Study of the Förster resonance energy transfer in composite films of carbon nanotubes

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ABSTRACT

We study excitonic energy transfer in a network of carbon nanotubes (CNTs), a promising light-absorbing material for next-generation organic solar cells. We calculate the exciton energy dispersion curves through solving the Bethe-Salpeter equation in the basis of tight-binding wave functions. Furthermore, we compute the Coulomb-coupling matrix element between bright excitonic states, in order to obtain the exciton transfer rate between similar and dissimilar carbon nanotubes with an arbitrary orientations. The conservation of momentum imposes a limitation on the energy transfer rate between parallel nanotubes of different chiralities. However, there is no such limitation for transfer between misoriented CNTs, which results in transfer rates of the same order of magnitude between carbon nanotubes of similar and dissimilar chiralities.

Keywords: Semiconducting carbon nanotube, Exciton, Resonance energy transfer

1. INTRODUCTION

The quasi-one-dimensional (1D) structure of carbon nanotubes (CNTs) leads to a very unique set of optical, electronic, and mechanical properties. The strong optical absorbitivity, tunable near-infrared band gaps, ultrafast exciton and charge transport, excellent chemical stability, and economical solution-processability of semiconducting CNTs (s-CNTs) have made their application as the light absorbing material in photovoltaics the subject of much research effort in the past few years.\(^1\)\(^2\)

Bilayer donor/acceptor heterojunction photovoltaic devices based on s-CNT as the light absorber have been shown to have excellent efficiency in the exciton dissociation step at the heterojunction (Figure 1). However, the overall efficiency of such s-CNT based photovoltaics is still poor due to low efficiency in the exciton migration process from the light absorbing layer to the heterojunction. The exciton transport process in a film of s-CNT happens through two different mechanisms: wavelike (intratube) and hopping (intertube) transport. It has been shown that the exciton diffusion length along the CNT axis is on the order of 100 nm due to the relatively fast intratube exciton transport.\(^3\) However, the intertube exciton transport is a much slower process yielding to much smaller diffusion lengths. Wu et al.\(^4\) and Grechko et al.\(^2\) have recently studied the exciton transport in a network of CNTs using phenomenological models. However, the role of CNT chirality and the excitonic energy dispersion in the transport process are not fully understood.

The quantum-mechanical study of intertube exciton hopping in s-CNT composites is the focus of this study. We use the tight-binding single-particle wave functions as a basis to solve the Bethe-Salpeter equation and calculate the excitonic energies and wave functions. The intertube excitonic energy transfer happens via a hopping mechanism, which originates in the Coulomb coupling between electrons on the two s-CNTs. We calculate the energy transfer rate through the transition monopole approximation (TMA). Our result show that momentum conservation plays an important role in determining the energy transfer rate between parallel tubes with dissimilar chiralities: the energy transfer rate between CNTs of similar chiralities is about 3 orders of magnitude faster than between CNTs with dissimilar chiralities. However, momentum conservation is not an issue in the case of unparallel CNTs and the energy transfer rates between similar and dissimilar tubes have the same order of magnitude.

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Figure 1: Structure of a bilayer donor/acceptor heterojunction photovoltaic device based on a s-CNT light absorber. The incident light is absorbed by the s-CNTs in the vicinity of transparent ITO contacts and excitons are created. The excitons diffuse through the s-CNT film and dissociate into free electrons and free holes at the CNT-C60 heterojunction.

This paper is organized in the following way. Section 2 reviews the Bethe-Salpeter equation in the basis of tight-binding wave functions based on the work by Jiang et al. We show a calculation of the exciton energies and eigenstates in CNTs and discuss various categories of excitons based on their symmetry and spin. In section 3, we talk about the Coulomb coupling process and derive the long-range resonance energy transfer rates for different geometries. Further, we discuss the results of the transfer rate calculation between CNTs of (7,5) and (8,6) chirality. Section gives a summary of the paper.

