Concerning the stability of hybrid biexcitons in organic polymer aggregates

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Frenkel excitons are the primary photoexcitations in organic semiconductors and are ultimately responsible for the optical properties of such materials. They are also predicted to form bound exciton pairs, termed biexcitons, which are consequential intermediates in a wide range of photophysical processes. Generally, we think of bound states as arising from an attractive interaction. However, here we report on our recent theoretical analysis predicting the formation of stable biexciton states in a conjugated polymer material arising from both attractive and repulsive interactions. We show that in J-aggregate systems, JJ-biexcitons can arise from repulsive dipolar interactions with energies \( E_{JJ} > 2E_J \) while in H-aggregates, HH-biexciton states \( E_{HH} < 2E_H \) corresponding to attractive dipole exciton/exciton interactions. These predictions are corroborated by using ultrafast double-quantum coherence spectroscopy on a PBTTT material that exhibits both J- and H-like excitonic behavior.

I. INTRODUCTION

It is generally understood that the primary photoexcitations in organic semiconducting materials are molecular \( \pi - \pi^* \) electronic singlet states \( (S_1) \) termed Frenkel excitons \[1\]. While local in nature, at sufficiently high packing densities, excitons can delocalized over several molecular units and sufficiently higher excitation densities, exciton-exciton interactions begin to dominate the optical properties of such materials \[2\]. Biexcitons, bound pairs of excitons, are consequential intermediates in a wide range of photophysical processes such as exciton dissociation into electrons \( (e^-) \) and holes \( (h^+) \) \[3\],

\[
S_0 + 2h\omega \longrightarrow [2S_1]^\dagger \longrightarrow 2e^- + 2h^+ \tag{1}
\]

bimolecular annihilation \[4\],

\[
S_1 + S_1 \longrightarrow [2S_1]^\dagger \longrightarrow S_0 + S_0 \tag{2}
\]

and singlet fission producing triplet \( (T_1) \) states \[5\]

\[
S_0 + 2h\omega \longrightarrow [2S_1]^\dagger \longrightarrow T_1 + T_1. \tag{3}
\]

Ref. \[4\] notes that bimolecular annihilation may be mediated both by resonance energy transfer and diffusion-limited exciton-exciton scattering, but in either case we invoke the key intermediate \([2S_1]^\dagger\). Examples of this occur in biological light harvesting complexes where multi-exciton interactions may play important roles \[6\] in the excitonic transport process, and biexcitons can be crucial in cascade quantum emitters as a source of entangled photons \[7\]. While ample theoretical work points towards the existence of biexcitons in organic solids \[8–14\], and in optical lattices \[15\], there has been only indirect evidence of the dynamic formation of two-quantum exciton bound states in polymeric semiconductors by incoherent, sequential ultrafast excitation \[3\] \[5\] \[16\] \[17\].

Recently, we reported upon the the direct spectroscopic observation of bound Frenkel biexcitons, \( i.e., \) bound two-exciton quasiparticles \([2S_1]^\dagger\), in a model polymeric semiconductor, \[poly(2,5-bis(3-hexadecylothiophene-2-yl)thieno[3,2-b]thiophene)]\[18\] (PBTTT) using coherent two-dimensional ultrafast spectroscopy. \[19\] The chemical structure of PBTTT is given in Fig. 1(A). PBTTT is unique in that depending upon processing conditions, it can support the formation of both H and J aggregate single exciton states, suggesting an arrangement as sketched in Fig. 1(B) in which intra-chain J-like excitons can form along the chains spanning over several PBTTT subunits, while inter-chain H-like excitons can form due to parallel stacking of several chains within the aggregate. The experimental observations revealed a correlation between peaks in the single and double quantum spectra the correspond to the formation of HH and JJ biexciton species. This conclusion was supported by both a computational model and theoretical analysis based upon a quasi-one-dimensional continuum model.

