exciton states are linear combinations of configuration ...1120111..., where the numbers denote site occupancies, that the exciton energy is $U - V$. The electron-hole continuum consists of all states in which the double occupancy (electron) and the empty site (hole) are separated by more than one site (e.g., ...11120111..., which has energy $U$. Thus the binding energy is $V$. Another prediction from our theory is that the $2A_g$ state has a lower energy than the $1B_u$, which is the observed ordering in many non-luminescent conjugated polymers. The strong Coulomb interaction regime we consider here is the reason for this ordering in our model.

### D. Optical absorption

We will calculate the optical absorption from Fermi’s golden rule

$$\alpha(\omega) \propto \frac{1}{\omega} \sum_n |\langle n|g|\rangle|^2 \delta(\omega - E_n), \quad (2.93)$$

where $J$ is the current operator and $|n\rangle$ is the excited state with one electron-hole pair. This expression can be written in a more general form if we denote $|\nu\rangle = |g\rangle$,  

$$\alpha(\omega) \propto -\frac{1}{\pi \omega} \lim_{\varepsilon \to 0^+} \Im \langle \nu | \frac{1}{\omega + i\varepsilon - H} | \nu \rangle. \quad (2.94)$$

Hamiltonian $H$ referred to here is that determining the energy of the electron-hole pair with $K = 0$. The current operator in the polymers reads

$$J = i t \sum_{l, \sigma} [1 - (-1)^l] \delta (c_{l+1, \sigma}^\dagger c_{l, \sigma} - c_{l, \sigma}^\dagger c_{l+1, \sigma}). \quad (2.95)$$

Using the spinless fermions $\eta_l$ and $\gamma_l$ defined in Sec. II.A, we rewrite Eq. (2.95) as

$$J = -it \delta \sum_l (\eta_{l+1} \gamma_l - \gamma_{l+1}^\dagger \eta_l^\dagger + \eta_l \gamma_{l+1} - \gamma_l^\dagger \eta_{l+1}^\dagger). \quad (2.96)$$

Thus the optical absorption can be expressed by the electron-hole Green’s function

$$\alpha(\omega) \propto -\frac{t^2 \delta^2}{\pi \omega} \Im [\tilde{G}(0; \omega) + \tilde{G}(2; \omega)], \quad (2.97)$$

where $\tilde{G}(l; \omega)$ is the Green’s function of $H$, satisfying

$$\tilde{G}(z) = G(z) + G(z) T(z) G(z). \quad (2.98)$$

If we denote $G(n; \omega) = G_n$, then

$$\alpha(\omega) \propto -\frac{t^2 \delta^2}{\pi \omega} \Im \left\{ \left[ (G_0 + G_{-2}) - \frac{V}{D(\omega)} [(G_0 + G_2)^2 + V(G_0^3 - G_0 G_2^2 + G_0^2 G_2 - G_2^3)] \right] \right\} \quad (2.99)$$

and $D(\omega) = [1 + (G_0 - G_2)V][1 + (G_0 + G_2)V]$.

From Fig. 3, the $B_u$ exciton has acquired 52% oscillator strength when $U = 5t$ and $V = t$. If we increase $V$ and thus have an exciton with a larger binding energy, the $B_u$ exciton will gain more oscillator strength. For $U = 5t$ and $V = 2t$, the $B_u$ exciton has achieved 95% strength, and the strength of the transition to the continuum is correspondingly diminished, as shown in Fig. 4. The large transition strength for the exciton state is a characteristic feature of one-dimension.
III. IMPURITIES AND THE COHERENT MOTION OF EXCITON

As stated in the introduction, “pristine” samples of a polymer cannot eliminate all impurities and defects. Moreover, the fluctuations (both quantum and thermal) of the lattice are also a kind of intrinsic disorder for the electronic states in polymers. Excitons represent a coherent composite particle motion of correlated electrons and holes, whereas impurities tend to produce localized wavefunction. We know that an impurity has a strong effect on transport properties in many systems, especially low-dimensional materials, so a natural question arises: how do the impurities affect the coherent motion of the exciton?

In polymers, two kinds of impurity are often referred to in the literature. A site impurity is represented by a local potential at site 0:

\[ H_1 = V_0 \sum_\sigma c^\dagger_0 \sigma c_0 \sigma, \]  
(3.1)

and a bond impurity which acts on the bond between sites 0 and 1:

\[ H_2 = -W_0 \sum_\sigma (c^\dagger_0 \sigma c_1 \sigma + \text{H.c.}) . \]  
(3.2)

Both of these impurities have very localized (on-site) potentials. However, for a charged impurity, its potential, in principle, may be of long-range. Thus we have two length scales here: one is the range of the impurity potential \( l_i \) and the other the range of the (screened) Coulomb interaction \( l_V \). The latter is equal to one lattice constant in our model. Since the impurity competes with the Coulomb interaction (in exciton states) differently in the two regimes \( l_V > l_i \) or \( l_V < l_i \), impurity effects are expected to be different.

A. On-site impurity potentials

For the site and bond impurities described above, we can rewrite them in the spinless fermion representation, giving

\[ H_1 = V_0 (-\eta^\dagger_0 \eta_0 + \gamma^\dagger_0 \gamma_0) , \]  
(3.3)

\[ H_2 = -W_0 (-\eta_0 \gamma_1 - \gamma^\dagger_1 \eta_0 + \gamma^\dagger_0 \eta_1 + \eta_1 \gamma_0) . \]  
(3.4)

Since \( H_2 \) involves the creation and annihilation of an electron-hole pair, it must be less important than \( H_1 \) by order \( 1/U \). This can be seen more clearly by using the unitary transformation \( H^S = e^{-S} H e^S \),

\[ H_2^S = \frac{W_0^2}{U + 2J(1 - \delta^2)}(-\eta^\dagger_0 \eta_0 - \eta^\dagger_1 \eta_1 - \gamma^\dagger_0 \gamma_0 - \gamma^\dagger_1 \gamma_1) . \]  
(3.5)

Although the site impurity seems more realistic from the above analysis, we will study three kinds of impurity to arrive at a unified picture of impurity effects:

\[ H_1^{\text{imp}} = V_0 (-\eta^\dagger_0 \eta_0 + \gamma^\dagger_0 \gamma_0) , \]  
(3.6)

\[ H_2^{\text{imp}} = V_0 (-\eta^\dagger_0 \eta_0 - \gamma^\dagger_0 \gamma_0) , \]  
(3.7)

\[ H_3^{\text{imp}} = V_0 (\eta^\dagger_0 \eta_0 + \gamma^\dagger_0 \gamma_0) . \]  
(3.8)

Hamiltonian \( H_1^{\text{imp}} \), in which the impurity attracts the hole and repels the electron, or vice versa, imitates a local charged impurity. Hamiltonian \( H_2^{\text{imp}} \), in which the impurity attracts both the electron and hole, acts as a trap for particles. In Hamiltonian \( H_3^{\text{imp}} \), the impurity potentials are repulsive for both the electron and hole, describing a barrier effect. The last two types of impurity can be viewed as simulating the cross-linking and conjugation breaking effects in conjugated polymers.

