

Simulation of Resonance Energy Transfer in Carbon Nanotube Composites for Photovoltaic Applications

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Abstract—Carbon nanotubes (CNTs) are interesting for use as the light-absorbing material in photovoltaic devices. We study the intertube exciton transfer rates in CNT films. The excitonic states in semiconducting CNTs are calculated by solving the Bethe-Salpeter equation. The resonance energy transfer rates are calculated using Fermi's golden rule. We calculate the exciton transfer rate between two CNTs as a function of their relative angle and also the effect of exciton confinement on the energy transfer rate. Our results show that the exciton confinement decreases the transfer rate between CNTs with similar chiralities. However, the transfer rate between CNTs with dissimilar chiralities increases as a result of exciton confinement.

I. INTRODUCTION

Carbon nanotubes (CNTs) are quasi-one-dimensional materials with a very unique set of optical and electronic properties. Recently, the tunable optical band-gap and high optical absorption of CNTs have drawn the attention of researchers as the light absorbing material in bilayer donor/acceptor heterojunction photovoltaic devices [1], [2]. A schematic of such photovoltaic devices is shown in Figure 1. The electron-hole pairs (excitons) are created by the absorbed photons in the CNT layer, which then diffuses to the CNT/C₆₀ interface. It has been shown that the exciton dissociation at CNT/C₆₀ interface is very efficient [3]. However, the performance of these solar cells is limited by the poor diffusion of excitons in CNT layer. The exciton transport inside a single CNT is shown to be relatively fast, with a diffusion length of about 90 nm [4], [5]. However, exciton transport between two CNTs is hopping in nature and the associated diffusion length is therefore much smaller.

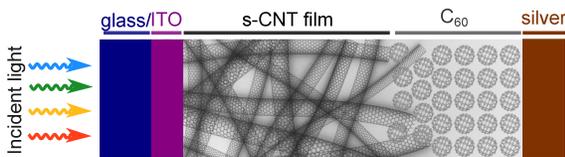


Fig. 1. Schematic of a CNT-based bilayer donor/acceptor heterojunction photovoltaic devices.

Here, we study the intertube exciton transport in CNT films. We calculate the many-body excitonic states in CNTs by solving the Bethe-Salpeter equation in the basis of tight binding wavefunction. By treating the Coulomb interaction between electrons of two CNTs as the perturbation Hamiltonian, we calculate the exciton transfer rate between CNTs via Fermi's golden rule. In a realistic CNT film, the excitons can be confined in quantum wells created by defects or inhomogeneity of the film. In this paper, we look at the effect of the exciton confinement on the exciton transfer rate.

This paper is structured as follows. In section II, we explain the excitonic states in CNTs. In section III, we introduce the formulation for the calculation of the exciton transfer rate. In section IV, we discuss the results of the calculation of the exciton transfer rate for two cases: free and confined excitons.

II. EXCITONS IN CARBON NANOTUBES

The photo-induced electronic transition energies in CNTs are known to differ significantly from those predicted by a simple tight-binding models [6]. It is shown experimentally that the photogenerated electrons and holes in CNTs form neutrally charged bound states, known as excitons [7], [8]. According to the Tamm-Dancoff approximation, these many-body states can be described by a linear expansion in the basis of the free-electron and free-hole states

$$|s\rangle = \sum_{\mathbf{k}_c, \mathbf{k}_v} A_s(\mathbf{k}_c, \mathbf{k}_v) \hat{u}^\dagger(\mathbf{k}_c) \hat{v}(\mathbf{k}_v) |GS\rangle. \quad (1)$$

Here, $\hat{u}^\dagger(\mathbf{k}_c)$ is the creation operator of an electron in the conduction band with wave vector \mathbf{k}_c , and $\hat{v}(\mathbf{k}_v)$ is the annihilation operator of an electron from the valence band with wave vector \mathbf{k}_v . $|GS\rangle$ is the system ground state. s is a quantum number analogous to the principal quantum number in a hydrogen atom. $A_s(\mathbf{k}_c, \mathbf{k}_v)$ is the expansion coefficient which is calculated by solving the Bethe-Salpeter equation (BSE) [9], [10]

$$[E_c(\mathbf{k}_c) - E_v(\mathbf{k}_v)] A_s(\mathbf{k}_c, \mathbf{k}_v) + \sum_{\mathbf{k}'_c, \mathbf{k}'_v} \mathcal{K}(\mathbf{k}_c, \mathbf{k}_v; \mathbf{k}'_c, \mathbf{k}'_v) A_s(\mathbf{k}'_c, \mathbf{k}'_v) = \Omega_s A_s(\mathbf{k}_c, \mathbf{k}_v), \quad (2)$$

where $E_c(\mathbf{k}_c)$ and $E_v(\mathbf{k}_v)$ are the quasiparticle energies of electrons with wave vectors \mathbf{k}_c and \mathbf{k}_v in the conduction and