Here present an overview of the theoretical model we developed for biexcitons and use it to discuss biexcitons in related organic polymer materials. First, we show how one can reduce the two-dimension lattice problem into two separate one-dimensional problems and use a Greens function approach to account for the contact interaction...
which enforces Pauli exclusion since given site, they obey the Fermion relation \( a_n^\dagger a_m = a_m^\dagger a_n = 0 \). These operators are Paulion operators that create and remove single excitations on to a site labeled by \( n \). Further, we can write a generic multi-exciton Hamiltonian as

\[
H = \sum_{nm} h_{nm} a_n^\dagger a_m + \frac{1}{2} \sum_{nm} U_{nm} a_n^\dagger a_m a_n a_m. \tag{5}
\]

where \( h_{nm} \) describes the single-exciton dynamics and \( U_{nm} \) is the exciton/exciton interaction. In principle, the parameters entering into the Hamiltonian in Eq. \( 5 \) are defined by the system of interest. For the case of excitons, the diagonal elements of the single particle term defines the energy to place an exciton in site \( n \), and we write \( h_{nn} = \epsilon_n \). For a homogeneous lattice, all site energies are the same, and \( \epsilon_n = \epsilon_0 \). Similarly, the off-diagonal elements of \( h_{nm} \) correspond to the matrix elements for transferring an excitation from site \( n \rightarrow m \).

To a good approximation, the single-exciton transfer interaction can be described within the dipole-dipole approximation as described above. This model differs from the Hubbard model commonly studied in condensed matter physics in that we explicitly exclude double occupancy of each lattice and the exciton/exciton interaction is taken to be between occupied neighbors. Formally, a Frenkel exciton corresponds to a single electron/hole excitation on a given site. However, molecules are not point particles and excitons may acquire some intramolecular charge-transfer character. Therefore, we anticipate that \( U_{nm} \) is also dipole-dipole like and reflects the relative orientation of the static exciton dipole moments.

For a one-dimensional chain with lattice spacing \( a \), \( n \) is simply an index along the chain such that the site location is given by \( r_n = na \). However, for 2- and 3-dimensional systems, we shall take it as an \( n \)-tuple index specifying the site location. For the single particle term, \( h_{nn} \) is the excitation energy for single site \( (\epsilon_n) \) and \( h_{nm} \) (for \( n \neq m \)) corresponds to the hopping integral between sites. Upon transforming into the reciprocal space, one finds the single particle energy dispersion as

\[
(\epsilon(k) - E)e^{ikn} = \sum_m h_{nm}e^{ikm}. \tag{7}
\]

To determine the 2-exciton states, we begin by writing

\[
|\psi\rangle = \sum_{kk'} c_{kk'} a_k^\dagger a_{k'}^\dagger. \tag{8}
\]

where \( c_{kk'} \) are the expansion coefficients for this state. At this point, there are various approaches one can take to find the general solutions for the Schrödinger equation for the 2-exciton system. Indeed, for a small enough lattice, one can simply directly diagonalize the Hamiltonian in Eq. \( 5 \) for a finite sized grid. However, we are not interested the full solution of this problem. Rather, we are focused upon only solutions corresponding to bound exciton pairs, and especially those bound pairs that retain their J- or H-like excitonic character. With this in mind, we develop an analytical solution that naturally extends to the full model.
B. Greens function approach

Exact solutions for the biexciton problem can be obtain for homogeneous 1-, 2-, and 3-dimensional systems in which the hopping integral between nearest neighbours is the same in any direction, all the site-energies are the same, and the exciton/exciton interaction only involves nearest neighbor terms. Employing the Greens function approach developed by Vektaris,9 those solutions are given by

\[ \phi_K(n) = \sum_m \left( G_{nm} - \frac{G_{n0}G_{m0}}{G_{00}} \right) U_m \phi_K(m) \]  

(9)

where \( 2K = k + k', 2q = k - k' \) define the center of mass and relative motions,

\[ G_{nm} = \frac{1}{N} \sum_q e^{-i\mathbf{q}(n-m)} \]  

(10)

is a Greens function, and

\[ \phi_K(n) = \frac{1}{\sqrt{N}} \sum_{k+k'=2n} \exp(i\mathbf{n} \cdot (\mathbf{k} - \mathbf{k}')) \tilde{c}_{kk'} \]  

(11)

is the 2-exciton wave function written in terms of the coefficients \( \tilde{c}_{kk'} \). Finally, we have assumed the interaction \( U_{nm} \) to be translationally invariant such that

\[ U_{nm} = \sum_{n'} U_{n'n} \delta_{n,m+n'}. \]  

(12)

Note that \( \phi_K(0) = 0 \), which enforces the exclusion principle.