There is no translation invariance once the impurity is included, so we will work in real space and the Hamiltonian we must study reads
\[ H_i = \sum_i \left\{ J(1 + \delta^2)\eta_i^\dagger \eta_i + \frac{1}{2} J(1 - \delta^2)(\eta_{i+1}^\dagger \eta_i + \eta_i^\dagger \eta_{i+1}) + [U + J(1 - 3\delta^2)]\gamma_i^\dagger \gamma_i \\
+ \frac{1}{2} J(1 - \delta^2)(\gamma_i^\dagger \gamma_{i+2} + \gamma_{i+2}^\dagger \gamma_i) \right\} + V \sum_i (\eta_{i+1}^\dagger \eta_i \eta_{i+1} + \gamma_{i+1}^\dagger \gamma_i \gamma_{i+1} - \eta_{i+1}^\dagger \gamma_i \eta_{i+1} - \gamma_{i+1}^\dagger \gamma_i \eta_{i+1}) + H_i^{\text{imp}}. \] (3.9)

The key issue here is how to measure the coherence in the excitonic composite particle. We can do this by defining the correlation function between the electron and hole in the lowest state in the one electron and one hole subspace:

\[ \mathcal{R}(l, l') = \frac{\langle \delta \rho_h(l) \delta \rho_e(l') \rangle}{\sqrt{\langle (\delta \rho_h(l))^2 \rangle \langle (\delta \rho_e(l'))^2 \rangle}}, \] (3.10)

where the deviations are

\[ \delta A = A - \langle A \rangle, \] (3.11)

and the density operators of electron and hole are

\[ \rho_h(l) = \eta_i^\dagger \eta_i, \] (3.12)
\[ \rho_e(l) = \gamma_i^\dagger \gamma_i. \] (3.13)

In the impurity-free system, this correlation function (3.10) is connected with the relative wavefunction of the lowest exciton state \( |\Psi_0\rangle \) by

\[ \mathcal{R}^{\text{free}}(l, l') = |B_{l-l'}|^2. \] (3.14)

When we add an impurity, the correlation is expected to decrease. The closer \( \mathcal{R} \) is to \( \mathcal{R}^{\text{free}} \), the more correlated are the electron and hole in the lowest excitonic states, while \( \mathcal{R} \) approaching zero means that there is no correlation between the electron and hole; in other words, this excitonic state has lost all its coherence.

The effects of the first kind of impurity are illustrated in Fig. 5, which shows the electron-hole correlation functions for different sites in a finite system of size \( N = 10 \). We emphasize that the parameters we use \( (U = 10t \) and \( V = t \)) ensure that the exciton has a very localized relative wavefunction, so that finite system corrections and the boundary condition effects are not important. In Fig. 5, all the correlation functions exhibit a crossover behavior around \( V_0 \sim 0.1t \). This can be understood in terms of a relevant energy scale of the exciton, namely, the width of the exciton band, which equals \( J = 2t^2/U \). This crossover behavior, which occurs at \( V_0 \sim J \), describes the localization of the exciton, i.e., the free exciton becomes trapped. We can also calculate the charge density at the impurity site as the impurity strength increases. Since in an impurity-free system the hole (electron) is uniformly distributed, and from our exciton theory the electron and hole do not tend to occupy the same site, the hole density at the impurity site is \( 2/N \). We see a crossover again in Fig. 6 when \( V_0 \) is comparable to the bandwidth \( J \). After this crossover, the hole density at the impurity site approaches 1, clearly showing that the exciton is trapped by the impurity, and the correlation between the electron and hole gradually vanishes, although, as indicated in Fig. 7, they are bound together near the impurity.

For the second type of impurity, from Fig. 8, a crossover is also observed if the impurity strength is similar to the exciton bandwidth, again indicating that the exciton is trapped. But when \( V_0 \) is larger than \( V \), the correlation function abruptly falls to zero, which implies the total breakdown of the exciton as a composite particle. This is because, when \( V_0 \) is large enough, it is a lower energy for the impurity to trap the electron and hole separately rather than the impurity trapping the hole and then the electron being trapped near the hole due to the Coulomb interaction (as for the first kind of impurity). Thus the electron and the hole occupy the same site and they have no Coulomb interaction. This is not an exciton.

Now we consider the third type of impurity. The correlation function behaviors in Fig. 9 seem more complicated than for the other two types of impurity. The correlation function in which the hole is at the impurity site shows an analogous crossover behavior when \( V_0 \) is near the exciton bandwidth \( J \) to the first and second types of impurity. However, if both the electron and the hole are left (or right) of the impurity, from the correlation function we see that they have not felt the impurity. On the other hand, if the electron and the hole sit on different sides of the impurity, there is a crossover at \( V_0 \sim J \), but part of correlation between the electron and hole survives.

The different effects of these three kinds of impurity can be further understood if we project the lowest excitonic state to the free exciton states with momentum \( K \). We depict in Figs. 10, 11 and 12 the distribution \( |Z_K|^2 \), where
$Z_K = \langle \Psi_K | \Psi \rangle$, and $| \Psi \rangle$ is the lowest excitonic state in these three disordered systems. In the impurity-free system, the lowest state is the linear combination of exciton states with $K = 0$ and $K = \pi$ (they are degenerate). In the presence of an impurity, the exciton state will be scattered to other exciton states with different $K$ and the distribution of momenta will broaden from the $\delta$ function. A free exciton state with a specific $K$ can be defined only when the width of the distribution of momentum is narrow enough (i.e., the lifetime of this state is long enough). This is analogous to the quasi-particle in Landau’s Fermi Liquid theory. From these figures, we see that for the first and second types of impurities, after the crossover at $V_0 \sim J$ the distribution in momentum space becomes so broad that we can hardly identify the original exciton state with momentum $K = 0$ or $K = \pi$. For the second type of impurity, when $V_0$ is larger than $V$, the final state has no distribution at all on any free exciton state, also indicating that the final state is no longer excitonic. However, for the third kind of impurity, after the crossover at $V_0 \sim J$, the distribution in momentum space still has two sharp peaks at $K = 0$ and $K = \pi$. This is the reason why the exciton is still coherent, as shown in the correlation functions, and in this sense the exciton can be regarded as a quasi-particle in this disordered system.