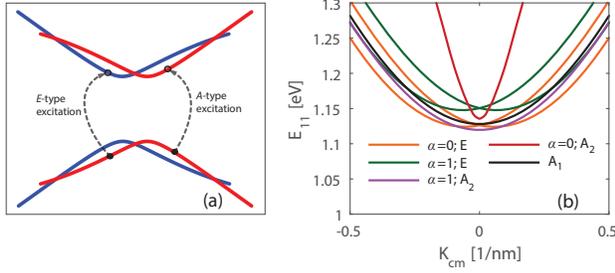


Fig. 2. (a) Schematic of valley degeneracy in the CNT band structure. (b) Energy dispersion for different types of excitons in a (7,5) CNT.

valence bands, respectively. Ω_s is the exciton energy. \mathcal{K} is the interaction kernel that describes the electron-electron interaction. We use the tight binding states as the basis to calculate the interaction kernel. The tight binding wavefunction for CNT is

$$\psi_{ak}(r) = \frac{1}{\sqrt{N_u}} \sum_b \sum_u C_{ab}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}_{ub}} \phi(\mathbf{r} - \mathbf{R}_{ub}), \quad (3)$$

where u runs over all the N_u graphene unit cells, $b = A, B$ runs over all the basis atoms in graphene unit cell, and a is the band index.

The band structure of CNTs has two degenerate valleys (Figure 2a). In an exciton, the electron and hole can belong to the same valley (A -type excitation) or different valleys (E -type excitation). It is shown that A -type excitons are optically active [9]. Furthermore, A -type excitons are divided into symmetric excitons (A_1) and antisymmetric excitons (A_2) under C_2 rotation around the axis perpendicular to the nanotube axis. Based on group symmetry consideration, A_2 excitons are optically active and A_1 excitons are inactive. Figure 2b shows the energy dispersion of excitonic states in a (7,5) CNT. α is the exciton total spin. Also, the singlet excitons ($\alpha = 0$) are optically active and triplet excitons ($\alpha = 1$) are optically inactive.

III. RESONANCE ENERGY TRANSFER IN CARBON NANOTUBES

When the exciton is transferred from a donor CNT (system 1) to an acceptor CNT (system 2), the system transitions between the following states

$$|I\rangle = |1^*\rangle \otimes |2\rangle \rightarrow |F\rangle = |1\rangle \otimes |2^*\rangle. \quad (4)$$

Here, the (un)starred states represent the (ground) excited state of the systems. This process happens through a direct or exchange Coulomb interaction between electrons of the donor and acceptor CNTs. Figure 3 shows a schematic of the exciton transfer process. Here, we only consider the direct exciton transfer process as the wall-to-wall distance between donor and acceptor CNTs are large compared to atomic orbitals and exchange interaction is negligible [11].

The direct interaction matrix element can be written

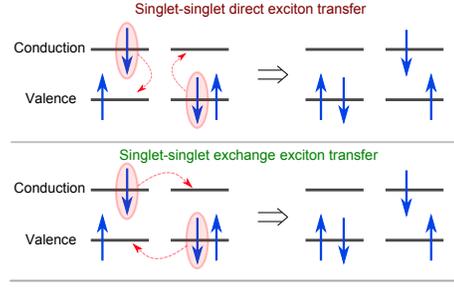


Fig. 3. Direct and exchange interaction between donor and acceptor systems.

$$\begin{aligned} \mathcal{M}_d &= \langle s_1, \mathbf{K}_1; \text{GS}_2 | v(\mathbf{r} - \mathbf{r}') | \text{GS}_1; s_2, \mathbf{K}_2 \rangle \\ &= \frac{1}{\sqrt{N_{u_1} N_{u_2}}} J_\theta(\mathbf{K}_1, \mathbf{K}_2) \times Q_{s_1, s_2}(\mathbf{K}_1, \mathbf{K}_2) \end{aligned} \quad (5)$$