In general, the complete solution of Eq[9] would produce both bound and unbound biexciton states.

However, here we are solely interested in bound exciton pairs. In order to be bound, the state must exist outside the energy band for free exciton pairs. That is to say, \( |E - 2\varepsilon| \geq 2|t| \) to produce a bound biexciton state.

C. Local exciton approximation

Now, we wish to apply the Greens function approach to the case at hand in which motion in direction is different from motion in the perpendicular direction. For this, let us define a new set of exciton operators, \( \hat{J}_{k_x}(n) \) and \( \hat{J}_{k_y}(n) \) which creates or removes an exciton with wavevector \( k_x \) in the \( x \)-direction localized on the \( n \)th row of sites. Similarly, we define operators \( \hat{H}_{k_x}(m) \) and \( \hat{H}_{k_y}(m) \) which create and remove excitons with wavevector \( k_y \) in the \( y \)-direction, but localized to the \( m \)th column, as sketched in Fig. 2. These can be written in terms of the original lattice operators

\[ \hat{J}_{m,k_x} = \frac{1}{\sqrt{N}} \sum_n e^{ik_x n} a_{(n,m)} \]  

(13)

\[ \hat{H}_{n,k_y} = \frac{1}{\sqrt{N}} \sum_m e^{ik_y m} a_{(n,m)}. \]  

(14)

FIG. 2. Sketch of 2D lattice model with superimposed transition dipole for each site. In (A), we define a J-aggregate basis and create JJ biexciton configurations along each row. In (B), we define an H-aggregate basis along each column. As discussed in the text, these are equivalent representations of the full 2D problem and are useful for reducing the 2D problem into two separate (but formally identical) 1D problems.

Both are equivalent representations and we can choose to use either (but not both) to rewrite the original problem in this new representation.

Thus, we can write

\[ \sum_{nm} \hat{h}_{nm} a_n^\dagger a_m = \sum_{k_x,m,m'} (\varepsilon_J(k_x) \delta_{mm'} + t_H(mm') \hat{J}_{m,k_x}^\dagger \hat{J}_{m',k_x}) \]  

(15)

\[ = \sum_{k_y,n,n'} (\varepsilon_H(k_y) \delta_{nn'} + t_J(nn') \hat{H}_{n,k_y}^\dagger \hat{H}_{n',k_y} \]  

where in the first line we diagonalized in the J-direction and in the second, we diagonalized in the H-direction. This implies that we can think of a J-exciton state as moving in the H-direction with hopping integral \( t_H \) and H-exciton states as moving in the J-direction with hopping integrals \( t_J \). The dispersion relations are then as usual

\[ \varepsilon_J(k_x) = \varepsilon_0 + 2t_J \cos(k_x) \]  

(16)

\[ \varepsilon_H(k_y) = \varepsilon_0 + 2t_H \cos(k_y) \]  

(17)

where \( t_J < 0 \) is the nearest-neighbor coupling along the \( x \)-direction and \( t_H > 0 \) is the nearest-neighbor coupling taken in the \( y \)-direction. To remind, throughout we are taking the wavevector \( k \in [-\pi, \pi] \). Since the problem is formally separable between \( x \) and \( y \) directions, the single-particle terms do not mix wavevector components since \( k_x \) and \( k_y \) are “good” quantum numbers for this system. Using the \( \hat{J} \) and \( \hat{H} \) operators, we can reduce the 2-particle/2-dimensional problem into a one for pair of particles within a 1 dimensional frame without loss of generality.

This decomposition suggest that motion in one direction can be very different than motion in the perpendicular direction due to the orientations of the transition dipoles between neighboring units. In Fig. 1B we suggest how this can be accomplished within the context of molecular aggregates with \( \pi \)-stacking. Here, excitonic sites are denoted as blue ellipsoids along with their
D. Optical Transitions

It is important to keep in mind that two types of excitons sketched in Fig. 1 occur at different wave-vectors. In Fig. 1(a) the J-like exciton has its longest wavelength in the x-direction (corresponding to $k_x = 0$) while having the shortest possible wavelength in the y-direction (i.e. $k_y = \pm \pi/a$). Transitions to this state from the exciton vacuum (ground states) are allowed under the dipole approximation for the transition moment. Consequently, double excitations can create either pairs of free J-like excitons or bound 2J excitons. Similarly, optically allowed H-like single excitons are delocalized along the y-direction but localized along the x-direction (i.e. $k = \{\pm \pi/a, 0\}$) implying that the double excitations must also occur at these wave-vectors. Bearing this in mind, the dispersion curves plotted in Fig. 3 need to be taken at the corresponding points in k-space with a corresponding shift in the energy origins for each exciton species.