### B. Extended impurity potentials

For a charged impurity, the range of (screened Coulomb) potential can be extended over several lattice constants. As an illustration, here we consider a specific impurity potential

$$H_4^{\text{imp}} = V_0(-\eta_0^+ \eta_0 + \gamma_0^+ \gamma_0) + \frac{V_0}{2}(-\eta_1^+ \eta_1 + \gamma_1^+ \gamma_1 - \eta_{-1}^+ \eta_{-1} + \gamma_{-1}^+ \gamma_{-1}) .$$

Its range ($l_4$) is three lattice constants which is longer than that of the Coulomb interaction ($l_V$). The correlation functions are illustrated in Fig. 13, from which we observe again a crossover around $V_0 \sim J$, indicating the free exciton becomes trapped. Interestingly, when $V_0$ is sufficiently large compared to $V$, the correlation functions falls further abruptly to zero, indicating the dissociation of the exciton into an uncorrelated electron-hole pair. Note that this does not occur for the charged impurity $H_1^{\text{imp}}$ with the on-site potential, since the impurity range is then less than the trapped exciton size. From charge densities shown in Fig. 14, we find that for $V_0 = 0.5t$ (just after the first crossover), both the electron and the hole (thus the exciton) are trapped around the impurity. For $V_0 = 5t$ (after the correlation goes to zero), the hole is trapped by the impurity while the electron is repelled from the impurity. The dissociation of excitons here is easily understood. Because the impurity attracts the hole and repels the electron, when the impurity strength becomes sufficiently strong, the Coulomb attraction cannot overcome the impurity repulsion to bind the electron and hole together. This impurity-induced exciton dissociation may be invoked to interpret impurity-enhanced photoconductivity observed in certain experiments. We can project the lowest excitonic state in the system with the impurity to free exciton states with different momenta. In Fig. 15, the distribution in momentum space changes from a sharply localized one ($V_0 = 0.1t$, before the crossover) to a very broad Gaussian distribution ($V_0 = 0.5t$, after the crossover) and finally goes to zero ($V_0 = 5t$). This is consistent with the picture that the free exciton becomes trapped, then dissociates into an uncorrelated electron-hole pair with increasing impurity strength.

### IV. INTERCHAIN COUPLING AND INTERCHAIN EXCITONS

The interchain coupling can strongly influence the energy and stability of the nonlinear excitations such as solitons and polarons. Current interest in interchain coupling and the intrachain and interchain exciton crossover in polymers stems from the experimentally observed large amount of interchain excitations in luminescent polymers like PPV. However, the concept of an interchain exciton and how to distinguish the interchain and intrachain excitons, are not very clear. The wavefunction is not so useful to specify whether a state is an interchain or intrachain exciton, because the wavefunction of any state, in principle, will spread over the whole system if interchain coupling is present. To demonstrate interchain exciton states in our approach, we study a two-chain system coupled by the nearest-neighbor hopping,

$$H_{\text{hop}} = -t_{\perp} \sum_{l \sigma} (c_{1l\sigma}^\dagger c_{2l\sigma} + \text{H.c.}) ,$$

and nearest-neighbor interchain Coulomb interaction,

$$H_{\text{Cou}} = V_{\perp} \sum_{l} (\rho_{1l} - 1)(\rho_{2l} - 1) .$$
Here 1, 2 are chain indices. Now the unperturbed Hamiltonian in the large-\( U \) limit becomes

\[
\tilde{H}_0 = H'_0 + H_{\text{hop}} = \sum_{i,k} (\epsilon_k \eta_{ik}^\dagger \eta_{ik} + \tilde{\epsilon}_k \gamma_{ik}^\dagger \gamma_{ik}) + t_\perp \sum_l (\eta_{2l}^\dagger \eta_{l1} - \gamma_{1l}^\dagger \gamma_{2l} + \text{H.c.}) .
\]  

(4.3)

In momentum space, this is

\[
\tilde{H}_0 = \sum_{i,k} (\epsilon_k \eta_{ik}^\dagger \eta_{ik} + \tilde{\epsilon}_k \gamma_{ik}^\dagger \gamma_{ik}) + t_\perp \sum_k (\eta_{2k}^\dagger \eta_{1k} - \gamma_{1k}^\dagger \gamma_{2k} + \text{H.c.}) ,
\]

(4.4)

which can be readily diagonalized, yielding

\[
\tilde{H}_0 = \sum_{I,k} (E_k^I \gamma_{I1k}^\dagger \gamma_{I1k} + \tilde{E}_k^I \gamma_{I1k}^\dagger \gamma_{I1k}) .
\]

(4.5)

Here \( I = 1, 2 \) is the band index (hereafter we use small \( i, j \) for the chain indices, and capital \( I, J \) for the band indices). The details of the diagonalization are given in Appendix B. Now we have two conduction and two valence bands with the dispersion relations

\[
E_k^{1,2} = \epsilon_k \mp t_\perp ,
\]

(4.6)

\[
\tilde{E}_k^{1,2} = \tilde{\epsilon}_k \mp t_\perp .
\]

(4.7)

The interaction Hamiltonian now contains two parts

\[
H_V = H_{\text{int}} + H_{\text{Cou}} .
\]

(4.8)

The electron-hole interaction part of \( H_V \), which is relevant to the exciton state, is

\[
H_V^{e-h} = -V \sum_{i,l} (\eta_{il+1}^\dagger \gamma_{il}^\dagger \gamma_{il+1} + \gamma_{il+1}^\dagger \eta_{il}^\dagger \gamma_{il} \gamma_{il+1} ) - V_\perp \sum_l (\eta_{2l}^\dagger \gamma_{2l} \gamma_{2l+1} + \gamma_{2l+1}^\dagger \eta_{2l} \gamma_{2l+1} ) .
\]

(4.9)

If we define local fermion operators

\[
\tilde{\eta}_I = \frac{1}{\sqrt{N}} \sum_k e^{ikl} \eta_{Ik} ,
\]

(4.10)

\[
\tilde{\gamma}_I = \frac{1}{\sqrt{N}} \sum_k e^{ikl} \gamma_{Ik} ,
\]