2. EXCITON WAVE FUNCTION

According to the Tamm-Dancoff approximation the electron-hole excitation (exciton) wave function is a linear combination of free electron-free hole wave functions

\[ |s\rangle = \sum_{k_c,k_v} A_s(k_c,k_v) \hat{a}^\dagger(k_c) \hat{\psi}(k_v) (\text{GS}). \]  

Here, \( A_s(k_c,k_v) \) is the expansion coefficient, \( \hat{a}^\dagger(k_c) \) is the creation operator of an electron in conduction band with wave vector \( k_c \), and \( \hat{\psi}(k_v) \) is the annihilation operator of an electron from the valence band with wave vector \( k_v \). \( s \) is a quantum number analog of the principal quantum number in hydrogen atom. We use the tight-binding single-particle wave functions as the basis functions. The expansion coefficients in the exciton wave function and the excitonic eigen energies are calculated by solving the Bethe-Salpeter (BS) equation

\[ [E_c(k_c) - E_v(k_v)] A_s(k_c,k_v) + \sum_{k'_c,k'_v} K(k_c,k_v;k'_c,k'_v) A_s(k'_c,k'_v) = \Omega_s A_s(k_c,k_v), \]  

where \( E_c(k_c) \) and \( E_v(k_v) \) are the quasiparticle energies of electrons with wave vectors \( k_c \) and \( k_v \) in the conduction and valence band. \( \Omega_s \) is the exciton energy. \( K \) is the interaction kernel which describes the particle-particle interaction. Using the GW approximation, we can divide the interaction kernel into direct and exchange terms

\[ K(k_c,k_v;k'_c,k'_v) = 2\delta_{sA} K^x(k_c,k_v;k'_c,k'_v) - K^d(k_c,k_v;k'_c,k'_v), \]  

where

\[ K^d(k_c,k_v;k'_c,k'_v) = W(k_c,k'_c;k_v,k'_v) = \int d^3r d^3r' \psi^*_k(r') \psi_k(r) w(r,r';\omega = 0) \psi_{k'_v}(r) \psi_{k'_c}(r'), \]  

and

\[ K^x(k_c,k_v;k'_c,k'_v) = V(k_c,k_v;k'_c,k'_v) = \int d^3r d^3r' \psi^*_k(r') \psi_k(r) v(r,r') \psi_{k'_v}(r) \psi_{k'_c}(r). \]
Here, $\psi_k$ is the quasiparticle wave function. $w$ and $v$ are the screened and bare Coulomb interactions. $\alpha$ is the exciton spin and $\delta_\alpha = 1$ for singlet exciton ($\alpha = 0$) and $\delta_\alpha = 0$ for triplet excitons ($\alpha = 1$).

The screened Coulomb interaction is in the frequency domain and can be calculated using the random phase approximation:7

$$W(a_1k_1, a_2k_2; a_3k_3, a_4k_4) = \frac{V(a_1k_1, a_2k_2; a_3k_3, a_4k_4)}{\kappa(k_1 - k_2, \omega = 0)}. \tag{4}$$

Here, $a_i$ shows the conduction or valence band of graphene. $\kappa$ is the static dielectric function which accounts for the effect of core electrons. We take $\kappa = 2$ in this paper. The effect of $\pi$ bond electrons is considered in the dielectric function $\epsilon(q, w)$ which is calculated through the Lindhard formula.7

We use the tight binding (TB) wave function,

$$\psi_{ak}(r) = \frac{1}{\sqrt{N_u}} \sum_s \sum_u C_{as}(k) e^{ik \cdot R_{us}} \phi(r - R_{us}), \tag{5}$$

to calculate the interaction kernels. Here, $u$ runs over all the $N_u$ graphene unit cells and $s$ runs over all the basis atoms in graphene unit cell.