E. Biexciton stability

According to our model, Frenkel biexcitons mix J-like and H-like character in terms of their collective quantum behavior with the requirement that the ratio of the exciton/exciton interaction and the perpendicular hopping term be $U/\Delta > 0$ which gives rise to localized biexciton states in the perpendicular direction. For the 1D $\delta$-function potential, any attractive interaction with $U/\Delta > 0$ produces a localized state with localization length $\lambda = \kappa^{-1} = 2t/U. [20]$ For the 1D lattice, bound biexciton states occur outside the band for free biexcitons.

1. One-dimensional impurity model

To gain further insight into the stability of these states, we turn to a continuum model and work in a relative coordinate reference frame where $x = |r_1 - r_2|$ is the separation between two localized excitons. Thus, the biexciton Schrödinger equation can be approximated as

$$t\psi'' + U\delta(x)\psi = E\psi \quad (19)$$

where $U$ is the contact interaction between the two excitons. For bound states, $\psi(x)$ must vanish as $x \to \pm \infty$, giving that

$$\psi(x) = \begin{cases} \sqrt{\kappa}e^{-\kappa x} & x > 0 \\ \sqrt{\kappa}e^{\kappa x} & x < 0 \end{cases} \quad (20)$$

where $\kappa = U/2t$ is a positive constant and $E = tk^2$. In general, we take $t = \hbar^2/2\mu_{ef}$ and $U < 0$ for an attractive potential giving rise to a bound state energetically below the continuum for the scattering states.
2. Lattice reorganization in the impurity model

Generally speaking, one cannot discount the role of lattice reorganization and relaxation when discussing excitons and biexcitons in organic polymer semiconducting systems. To study this, we append to the 1D impurity model a continuum model for the medium a term coupling the biexciton to the lattice as per the Davydov model. \[21\] The resulting equations of motion read

\[ i\hbar \dot{\psi}(x) = \left( t \nabla^2 + U\delta(x) + (E_o + 2\chi \nabla u(x)) \right) \psi(x) \]

\[ \ddot{u} - \frac{k}{m} \nabla^2 u = 2\frac{\chi}{m} \nabla |\psi|^2 \] \tag{21}

where \( u(x) \) is the lattice deformation, \( \chi \) describes the linear coupling between the biexciton and the lattice, \( m \) is the mass of the lattice “atoms” and \( k \) is the elastic modulus. If we seek traveling wave solutions, \( u(x,t) = u(x-\nu t) \) where \( \nu \) is the group velocity, we find a closure relation

\[ \nabla u = -\frac{2\chi}{k(1-(\nu/c)^2)} |\psi|^2 \] \tag{22}

that gives us a non-linear Schrödinger equation

\[ i\hbar \dot{\psi} = \left( \frac{t}{\hbar} \nabla^2 + g|\psi|^2 + U\delta(x) \right) \psi \]

where \( g = -4\chi^2/(k(1-(\nu/c)^2)) \) and \( c \) is the sound velocity. Note that \( E_o \) is a constant given by

\[ E_o = E - 2t + \frac{1}{2} \int_{-\infty}^{\infty} \left( m\dot{u}^2 + k\ddot{u}'' \right) dx. \] \tag{24}

that we can ignore for purposes of this analysis. The \( \delta \)-function potential implies the wave function should have the form in Eq.\[20\]. Taking \( \kappa \) as a variational parameter and minimizing the total energy, one obtains

\[ \kappa = \frac{U}{2t^2} + \frac{g}{8t}. \] \tag{25}

\( \kappa > 0 \) is necessary to produce a localized state and from above we know that \( U/t > 0 \) and \( g < 0 \) from its definition above, we have a stability requirement that if \( U > 0 \) and \( t > 0 \), then \( g < 4U \). Solving for the energy,

\[ E = -\frac{(4U + g)^2}{64t}. \] \tag{26}

This implies that while lattice reorganization would stabilize the attractively bound 2H biexciton, it destabilizes the 2J biexciton.