(4.11)

we can rewrite Eq. (4.3) as

\[
H_V^{e-h} = \frac{V}{2} \sum_{IJ} \sum_l (\tilde{\eta}_{I l+1}^\dagger \tilde{\gamma}_{J l} \tilde{\gamma}_{J l+1} + \tilde{\gamma}_{I l+1}^\dagger \tilde{\eta}_I \tilde{\gamma}_{I l+1} + \tilde{\gamma}_{I l+1}^\dagger \tilde{\eta}_I \tilde{\gamma}_l ) + \frac{V_\perp}{2} \sum_l (\tilde{\eta}_{I 2l}^\dagger \tilde{\gamma}_l + \tilde{\gamma}_l^\dagger \tilde{\eta}_{I 2l} + \tilde{\gamma}_l^\dagger \tilde{\eta}_{I 2l} ) (4.12)
\]

Thus we can construct the exciton wavefunction in this two-chain system as

\[
|\Psi_K \rangle = \sum_{IJ} \sum_s B_{s, K}^{IJ} |\psi_{s, K}^{IJ} \rangle .
\]  

(4.13)

Here the center-of-mass momentum \( K \) is still a good quantum number, and the basis is

\[
|\psi_{s, K}^{IJ} \rangle = \frac{1}{\sqrt{N}} \sum_l e^{ikl} \tilde{\eta}_{I l}^\dagger \tilde{\gamma}_{J l}^\dagger |g \rangle ,
\]  

(4.14)
which means the exciton state is a combination of every possible electron-hole excitation in different conduction and valence bands. The free electron-hole pair Green’s function under the basis Eq. (4.14) is

$$
\langle \psi_{r,K}^{J',J'} | H_{V}^{<} | \psi_{s,K}^{J,J} \rangle = \delta_{J'J} \delta_{J'J'} G^{JJ}(r - s; z_K) \tag{4.15}
$$

$$
G^{JJ}(l; z_K) = \frac{1}{N} \sum_{k} \frac{e^{ikl}}{z_K - (E_k^l + E_{-k+l}^l)} ,
$$

and the scattering potential is written as

$$
\langle \psi_{s,K}^{J,J'} | H_{V}^{>h} | \psi_{s',K}^{J',J'} \rangle = \delta_{ss'} \left( \frac{-V}{2} \delta_{s1} - \frac{V}{2} \delta_{s-1} - \frac{V}{2} \delta_{s0} \right) F(I', J'; I, J) \tag{4.17}
$$

with $F(I, J; I, J) = 1$ and $F(1, 1; 2, 2) = F(2, 2; 1, 1) = F(1, 2; 2, 1) = F(2, 1; 1, 2) = 1$, and otherwise $F = 0$. We can solve for the exciton states by locating the roots of the determinant $\det(1-\mathbf{G})$ according to $\mathbf{t}$ matrix theory. The whole determinant can be decomposed into blocks by appropriate transformations and we achieve two subdeterminants,

$$
D_1 = \begin{vmatrix}
1 + \frac{V_1}{2} G^{11}(0; z_K) & \frac{V_1}{2} G^{11}(0; z_K) \\
\frac{V_1}{2} G^{12}(0; z_K) & 1 + \frac{V_1}{2} G^{22}(0; z_K)
\end{vmatrix}
$$

and

$$
D_2 = \begin{vmatrix}
1 + \frac{V_1}{2} G^{12}(0; z_K) & \frac{V_1}{2} G^{12}(0; z_K) \\
\frac{V_1}{2} G^{21}(0; z_K) & 1 + \frac{V_1}{2} G^{21}(0; z_K)
\end{vmatrix}
$$

$D_1$ and $D_2$ are determined only by interchain Coulomb interaction $V_\perp$ corresponding to interchain excitons, and two subdeterminants,

$$
D_3 = \begin{vmatrix}
1 + \frac{V_2}{2} \left[ G^{11}(0; z_K) + G^{22}(0; z_K) \right] & \frac{V_2}{2} \left[ G^{11}(-2; z_K) + G^{22}(-2; z_K) \right] \\
\frac{V_2}{2} \left[ G^{12}(2; z_K) + G^{21}(2; z_K) \right] & 1 + \frac{V_2}{2} \left[ G^{12}(0; z_K) + G^{21}(0; z_K) \right]
\end{vmatrix}
$$

and

$$
D_4 = \begin{vmatrix}
1 + \frac{V_2}{2} \left[ G^{12}(0; z_K) + G^{21}(0; z_K) \right] & \frac{V_2}{2} \left[ G^{12}(-2; z_K) + G^{21}(-2; z_K) \right] \\
\frac{V_2}{2} \left[ G^{12}(2; z_K) + G^{21}(2; z_K) \right] & 1 + \frac{V_2}{2} \left[ G^{12}(0; z_K) + G^{21}(0; z_K) \right]
\end{vmatrix}
$$

which are determined only by the intrachain Coulomb interaction $V$ corresponding to intrachain excitons. Equations $D_1 = 0$ and $D_2 = 0$ have a single root, respectively, whereas both $D_3 = 0$ and $D_4 = 0$ have two roots. Thus there are a total of six exciton bands: two interchain exciton bands and four intrachain exciton bands. Figures 16 and 17 show these intrachain and interchain exciton bands. The relative energy ordering of the interchain and intrachain excitons depends on the ratio $V_\perp/V$.

It is interesting to study the wave function of the interchain excitons. The static interchain exciton can be represented in real space as

$$
|\Psi_{K=0}\rangle = \sum_{ij} \sum_{s} A_{s}^{ij} \frac{1}{\sqrt{N}} \sum_{l} \gamma_{l+s}^\dagger \eta_{l+j}^\dagger g^l .
$$

For the lower exciton state determined by $D_1(z_0) = 0$, we obtain

$$
A_{s1}^{11} = -A_{s2}^{12} = -\frac{G^{11}(s; z_0) - G^{22}(s; z_0)}{2\sqrt{\left[ G^{11}(0; z_0) + G^{22}(0; z_0) \right]'}} ,
$$

$$
A_{s2}^{11} = -A_{s1}^{12} = -\frac{G^{11}(s; z_0) - G^{22}(s; z_0)}{2\sqrt{\left[ G^{11}(0; z_0) + G^{22}(0; z_0) \right]'}} ,
$$

$$
A_{s1}^{11} = -A_{s2}^{12} = -\frac{G^{11}(s; z_0) - G^{22}(s; z_0)}{2\sqrt{\left[ G^{11}(0; z_0) + G^{22}(0; z_0) \right]'}} ,
$$

$$
A_{s2}^{11} = -A_{s1}^{12} = -\frac{G^{11}(s; z_0) - G^{22}(s; z_0)}{2\sqrt{\left[ G^{11}(0; z_0) + G^{22}(0; z_0) \right]'}} ,
$$

$$
A_{s1}^{11} = -A_{s2}^{12} = -\frac{G^{11}(s; z_0) - G^{22}(s; z_0)}{2\sqrt{\left[ G^{11}(0; z_0) + G^{22}(0; z_0) \right]'}} .
$$