The final expression for the interaction kernels has the following format

$$K^d(k_c, k_v; k_c', k_v') = \delta(k_c' - k_c, k_v' - k_v) \sum_{s,s'} C_{cs}(k_c)C_{cs'}(k_v)C_{cs'}(k_v') C_{vs}(k_c' - k_c), \tag{6a}$$

$$K^x(k_c, k_v; k_c', k_v') = \delta(k_c - k_c', k_v - k_v') \sum_{s,s'} C_{cs}(k_c)C_{us}(k_v)C_{cs'}(k_v') C_{vs}(k_c - k_v), \tag{6b}$$

where $v_{s,s'}(q)$ is the Fourier transform of the overlap matrix between two $p_z$ orbitals

$$v_{s,s'}(q) = \frac{1}{N_u} \sum_{u,u'} e^{iq \cdot R_{u''u'''} - R_{us'}} I(R_{u''u'''} - R_{us'}) \tag{7a}.$$

$$I(R_{u''u'''} - R_{us'}) = \int d^3r d^3r' |\phi(r - R_{us'})|^2 |\phi(r' - R_{u''u'''})|^2 \approx \frac{U}{\sqrt{(4\pi\epsilon_0 U |R_{u''u'''} - R_{us'}|)^2 + 1}} \tag{7b}.$$

The last expression is the Ohno potential were we take the parameter $U = 11.3 \text{ eV}$. Note that due to the delta functions in equation 6 we can write the interaction kernels in terms of center-of-mass and relative motion wave vectors

$$k = \frac{k_c - k_v}{2}, \quad k_r = \frac{k_c + k_v}{2}. \tag{8}$$

Consequently, the center-of-mass wave vector is a good quantum number in solving the BS equation. The excited state in equation 1 can now be written as

$$|s, K\rangle = \sum_{k_c} A_s(K, k_r) \hat{u}^\dagger(k_r + K) \hat{v}(k_r - K)|\text{GS}\rangle. \tag{9}$$

In addition, it can be easily shown that

$$K^d(k_r, k_r'; K) = K^d(-k_r, -k_r'; K), \tag{10a}$$

$$K^x(k_r, k_r'; K) = K^x(-k_r, -k_r'; K), \tag{10b}$$

$$K^x(k_r, k_r'; K) = K^x(-k_r, -k_r'; K), \tag{10c}$$

which results in the existence of symmetric ($A_1$) and antisymmetric ($A_2$) excitons:5

Symmetric exciton $\rightarrow A_s(K, k_r) = -A_s(K, -k_r),$
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Figure 2: Energy dispersion of $A_1$ singlet and triplet (left panel), $A_2$ singlet (center panel), and $A_2$ triplet (right panel) excitons for $E_{11}$ transition in (7,5) carbon nanotube.

Antisymmetric exciton $\rightarrow A_s(K, k_r) = +A_s(K, -k_r)$.

Figure 2 shows the energy dispersions for singlet and triplet excitons with $A_1$ and $A_2$ symmetry. It should be denoted that singlet and triplet excitons with $A_1$ symmetry are degenerate.

Among the various types of excitons discussed here, only the singlet $A_2$ excitons are bright and the rest are dark excitons. Therefore, from now on, we focus our attention on the $A_2$ singlet excitons (Figure 2 center panel.) Figure 3 shows the real part of the expansion coefficient $A^S(K = 0, k_r)$ in equation 9 for $S = 1$ and $S = 2$. One should notice the resemblance to the simple wave function of a particle in a one-dimensional finite potential.

Figure 3: wave function in $k_r$-space for an $A_2$ singlet exciton in (7,5) exciton with $K = 0$.

3. RESONANCE ENERGY TRANSFER

In this section, first we explain the theory of resonance energy transfer and then introduce the energy transfer rate between two CNTs. The Hamiltonian of two isolated systems is expressed as

$$\hat{H}_1 = \sum_{i_1,j_1} \frac{\hbar^2}{2m} \langle i_1 | r^2 | j_1 \rangle \hat{c}_{i_1}^\dagger \hat{c}_{j_1} + \frac{1}{2} \sum_{i_1,j_1,k_1,l_1} \frac{e^2}{4\pi\epsilon} \langle i_1,j_1 | k_1 \rangle \frac{1}{|r_1 - r_2|} |k_1 l_1\rangle \hat{c}_{i_1}^\dagger \hat{c}_{j_1} \hat{c}_{k_1} \hat{c}_{l_1}, \quad (11a)$$