J_θ is the geometric part of the matrix element

$$J_\theta(\mathbf{K}_1, \mathbf{K}_2) = \sum_{u, u'} e^{i(-2\mathbf{K}_1 \cdot \mathbf{R}_u + 2\mathbf{K}_2 \cdot \mathbf{R}_{u'})} \frac{1}{|\mathbf{R}_u - \mathbf{R}_{u'}|}, \quad (6)$$

which changes with the relative orientation of donor and acceptor CNT and the confinement of excitons. Q_{s_1, s_2} is the k -space part of matrix element

$$\begin{aligned} Q_{s_1, s_2}(\mathbf{K}_1, \mathbf{K}_2) &= \frac{e^2}{4\pi\epsilon\sqrt{N_{u_1} N_{u_2}}} \sum_{\mathbf{k}_{r_1}} \sum_{\mathbf{k}_{r_2}} A_{s_1}^*(\mathbf{K}_1, \mathbf{k}_{r_1}) A_{s_2}(\mathbf{K}_2, \mathbf{k}_{r_2}) \\ &\quad \times \sum_{b, b'} C_{cb}^*(\mathbf{k}_{c_1}) C_{vb}(\mathbf{k}_{v_1}) C_{cb'}(\mathbf{k}_{c_2}) C_{vb'}^*(\mathbf{k}_{v_2}) \\ &\quad \times e^{i(-2\mathbf{K}_1 \cdot \mathbf{d}_b + 2\mathbf{K}_2 \cdot \mathbf{d}_{b'})}. \end{aligned} \quad (7)$$

\mathbf{d}_b is the relative coordinate of basis atom b from the center of unit cell. \mathbf{K} is the exciton center-of-mass wave vector and \mathbf{k}_r is the relative wave vector of electron and hole

$$\mathbf{K} = \frac{\mathbf{k}_c - \mathbf{k}_v}{2}, \quad \mathbf{k}_r = \frac{\mathbf{k}_c + \mathbf{k}_v}{2}. \quad (8)$$

The exciton transfer rate is calculated as

$$\kappa_{12} = \frac{2\pi}{\hbar} \sum_{s_1, s_2} \sum_{\mathbf{K}_1, \mathbf{K}_2} \frac{e^{-\beta\Omega_{s_1}}}{\mathcal{Z}} |\mathcal{M}_d|^2 \delta(\Omega_{s_1} - \Omega_{s_2}), \quad (9)$$

where \mathcal{Z} is the partition function.

IV. RESULTS AND DISCUSSION

In this section, we show the result of exciton transfer rate calculation between (7,5) and (8,7) semiconducting CNTs.

Figure 4a shows the exciton transfer rate between two CNTs with similar chiralities as a function of the relative angle between donor and acceptor CNTs. When the exciton is free along the CNTs axes, we observe an ultrafast exciton transfer between parallel (bundled) CNTs. However, as the CNTs rotate to a more perpendicular orientation, the transfer rate drops by more than an order of magnitude. Exciton

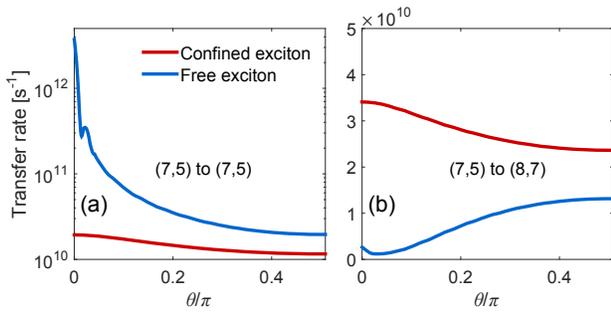


Fig. 4. (a) Transfer rate from a donor (7,5) CNT to an acceptor (7,5) CNT. (b) Transfer rate from a donor (7,5) CNT to an acceptor (8,7) CNT. Length of the one-dimensional quantum well in the confined case is 10 nm

confinement in quantum wells, introduced by defects or inhomogeneities in the CNT film, reduces the exciton transfer rate between bundled CNTs by about two orders of magnitude. The confinement effect is less pronounced as we move towards perpendicular geometry.

On the contrary, the free exciton transfer process between CNTs with different chiralities is relatively slow when the CNTs are parallel (Figure 4b). As the CNTs rotate towards a perpendicular geometry the exciton transfer rate increases by about one order of magnitude. The exciton transfer rate between bundled CNTs increases by introducing exciton confinement. The effect of confinement is less important as we move towards perpendicular orientation.

The pronounced effect of confinement on the exciton transfer rate between bundled CNTs is explained by looking at the geometric part of the matrix element (Figure 5). When the excitons are free and the CNTs are parallel to each other, the geometric matrix element is diagonal, which means the transition happens through the states that conserve both momentum and energy (Figure 5, left bottom). The number of excitonic states in donor and acceptor CNTs that obey these selection rules are limited when the CNT have dissimilar chiralities, resulting in a slow exciton transfer process. However, the numbers of contributing states are considerably higher when both donor and acceptor CNTs have similar chiralities, which yields a fast exciton transfer rate [12].

When the excitons are confined or the donor and acceptor rotate towards a perpendicular orientation, the off-diagonal elements increase and the diagonal elements decrease (Figure 5, bottom right and top left). Therefore, the number of contributing states to the transfer process increases. In the cases of CNTs with dissimilar chirality, this leads to an increase in the exciton transfer rate. However, when the CNTs have similar chiralities, the drop in diagonal elements decreases the total exciton transfer rate.