16
which represents the amplitude for the electron and hole being on the same chain; while

$$A_s^{21} = -A_s^{12} = -\frac{G^{11}(s; z_0) + G^{22}(s; z_0)}{2\sqrt{-[G^{11}(0; z_0) + G^{22}(0; z_0)]}} \quad (4.24)$$

is the amplitude that the electron and hole are on different chains. Here

$$G^{11}(0; z) = -\frac{1}{\sqrt{(E_G - z - 2t_\perp)(E_G - z + 2t_\perp + W)}} \quad (4.25)$$

$$G^{22}(0; z) = -\frac{1}{\sqrt{(E_G - z + 2t_\perp)(E_G - z + 2t_\perp + W)}} \quad (4.26)$$

where $E_G$ is defined as Eq. (2.51) and $W = 4J(1 + \delta^2)$. Figure 18 illustrates the intrachain wavefunction $A_s^{11}$ and interchain wavefunction $A_s^{21}$ for this interchain exciton state. We can see that although the state is for an interchain exciton, there is still some probability for the electron and hole to be on the same chain.

For the higher interchain exciton determined by $D_2(z_0) = 0$, we have

$$A_s^{11} = A_s^{22} = 0 \quad (4.27)$$

$$A_s^{21} = A_s^{12} = -\frac{G^{12}(s; z_0)}{\sqrt{-[G^{12}(0; z_0)]}} \quad (4.28)$$

$$G^{12}(0; z) = -\frac{1}{\sqrt{(E_G - z)(E_G - z + W)}} \quad (4.29)$$

In this interchain exciton, there is no relative amplitude between the electron and hole if they are on the same chain. In Fig. 19, we plot the wavefunction $A_s^{21}$ for this interchain exciton.

For more complicated Coulomb interactions within and between the chains, the exact interchain and intrachain exciton poles are difficult to obtain analytically. Instead, we can measure the correlation between the electron and hole using Eq. (3.10). In Fig. 20, we depict the intrachain and interchain electron-hole correlation functions for our simple interchain coupling situation for two $N = 12$ chains. Here we choose a fixed interchain hopping $t_\perp/t = 0.2$. The transition at $V_\perp/V = 1.18$ shows that the lowest exciton state changes from an intrachain exciton to an interchain one.

V. CHARGE TRANSFER IN A MOLECULARLY-DOPED POLYMER

Photoinduced charge transfer from a polymer chain to an adjacent dopant molecule, such as in PPV/C$_{60}$ blends has attracted much recent attention, because it can greatly increase the photoconductivity in polymers. In recent theoretical work on this phenomenon, Rice and Gartstein proposed a mechanism to explain the observed ultrafast time scale of this process. In this section, instead of discussing the time scale, we attempt to calculate the final state wavefunction of the whole system comprising the polymer chain and dopant molecule. This can tell us what part of the electron in the exciton has transferred from the chain to the dopant. To make our idea more transparent, let us briefly describe this photoinduced charge transfer process. In the ground state, there is no overlap between the chain and the dopant. The photoexcitation produces an exciton state in the polymer chain. Then, due to the coupling between the polymer and the dopant molecule, the electron (or hole) will transfer from the chain to the adjacent molecule. As a simplified Hamiltonian, we consider

$$H = H_{\text{chain}} + \Delta_e \sum_m c_m^\dagger c_m + H_{\text{tran}}. \quad (5.1)$$

Here we are modeling the dopant molecule by assuming it has an acceptor level with energy $\Delta_e$, which couples to the polymer chain only by nearest-neighbor hopping

$$H_{\text{tran}} = -v \sum_m (c_m^\dagger \gamma_0 + \text{H.c.}) = -\frac{v}{\sqrt{N}} \sum_{m,k} (c_m^\dagger \gamma_k + \text{H.c.}). \quad (5.2)$$
A schematic diagram of our model is shown in Fig. 21. The whole system consists of a polymer chain and \( N_d \) dilute noninteracting dopants. Before the coupling between the polymer chain and the dopant is switched on, the system has an exciton state on the polymer chain. When we turn on the coupling, the electron in the exciton will transfer between the chain and the molecule. Thus we can construct a variational wavefunction

\[
|\Psi\rangle = a|\Psi_0\rangle + \frac{1}{\sqrt{N_d}} \sum_m \sum_k a_k c_m |\gamma_k\rangle |\Psi_0\rangle ,
\]

with the condition \( \langle \Psi | \Psi \rangle = 1 \). The first term describes the electron remaining on the chain as a component of the exciton and the second term describes that the electron with different momentum has different probability to transfer to the dopant molecule. Here \( |\Psi_0\rangle \) is the assumed static exciton state within the polymer chain,

\[
|\Psi_0\rangle = \sum_s B_s \frac{1}{\sqrt{N}} \sum_l \gamma_{l+s} \eta_l^\dagger |g\rangle ,
\]

which can be represented by the relative momentum between the electron and hole

\[
|\Psi_0\rangle = \sum_k B_k \frac{1}{\sqrt{N}} \gamma_k^\dagger \eta_k^\dagger |g\rangle .
\]

Its energy is

\[
\langle \Psi_0 | H_{\text{chain}} | \Psi_0 \rangle = E_0 .
\]

The variational state \( |\Psi\rangle \) must have a lower energy than \( E_0 \),

\[
\epsilon = \langle \Psi | H | \Psi \rangle - E_0 < 0 .
\]

From \( \frac{\partial \epsilon}{\partial a} = 0 \) and \( \frac{\partial \epsilon}{\partial a_k} = 0 \), we obtain two coupled equations:

\[
- \sqrt{\frac{N_d}{N}} a \epsilon = a_k \left[ \epsilon + E_0 - (\epsilon_k + \Delta_e) \right] ,
\]

\[
a \epsilon = \frac{1}{N} \sum_k a_k |B_k|^2 \sqrt{\frac{N_d}{N}} v .
\]

Using Eq. (5.8), \( a_k \) can be eliminated from Eq. (5.9) and we have the eigenvalue equation for \( \epsilon \)

\[
\epsilon = c \frac{1}{N} \sum_k a^2 |B_k|^2 \epsilon + E_0 - (\epsilon_k + \Delta_e) \equiv c F(\epsilon) .
\]