$$\hat{H}_2 = \sum_{i_2,j_2} \frac{\hbar^2}{2m} \langle i_2 | r^2 | j_2 \rangle \hat{c}_{i_2}^\dagger \hat{c}_{j_2} + \frac{1}{2} \sum_{i_2,j_2,k_2,l_2} \frac{e^2}{4\pi\epsilon} \langle i_2,j_2 | k_2 \rangle \frac{1}{|r_1 - r_2|} |k_2 l_2\rangle \hat{c}_{i_2}^\dagger \hat{c}_{j_2} \hat{c}_{k_2} \hat{c}_{l_2}, \quad (11b)$$

where $i_1, j_1, k_1, l_1$ and $i_2, j_2, k_2, l_2$ indices representing single-electron wave functions from the first and second system, respectively. $\hat{c}_i$ and $\hat{c}_i^\dagger$ are the annihilation and creation operators for the eigen state shown by $i$. $V_1(r)$ and $V_2(r)$ are the potential due to atoms and core electrons of the first and second systems, respectively. The eigen functions of $\hat{H}_1$ and $\hat{H}_2$ are the excitonic states calculated in the previous section. Here, we are interested
in the transition rate between the excited states of the first system, \(|I| = |1^+\rangle \otimes |2^\rangle\), and the excited states of the second system \(|F| = |1^\rangle \otimes |2^*\rangle\) via Coulomb interaction between electrons of the two systems.

The Coulomb interaction Hamiltonian between the electrons of the two systems is

\[
\hat{H}^{(1)} = \frac{e^2}{4\pi\epsilon} \times \frac{1}{2} \sum_{i_1, j_1, i_2, j_2} \langle i_1 j_1 | \frac{1}{|r_1 - r_2|} | i_2 j_2 \rangle \hat{c}^\dagger_{i_1} \hat{c}^\dagger_{j_1} \hat{c}_{i_2} \hat{c}_{j_2} + \text{(other permutations of choosing functions } i, j, k, \text{ and } l \text{ from the two systems)}.
\]  

(12)

We form the matrix elements of the above Hamiltonian between \(|I|\) and \(|F|\) which yields to non-zero results only for

\[
\begin{aligned}
\langle \hat{v}_{k_1} = \hat{c}_l | & \langle \hat{v}_{k_1} = \hat{c}_k | A_s(K_1, k_1) A_s(K_2, k_2) \langle k_{c_1}, k_{c_2} | v(r - r') | k_{v_1}, k_{v_2} \rangle c^*_s(K_1) c^*_s(K_2), \\
\hat{u}_{k_2} = \hat{c}_l | & \langle \hat{u}_{k_2} = \hat{c}_l | A_s(K_1, k_1) A_s(K_2, k_2) \langle k_{c_1}, k_{c_2} | v(r - r') | k_{v_1}, k_{v_2} \rangle c^*_s(K_1) c^*_s(K_2).
\end{aligned}
\]

(13)

The matrix element of the first two choices correspond to the so-called Förster resonance energy transfer in which the donor system radiates a virtual photon which is absorbed by the acceptor system instantaneously (Figure 4, top panel). The second two choices correspond to the so-called Dexter resonance energy transfer, which is an electron exchange process (Figure 4, bottom panel). The Förster process is known to be responsible for the long-range energy transfer due to its Coulomb nature. We neglect the Dexter matrix elements from now on.

The matrix element due to the Förster process is

\[
\mathcal{M}_I = \langle s_1, K_1 | \otimes \langle GS_2 | \hat{H}^{(1)} | GS_1 \rangle \otimes | s_2, K_2 \rangle
\]

\[
= \sum_{k_{c_1}} \sum_{k_{v_1}} A^*_s(K_1, k_1) A_s(K_2, k_2) \langle k_{c_1}, k_{c_2} | v(r - r') | k_{v_1}, k_{v_2} \rangle c^*_s(K_1) c^*_s(K_2),
\]

(14)