V. CONCLUSION

In summary, we calculated the manifold of excitonic states in CNTs by solving the BSE. We introduced a formula for calculating the exciton transfer rates between CNTs in the basis of

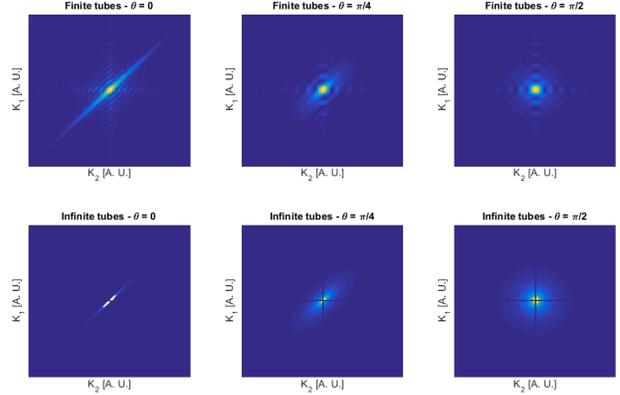


Fig. 5. Geometric part of the matrix element (Equation 6) for confined (top) and free (bottom) excitons as a function of the initial and final center-of-mass wave vector magnitudes.

single-particle tight binding wavefunctions. We show that the free exciton transfer rate between bundled CNTs is ultrafast when the donor and acceptor CNTs have similar chiralities. However, the transfer rate is three orders of magnitude slower when the donor and acceptor tubes have different chiralities. As a result of exciton confinement, the exciton transfer rate decreases (increases) when the CNTs have similar (dissimilar) chiralities.

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REFERENCES

- [1] R. M. Jain, R. Howden, K. Tvrđy, S. Shimizu, A. J. Hilmer, T. P. McNicholas, K. K. Gleason, and M. S. Strano, "Polymer-free near-infrared photovoltaics with single chirality (6,5) semiconducting carbon nanotube active layers," *Adv. Mater.*, vol. 24, p. 4436, 2012.
- [2] D. J. Bindl, A. S. Brewer, and M. S. Arnold, "Semiconducting carbon nanotube/fullerene blended heterojunctions for photovoltaic near-infrared photon harvesting," *Nano Res.*, vol. 4, p. 1174, 2011.
- [3] D. J. Bindl, M.-Y. Wu, F. C. Prehn, and M. S. Arnold, "Efficiently harvesting excitons from electronic type-controlled semiconducting carbon nanotube films," *Nano Lett.*, vol. 11, p. 455, 2011.
- [4] L. Cognet, D. A. Tsybouski, J. R. Rocha, S. D. Doyle, J. M. Tour, and R. B. Weisman, "Stepwise quenching of exciton fluorescence in carbon nanotubes by single-molecule reactions," *Science*, vol. 316, p. 1465, 2007.
- [5] L. Lüer, S. Hoseinkhani, D. Polli, J. Crochet, and T. Hertel, "Size and mobility of excitons in (6,5) carbon nanotubes," *Nature Phys.*, vol. 5, p. 54, 2009.
- [6] R. B. Weisman and S. M. Bachilo, "Dependence of optical transition energies on structure for single-walled carbon nanotubes in aqueous suspension: An empirical katura plot," *Nano Lett.*, vol. 3, p. 1235, 2003.
- [7] F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, "The optical resonances in carbon nanotubes arise from excitons," *Science*, vol. 308, p. 838, 2005.
- [8] J. Maultzsch, R. Pomraenke, S. Reich, E. Chang, D. Prezzi, A. Ruini, E. Molinari, M. S. Strano, C. Thomsen, and C. Lienau, "Exciton binding energies in carbon nanotubes from two-photon photoluminescence," *Phys. Rev. B*, vol. 72, p. 241402(R), 2006.

- [9] J. Jiang, R. Saito, G. G. Samsonidze, A. Jorio, S. G. Chou, G. Dresselhaus, , and M. S. Dresselhaus, "Chirality dependence of exciton effects in single-wall carbon nanotubes: Tight-binding model," *Phys. Rev. B*, vol. 75, p. 035407, 2007.
- [10] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, "Excitonic effects and optical spectra of single-walled carbon nanotubes," *Phys. Rev. Lett.*, vol. 92, p. 077402, 2004.
- [11] V. May and O. Kühn, *Charge and energy transfer dynamics in molecular systems*. John Wiley & Sons, 2008.
- [12] A. Davoody and I. Knezevic, "Study of the förster resonance energy transfer in composite films of carbon nanotubes;" in *SPIE OPTO*. International Society for Optics and Photonics, 2015, pp. 93580T–93580T.