III. COMPARISON TO EXPERIMENTAL MEASUREMENT

We have examined the theoretical concepts by means of two-dimensional coherent excitation spectroscopy on PBTMM, with structure depicted in Fig.\[1\](A), which we reported extensively in Ref. \[19\]. In that work, we identified spectral features associated with the 0–0 excitation peak of both the H- and J-aggregate components of the hybrid aggregate, with cross peaks between reflecting spectral correlations due to their shared ground state. The origin of the H-aggregate vibronic progression was centered at 2.06 eV, while a weaker peak at 1.99 eV was assigned to the J-aggregate vibronic origin. By performing two-quantum coherence measurements, we found spectral signatures of both HH and JJ biexcitons. A cross-section of the 2D spectral data is shown in Fig. \[4\]. We found that HH biexcitons displayed attractive biexciton binding with energy \(-64 \pm 6\) meV, whereas JJ biexcitons displayed repulsive correlations with binding energy \(+106 \pm 6\) meV; that is that the energy of the HH-biexciton resonance is lower than twice the H-aggregate resonance energy, while the corresponding energy for the JJ-biexciton resonance is higher.

We rationalized this observation as depicted in Fig. \[1\]: two quantum interactions for excitons dispersed along the polymer backbone (J aggregates) are with \( J < 0 \), while \( J > 0 \) for those for between excitons dispersed on several chains (H aggregates). Considering physically reasonable parameters, we concluded that biexcitons in PBTMM are stable by the arguments depicted in Fig. \[4\].

IV. CONCLUSIONS

We present here theoretical and experimental evidence supporting the formation of bound Frenkel biexcitons in a molecular aggregate material. In our theoretical analysis, we solved the full 2D interacting model and give the...
conditions necessary for the formation of stable, stationary states corresponding to bound exciton pairs. The model provides a road-map for developing a bi-exciton materials genome in terms of the properties of the J- and H-excitons. We show that for bound biexcitons, both the exciton-exciton interaction $U$ and the single-particle hopping integral $t$ must have the same sign. Furthermore, $U/t > 2$ so that the exciton/exciton potential interaction is greater than their total kinetic energy. Curiously, we find that while H-like excitons form bound biexcitons with attractive interactions, J-like exciton pairs form bound states arising from a repulsive interaction.

An open question, however, is the nature of the exciton-exciton interaction itself. Here, we introduce it as a parameter into our model with a dipole-dipole like form in that the exciton-exciton coupling in one direction is different from that in a perpendicular direction. It is also important to point out that while this interaction appears to have a dipole-like form, it necessarily must reflect the static dipole of the local Frenkel excitons rather than their transition dipole moments, which are responsible for the single exciton transfer between local sites. Computing these interactions from a first-principle $ab$ initio theory remains a formidable challenge since it necessitates the accurate calculation of doubly excited states with some degree of charge-separation.

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**Appendix A: Variational solution for NLSE + delta potential**

Starting from the NLSE,

$$i\hbar \psi' - t\psi'' - g|\psi|^2\psi - U(x)\psi = 0 \quad (A1)$$

we can write the equivalent Lagrange density as

$$\mathcal{L} = \frac{\hbar i}{2}(\psi\psi^* - \psi^*\psi) + t|\psi|^2 - U(x)|\psi|^2 - g\frac{|\psi|^4}{2}. \quad (A2)$$

Since we are seeking stationary solutions, we write

$$\psi = e^{-iEt/\hbar}\phi(x)$$

with $\phi(x)$ taking the exponential form in Eq 20 and write the Lagrangian

$$L = \int_{-\infty}^{\infty} \mathcal{L} dx \quad (A3)$$

$$= -E + t\kappa^2 - \kappa U_o - g\kappa \quad (A4)$$

The parameter $\kappa$ is obtained by solving the Euler Lagrange equations

$$\frac{d \partial L}{dt \partial \kappa} - \frac{\partial L}{\partial \kappa} = 0 \quad (A5)$$

subject to the constrain that $\phi$ is properly normalized. One then obtains that

$$\kappa = \frac{U}{2t} + \frac{g}{8t}$$

and the variational minimum energy

$$E = -\frac{(4U + g)^2}{64t}$$

Taking $g \to 0$ gives the result obtained in the absence of the deformable lattice.

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