(15)

where

\[
k_{c_1} = k_{v_1} + K_1 , \quad k_{c_1} = k_{v_1} - K_1 , \quad k_{c_2} = k_{v_2} + K_2 , \quad k_{v_2} = k_{v_2} - K_2.
\]

Assuming the wall to wall distance of the two CNTs is much larger than the size of atomic orbitals we can use the transition monopole approximation.8,9

After substituting the tight binding wave functions the matrix element for two parallel CNT comes out as

\[
\mathcal{M}_I = \frac{e^2}{4\pi\epsilon} \frac{1}{4\pi^2L \delta(K_1, K_2)} \times C(K_1) \sum_{k_{c_1}} \sum_{k_{v_1}} A^*_s(K_1, k_1) A_s(K_2, k_2) \sum_{s, s'} C^*_s(k_{c_1}) C_{ss'}(k_{v_1}) C_{ss'}(k_{c_2}) C_{ss'}(k_{v_2}),
\]

\[
C(K_1) = \int d\phi \, d\phi' \, K_0 \sqrt{(r_0 \cos \phi - r'_0 \cos \phi')^2 + (D + r_0 \cos \phi - r'_0 \cos \phi')^2}.
\]

(16a)

(16b)
The δ-function in the matrix element enforces the conservation of center-of-mass momentum.

The matrix element for the case of two unparallel CNTs forming an angle θ is

$$\mathcal{M}_f(\theta) = \frac{e^2}{4\pi R L \times L'^2} \times J_\theta(K_1, K_2) \sum_{k_{r_1}} \sum_{k_{r_2}} A^*_s(k_{r_1}) A(k_{r_2}) \sum_{s,s'} C_{cs}(k_{r_1}) C_{cs'}(k_{r_2}) C_{cs'}^*(k_{r_2}) C_{cs}^*(k_{r_1}),$$

(17a)

$$J_\theta(K_1, K_2) = \pi \int d\phi d\phi' \exp \left( 2i \frac{K_1(r'_0 \cos \phi' - r_0 \cos \phi \cos \theta) + K_2(r_0 \cos \phi' - r'_0 \cos \phi' \cos \theta)}{\sin \theta} \right) \times \exp \left( -2 \frac{[D + r'_0 \sin \phi' - r_0 \sin \phi] \sqrt{K_{r_1}^2 + K_{r_2}' - 2K_{r_1}K_{r_2}\cos \theta}}{\sqrt{K_{r_1}^2 + K_{r_2}'^2 - 2K_{r_1}K_{r_2}\cos \theta}} \right).$$

(17b)

Next, we calculate the energy transfer rate in the presence of a strong exciton-phonon interaction. The exciton-phonon scattering rates are of order $10^{14}$ s$^{-1}$, much higher than the rates associated with Coulomb-mediated processes, and are responsible for rapid exciton thermalization. In other words, we can assume that the exciton system in CNT 1 is in thermal equilibrium, with $Z = \text{tr}\{\exp(-\tilde{H}/k_B T)\}$ being the partition function. In this case, the Förster energy transfer rate from the donor CNT 1 to the acceptor CNT 2 is

$$k_{12} = \frac{2\pi}{\hbar} \sum_{s_1,s_2} \sum_{K_1,K_2} \frac{e^{-\Omega_i/k_B T}}{Z} |\mathcal{M}_f|^2 \delta(\Omega_1 - \Omega_2).$$

(18)

Substituting the matrix element for two parallel CNTs we get

$$k_{12} = \frac{2\pi}{\hbar} \left( \sum_{s_i} \int dK_i e^{-\Omega_i/k_B T} \right)^{-1} \sum_{k_{r_1},k_{r_2}} \sum_{s_1,s_2} e^{-\Omega_i/k_B T} |\mathcal{M}_f'|^2 \left( \frac{dK_i}{d\Omega_i} \right).$$

(19)