Here \( c \equiv N_d/N \) is the dopant concentration. Once we have found the negative solution of \( \epsilon \), the probability that the exciton remains on the chain is

\[
a^2 = \frac{1}{1 - c F'(\epsilon)} ,
\]

where \( F'(\epsilon) = \frac{dF(\epsilon)}{d\epsilon} \). So the probability of charge transfer is

\[
P = 1 - a^2 = \frac{-c F'(\epsilon)}{1 - c F'(\epsilon)} .
\]

For the \( B_u \) exciton in the polymer chain

\[
B_k = \sum_l B_l^+ e^{-ikl} .
\]

If we assume for demonstration purposes that the exciton is highly localized (this is not necessary in our theory), i.e., \( B_l^+ = B_{l+1}^+ = \frac{1}{\sqrt{2}} \) and \( B_l^+ = 0 \) for other \( l \), then
\[ B_k = \sqrt{2} \cos k \],

and we can write \( F(\epsilon) \) in a very compact form:

\[
F(\epsilon) = \frac{v^2}{J(1 - \delta^2)} \left( \sqrt{\frac{E + 2J(1 - \delta^2)}{E}} - 1 \right),
\]

with

\[ E = -(\epsilon + E_0 - \Delta_e - 2J\delta^2). \]

Figure 22 illustrates the probability of charge transfer to the dopant. The dopant concentration is set to be 0.2, a typical value for a molecularly-doped polymer. We see that when the acceptor level is near the exciton energy \( E_0 \), a crossover will occur. When the acceptor level is below this crossover value, the electron is mainly on the dopant. Otherwise, the electron is mainly on the polymer chain. The coupling strength \( v \) affects the charge transfer by controlling the width of the crossover. The smaller \( v \) is, the more rapid is the crossover.

For the \( A_g \) exciton, if we make the assumption \( B_{-1} = -B_{-2} = \frac{1}{\sqrt{2}} \), then

\[
|B_k| = \left| \sum_l B_l e^{ikl} \right| = \sqrt{2} \sin k,
\]

and we have

\[
F(\epsilon) = \frac{v^2}{J(1 - \delta^2)} \left( 1 - \sqrt{\frac{E}{E + 2J(1 - \delta^2)}} \right).
\]

We plot the charge transfer probability for the \( A_g \) state in Fig. 23. We can see that there is a threshold for \( \Delta_e \). Below this value, the electron will thoroughly transfer to the dopant molecule. However for the \( B_u \) state there is a long tail below the critical value, indicating some fraction of the electron can still be found in the polymer. Having gained the knowledge of how \( \Delta_e \), \( v \), and the exciton wavefunction influence the probability of charge transfer, one will be able to control this transfer process in the conjugated polymer.

VI. CONCLUDING REMARKS

In this paper, we have extensively studied the exciton states in conjugated polymers by emphasizing the dominant role of \( e-e \) correlations. The model we studied here is the widely-used Peierls-extended Hubbard model with frozen bond dimerization. First, in the large-\( U \) approximation, we mapped this model to a spinless fermion model with only nearest-neighbor Coulomb interaction in real space. The short range interaction enabled us to apply \( t \) matrix theory to analytically calculate the energy spectrum and wavefunction of bound (exciton) states. We have found that there always exists a stable \( A_g \) exciton as long as the nearest-neighbor Coulomb \( V \) is nonzero; for the \( B_u \) state, however, a stable exciton state can exist only when \( V \) is larger than the half width of the continuum band. This criterion has been proven based on Levinson’s theorem. In our results, we have a correct ordering for \( A_g \) and \( B_u \) states, i.e., \( 2A_g < 1B_u \), as observed in most conjugated polymers. The impurity effects on the coherent motion of the excitons were also investigated in this large-\( U \) approximation. The coherence of the exciton can be measured by an appropriately defined electron-hole correlation function. We have studied impurities with on-site potentials as well as a charged impurity with a more extended potential. There are three kinds of impurity with the on-site potential: the first is like a local charge, attracting holes but repelling electrons (or vice versa); the second acts as a well, attracting both electron and hole; the third is like a barrier which repels both electron and hole. We have found that for the first and second type of impurities, the electron-hole correlations exhibit a crossover when the impurity strength \( V_0 \) is comparable to the exciton bandwidth \( J \), which describes the exciton being trapped by the impurity. For the second type of impurity, if the impurity strength is larger than the Coulomb interaction \( V \), the deep well will trap the electron and hole separately, leading to the total de-correlation of the exciton as a particle. For the third type of impurity, the exciton coherence can survive the impurity and the distribution in momentum space has a sharp peak which means the exciton still moves freely. For the charged impurity with an extended potential of range greater than \( l_V \), the range of the Coulomb interaction, the free exciton becomes trapped at \( V_0 \sim J \), analogous to the situation for on-site impurity potentials. However, unlike the charged impurity with the on-site potential, the exciton dissociates into an uncorrelated electron-hole pair when \( V_0 \) is sufficiently large compared to the Coulomb strength \( V \).
We have also investigated the effects of interchain coupling and the resulting interchain exciton states within the strong correlation approximation by considering a two-chain system with nearest-neighbor interchain hopping $t_\perp$ and Coulomb interaction $V_\perp$. In this coupled system, we have two conduction bands and two valence bands. Within the $t$ matrix formalism, we have found six poles for every center-of-mass momentum $K$, in which two poles are determined solely by $V_\perp$, corresponding to interchain excitons, while the other four poles are determined solely by the intrachain Coulomb interaction $V$, corresponding to intrachain excitons. We have also illustrated the wavefunctions of the static interchain exciton. There is still some amplitude for the electron and hole being on the same chain for the interchain exciton state. For more complicated Coulomb potentials, we propose a way to distinguish the interchain and intrachain excitons, namely by comparing the interchain electron-hole correlation function with the intrachain one.

The charge transfer in a molecularly-doped conjugated polymer has been studied by constructing a variational wavefunction for the whole system including the polymer chain and dopant molecule. We modeled this coupled system by simply regarding the molecule has an acceptor level which interacts with the polymer chain by nearest-neighbor hopping $v$. Minimizing the energy of the state, we have obtained the energy of the variational state and, accordingly, the probability of charge transfer. We have shown that a crossover behavior will occur when the acceptor level is near to the exciton energy. When the acceptor level is higher than this crossover value, the electron mainly controls the width of this crossover, the larger $v$ is, the more gentle is the crossover. The wavefunction is also an important influence on the charge transfer. For the $A_g$ state, there is a threshold for the acceptor level. If $\Delta_e$ is less than this value, the charge transfers to the molecule thoroughly and the percentage of electron density in the polymer chain is zero.