The primed quantities in the last relations shows the energy and momentum conservation constraints, in the sense that the sum over $K_i$ goes over the points that conserve both energy and momentum in the transition. Figure 5a shows a comparison of the bright exciton dispersion in (7,5) and (8,6) CNTs. The black dots show that the number of points that conserve both momentum and energy are limited, which can lead to energy trapping in low-lying excited states in CNTs with larger band gaps. (Figure 5b) For example according to figure 5c, the exciton transfer rate from (7,5) to (7,5) CNTs is about 4 orders of magnitude larger than the downhill energy transfer between (7,5) to (8,6) energy transfer. The drop in energy transfer rate is due to the momentum conservation. Comparing these transfer rates with the uphill exciton transfer rate from (8,6) to (7,5) CNTs which is less than an order of magnitude smaller than the downhill transfer rates, we conclude that the major drop in the energy transfer rate is the result of the momentum conservation constraint.

Next, we calculate the exciton transfer rate between unparallel CNTs. Substituting the matrix element from Eqs. (17a) we get

$$k_{12} = \frac{2\pi}{\hbar} \frac{1}{2\pi L_c} \sum_{s_1,s_2} \sum_{K_{r_2}} e^{-\Omega_i/k_B T} |\mathcal{M}_f|^2 \left( \frac{dK_2}{d\Omega_i} \right) \Omega_i.$$

(20)

In the last equation, we have taken out the size dependence of the matrix element, $\mathcal{M}_f^+ = \mathcal{M}_f^+ \times L_c$, where $1/L_c$ is the linear density of crossing CNTs. The summation over $K_{r_2}$ only goes over all the final states that conserve the excitation energy.

Our calculation of the orientation dependence of energy transfer rate shows a different result from the point dipole approximation where each CNT is modeled by a single dipole. Figure 6a shows the energy transfer rate from a donor CNT to an array of acceptor CNTs with similar and dissimilar chirality as a function of the angle between the donor and acceptor CNTs, $\theta$. As expected, the energy transfer rate becomes divergent as the acceptor CNT array becomes parallel to the donor CNT. For unparallel orientations, the transfer rates drops by about an order of magnitude when we move to the right angle orientation, however, unlike the point dipole
approximation the energy transfer rate is still appreciable compared to the transfer rate between two parallel CNTs. (Figure 5c) This is mainly due to the large size of CNTs which is comparable to the spacial separation between the systems.\(^9\)

Next, we look at the energy transfer rates between different types of CNTs in unparallel orientations. As we can see in figure 6a, unlike the parallel geometry, the energy transfer rates have the same order of magnitude when energy is transferred between CNTs of similar and dissimilar chirality for large angles. We associate this behavior to the breakdown of momentum conservation rule. Figure 6b shows the angle dependence of the matrix element in equation 17b for different values of initial and final momentum mismatch. We observe that at near parallel orientations the transfer process is dominant by the states that conserve the momentum. However, as the donor and acceptor CNTs rotate towards perpendicular orientation, the energy transfer between the states that do not conserve the momentum become more important. The outcome of this phenomena is the smaller dependence of the energy transfer rate on the chirality of misoriented CNTs than what we obtained for parallel tubes.

### 4. SUMMARY

We have shown the calculation of exciton energy dispersion curves obtained through solving the Bethe-Salpeter equation within the \(GW\) approximation and using the tight-binding wave functions as basis functions. The exciton wave function is formed as a linear combination of free electron and free hole states. We have derived the expressions for the Förster energy transfer rate for parallel donor and acceptor geometries and when they are misoriented by an arbitrary angle. The Coulomb interaction matrix element shows that a the center-of-mass momentum has to be conserved in the parallel-tube geometry. This constraint, along with the energy
conservation rule, limits the transfer rates when the donor and acceptor CNTs have dissimilar chiralities and are parallel. In contrast, scattering processes between two unparallel CNT do not suffer from such limitation and the transfer rate has a much weaker dependence on the CNT chirality (merely due to the differences in the energy band gaps).

ACKNOWLEDGMENTS

This work was primarily funded by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under DOE Award No. DE-SC0008712. Preliminary efforts (prior to the start of DOE funding) were supported as part of the University of Wisconsin MRSEC, IRG2 (NSF Grant No. 1121288).

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