Our calculations in this paper presented a comprehensive picture of the exciton in conjugated polymers, in a limit in which the electron correlation effects have been taken seriously and consistently. Our exciton theory can be readily extended to a system with a relatively long range Coulomb interaction. Also using our spinless fermion representation for the Peierls-extended Hubbard model, biexciton states can be obtained either by the Heitler-London method or diagonalization of the Hamiltonian in two electron-hole pair space. Although for real conjugated polymers, the Hubbard $U$ is not so strong and our results cannot quantitatively match the energy levels in luminescent polymers, our theory is useful for understanding several puzzles which have arisen from correlation effects in conjugated polymers. Finally, we note that recent experimental evidence has demonstrated that there is an excitonic contribution to the static pairing mechanism in YBa$_2$Cu$_3$O$_{7-\delta}$. We expect that our exciton theory can give some guidance for exciton effects in high-T$_c$ superconductors by extending the formalism to two dimensions.

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**APPENDIX A: EXPLICIT EXPRESSIONS OF GREEN’S FUNCTIONS**

In this Appendix, we will give explicit expressions for $G(0; E_0)$ and $G(2; E_0)$ in different energy regions, calculated according to the definition Eq. (2.33). Here we use the same notation as in the text: $x = E_G - E_0$. When $E_0 > E_f$, i.e., $x < -4J(1 + \delta^2)$, the energy is above the top of the continuum band, and the Green’s functions are

\[
G(0; E_0) = \frac{1}{\sqrt{x^2 - 4J(1 + \delta^2)|x|}},
\]  

\[
G(2; E_0) = -\frac{1}{2J(1 + \delta^2)} + \left[\frac{|x|}{2J(1 + \delta^2)} - 1\right] \frac{1}{\sqrt{x^2 - 4J(1 + \delta^2)|x|}}.
\]  

When $E_i < E_0 < E_f$, i.e., $-4J(1 + \delta^2) < x < 0$, the energy is within the continuum band,

\[
G(0; E_0) = -i \frac{1}{\sqrt{-x^2 - 4J(1 + \delta^2)x}},
\]  

\[
G(2; E_0) = -\frac{1}{2J(1 + \delta^2)} + i \left[\frac{x}{2J(1 + \delta^2)} + 1\right] \frac{1}{\sqrt{-x^2 - 4J(1 + \delta^2)x}}.
\]
When $E_0 < E_i$, i.e., $x > 0$, the energy is in the gap,

$$G(0; E_0) = -\frac{1}{\sqrt{x^2 + 4J(1 + \delta^2)x}}, \quad \text{(A5)}$$

$$G(2; E_0) = -\frac{1}{2J(1 + \delta^2)} + \left[\frac{x}{2J(1 + \delta^2)} + 1\right] \frac{1}{\sqrt{x^2 + 4J(1 + \delta^2)x}}. \quad \text{(A6)}$$

**APPENDIX B: DIAGONALIZATION OF HAMILTONIAN (4.4)**

Hamiltonian (4.4) can be written as

$$\tilde{H}_0 = \sum_k (\eta_{1k} \eta_{2k}) \left( \begin{array}{c} \epsilon_k & t_\perp \\ t_\perp & \epsilon_k \end{array} \right) \left( \begin{array}{c} \eta_{1k} \\ \eta_{2k} \end{array} \right) + \sum_k (\gamma_{1k} \gamma_{2k}) \left( \begin{array}{c} \tilde{\epsilon}_k & -t_\perp \\ -t_\perp & \tilde{\epsilon}_k \end{array} \right) \left( \begin{array}{c} \gamma_{1k} \\ \gamma_{2k} \end{array} \right), \quad \text{(B1)}$$

Making the transformations

$$\left( \begin{array}{c} \eta_{1k} \\ \eta_{2k} \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 1 & 1 \\ -1 & 1 \end{array} \right) \left( \begin{array}{c} \tilde{\eta}_{1k} \\ \tilde{\eta}_{2k} \end{array} \right), \quad \text{(B2)}$$

and

$$\left( \begin{array}{c} \gamma_{1k} \\ \gamma_{2k} \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 1 & -1 \\ 1 & 1 \end{array} \right) \left( \begin{array}{c} \tilde{\gamma}_{1k} \\ \tilde{\gamma}_{2k} \end{array} \right), \quad \text{(B3)}$$

we have

$$\tilde{H}_0 = \sum_{Ik} (E_k^{\dagger} \tilde{\eta}_{1k} \tilde{\gamma}_{Ik} + \tilde{E}^{\dagger}_k \tilde{\gamma}_{1k} \tilde{\gamma}_{Ik}), \quad \text{(B4)}$$

and the relation between the two types of local operators $\eta_l (\gamma_l)$ and $\tilde{\eta}_l (\tilde{\gamma}_l)$:

$$\eta_{1l} = \frac{1}{\sqrt{2}} (\tilde{\eta}_{1l} + \tilde{\eta}_{2l}), \quad \text{(B5)}$$

$$\eta_{2l} = \frac{1}{\sqrt{2}} (\tilde{\eta}_{1l} - \tilde{\eta}_{2l}), \quad \text{(B6)}$$

$$\gamma_{1l} = \frac{1}{\sqrt{2}} (\tilde{\gamma}_{1l} - \tilde{\gamma}_{2l}), \quad \text{(B7)}$$

$$\gamma_{2l} = \frac{1}{\sqrt{2}} (\tilde{\gamma}_{1l} + \tilde{\gamma}_{2l}). \quad \text{(B8)}$$

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FIG. 1. Wave functions of the \(A_g\) and \(B_u\) bound exciton with \(U = 10t\), \(V = 0.5t\), and \(\delta = 0.2\). The dashed and solid lines correspond to the \(A_g\) and \(B_u\) states, respectively.
FIG. 2. Energy of excitons as a function of center-of-mass momentum $K$ with $U = 5t$, $V = 2t$, and $\delta = 0.2$.

FIG. 3. Optical absorption spectrum with $U = 5t$ and $V = t$. The $B_u$ exciton occupies 0.520 of the total oscillator strength. The arrow indicates the energy of the corresponding $A_g$ exciton.

FIG. 4. Optical absorption spectrum with $U = 5t$ and $V = 2t$. The arrow indicates the position of the $A_g$ exciton, and the $B_u$ exciton takes 0.949 of the total transition strength.

FIG. 5. Electron-hole correlation function as a function of the impurity strength $V_0$ for impurity potential $H_1^{\text{imp}}$ with $U = 10t$ and $V = t$. The impurity is situated at site 5 in a $N = 10$ site chain. The solid, long dashed, and short dashed lines correspond to $R(5, 6)$, $R(7, 8)$, and $R(3, 6)$, respectively.

FIG. 6. The hole density at the impurity site vs impurity strength $V_0$ for the impurity potential $H_1^{\text{imp}}$. The parameters here are the same as in Fig. 5.

FIG. 7. Distribution of charge density in real space for the first type of impurity, $H_1^{\text{imp}}$. The solid circles describe the hole density, while the open ones are for the electron density. Here $U = 10t$, $V = t$, and $V_0 = 0.5t$.

FIG. 8. Electron-hole correlation function, as a function of the impurity strength $V_0$ for the impurity potential $H_2^{\text{imp}}$ with $U = 10t$ and $V = t$. The impurity is located at site 5 in a $N = 10$ chain. The solid, dashed, and dot-dashed lines illustrate $R(5, 6)$, $R(3, 4)$, and $R(3, 6)$, respectively.

FIG. 9. Electron-hole correlation function as a function of the impurity strength $V_0$ for the third kind of impurity $H_3^{\text{imp}}$ in a $N = 10$ chain. Parameters are the same as for Fig. 8, $U = 10t$ and $V = t$. The solid, dashed, and dot-dashed lines are for $R(5, 6)$, $R(3, 4)$, and $R(3, 6)$, respectively.

FIG. 10. Distribution $|Z_K|^2$ for the impurity potential $H_1^{\text{imp}}$ with $U = 10t$ and $V = t$ in a $N = 12$ chain. There are two exciton branches ($A_g$ and $B_u$). The solid symbols indicate the amplitude of excitons in the $A_g$ branch, and the open ones give the amplitude of excitons in the $B_u$ branch. The circle corresponds to $V_0 = 0.1t$, the situation before the crossover, and the box corresponds to $V_0 = t$, which is larger than the crossover value.

FIG. 11. Distribution $|Z_K|^2$ for the second kind of impurity potential $H_2^{\text{imp}}$ with $U = 10t$ and $V = t$ in a $N = 12$ chain. The solid and open symbols have the same meanings as in Fig. 10. The circle describes the case of $V_0 = 0.1t$ and the box describes $V_0 = t$. The line is for the case $V_0 = 2t$. The vanishing amplitude in every exciton state shows the breakdown of the exciton.

FIG. 12. Distribution $|Z_K|^2$ for the third kind of impurity $H_3^{\text{imp}}$ with $U = 10t$ and $V = t$ in a $N = 12$ chain. The circle and box correspond to $V_0 = 0.1t$ and $V_0 = t$, respectively.

FIG. 13. Electron-hole correlation function as a function of the impurity strength $V_0$ for a charged impurity $H_4^{\text{imp}}$ in a $N = 10$ chain. Parameters are the same as for Fig. 8, $U = 10t$ and $V = t$. The solid and dashed lines are for $R(5, 6)$ and $R(3, 6)$, respectively.

FIG. 14. Distribution of charge density in real space for a charged impurity with extended potential $H_4^{\text{imp}}$. The solid symbols describe the hole density and the open ones are for the electron density. The circles and triangles correspond to $V_0 = 0.5t$ and $V_0 = 5t$, respectively. Here $U = 10t$, $V = t$.

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FIG. 15. Distribution $|Z_K|^2$ for a charged impurity with extended potential $H^{\text{imp}}_2$ for $U = 10t$ and $V = t$ in a $N = 12$ chain. The solid and open symbols have the same meaning as in Fig. 10. The circle describes the $V_0 = 0.1t$ case, the box describes $V_0 = t$, and the line is for $V_0 = 5t$. The vanishing amplitude in every exciton state indicates the dissociation of the exciton.

FIG. 16. Intrachain and interchain exciton bands with $U = 10t$, $V = t$, $t_\perp = 0.5t$ and $V_\perp = t$. The two solid lines describe the dispersion of the interchain exciton, and the four dashed lines are for intrachain excitons.

FIG. 17. Intrachain and interchain exciton bands with $U = 10t$, $V = t$, $t_\perp = 0.2t$ and $V_\perp = 1.5t$. Solid lines are the energy spectra for interchain excitons. Here the interchain exciton is the lowest excited state.

FIG. 18. Wavefunctions of the lower static interchain exciton with $U = 10t$, $V = t$, $t_\perp = 0.2t$, and $V_\perp = t$. The solid line gives the relative amplitude that the electron and hole are in the same chain, and the dashed line gives the amplitude that they are in different chains.

FIG. 19. Wavefunctions of the higher static interchain exciton with $U = 10t$, $V = t$, $t_\perp = 0.2t$, and $V_\perp = t$. Here the intrachain amplitude is zero.

FIG. 20. Intra/interchain electron-hole correlation vs $r = V_\perp/V$ in a two-chain system. Each chain has $N = 12$ sites and the parameters are $U = 10t$, $V = t$, and $t_\perp = 0.2t$. The intrachain correlation function illustrated here by the dashed line is $\mathcal{R}(5, 6)$, and the interchain correlation function given by the solid line is $\mathcal{R}(5, 17)$, where site $12 + i$ indicates site $i$ in the second chain.

FIG. 21. Schematic diagram of the charge transfer from a polymer chain to a dopant molecule. The dopant has an acceptor level which interacts with the polymer by nearest-neighbor hopping $v$.

FIG. 22. Probability of charge transfer of the $B_u$ state as a function of acceptor level $\Delta_e$. The parameters in the polymer are $U = 10t$, $V = t$, and $\delta = 0.2$, corresponding to the energy of the $B_u$ exciton, $E_0 = 9.537t$ (indicated by the arrow). The dopant concentration $c = 0.2$. In the solid line, $v = 0.212t$, and in the dashed line, $v = 0.566t$.

FIG. 23. Probability of charge transfer of the $A_g$ state as a function of acceptor level $\Delta_e$. The parameters are the same as those in Fig. 22, and the corresponding $A_g$ state has energy $E_0 = 9.140t$ (indicated by the arrow). The solid and dashed lines correspond to $v = 0.212t$ and $v = 0.566t$, respectively.
polymer

dopant
\[ P = f(\Delta_e) \]

Graph showing the relationship between \( P \) and \( \Delta_e \). The graph indicates a decrease in \( P \) as \( \Delta_e \) increases.