Theory and *Ab Initio* Calculation of Radiative Lifetime of Excitons in Semiconducting Carbon Nanotubes

Catalin D. Spataru,[1,2] Sohrab Ismail-Beigi,[3] Rodrigo B. Capaz,[1,2,4] and Steven G. Louie[1,2]
[1]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*Department of Applied Physics, Yale University, New Haven, Connecticut 06520, USA*
[4]*Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, Rio de Janeiro, RJ 21941-972, Brazil*
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We present a theoretical analysis and first-principles calculation of the radiative lifetime of excitons in semiconducting carbon nanotubes. An intrinsic lifetime of the order of 10 ps is computed for the lowest optically active bright excitons. The intrinsic lifetime is, however, a rapid increasing function of the exciton momentum. Moreover, the electronic structure of the nanotubes dictates the existence of dark excitons near in energy to each bright exciton. Both effects strongly influence measured lifetime. Assuming a thermal occupation of bright and dark exciton bands, we find an effective lifetime of the order of 10 ns at room temperature, in good accord with recent experiments.

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Single-walled carbon nanotubes (SWCNT) possess highly unusual mechanical, thermal, electronic, and optical properties, making them objects of great interest for basic scientific studies as well as potential applications [1]. Their optical properties have been studied intensively in the past, but most of the optical measurements were performed on aggregated samples containing bundles of SWCNTs [2,3], resulting in measured spectra broadened or even washed out by environmental interaction effects and preventing a detailed spectral analysis. Recently, fabrication of well-separated SWCNTs [4,5] allowed for much better resolved optical absorption spectra. More importantly, fluorescence was detected from individual semiconducting SWCNTs. Combining resonant fluorescence and Raman spectroscopy, it became possible to assign optical transitions to specific (n, m) semiconducting SWCNTs [6,7].

While first-principles calculations [8–10] have explicitly predicted huge exciton binding energies (of the order of 1 eV) for semiconducting tubes with prominent features in their optical spectra excitonic in nature, and there have been also several model studies [11–13], most experimental data have been interpreted by assuming one-electron interband transitions. Thus, any information on the photoexcited states of SWCNTs is very valuable. In particular, knowledge of the radiative lifetime would be helpful in understanding the nature of the excitations and essential for potential applications in photonics and optoelectronics.

Recent time-resolved flourescence experiments reported a radiative lifetime of excited nanotubes ranging from 10 [14] to 100 ns [15]. The variation in the measured radiative lifetime is probably due to uncertainty in the quantum efficiency of fluorescence of the semiconducting SWCNTs that contribute to the fluorescence signal.

In this work, we carry out *ab initio* calculations of the radiative lifetime of the lowest electronic excitations in several semiconducting SWCNTs. The electronic excited states are found by solving the Bethe-Salpeter equation, including band-structure, self-energy, and electron-hole interaction effects [8,9,16,17]. Solution of the Bethe-Salpeter equation provides the excitation energies and quantum amplitudes (or wave functions) for excitons. Specifically, for an excited state with center of mass momentum $\hbar\vec{Q}$ labeled by index S, we have the excitation energy $\hbar\Omega_S(\vec{Q})$ and the amplitude

$$\chi(\vec{r}_e, \vec{r}_h) = \langle G|\Psi(\vec{r}_h)^\dagger \Psi(\vec{r}_e)|S(\vec{Q})\rangle. \tag{1}$$

Here, $\Psi(\vec{r})^\dagger$ and $\Psi(\vec{r})$ are the creation and annihilation field operators that create or destroy an electron at position $\vec{r}$. The square amplitude $|\chi(\vec{r}_e, \vec{r}_h)|^2$ is the probability density of finding the electron at $\vec{r}_e$ and hole at $\vec{r}_h$. Within the Tamm-Damcoff approximation [18], the amplitude takes the form of a coherent superposition of electron-hole pairs,

$$\chi(\vec{r}_e, \vec{r}_h) = \sum_{vc\vec{k}} A^{S(Q)}_{vc\vec{k}} \psi_{c\vec{k}+\vec{Q}}(\vec{r}_e)\psi_{v\vec{k}}(\vec{r}_h)^*. \tag{2}$$

Here, $\psi_{n\vec{k}}(\vec{r})$ are Bloch states with wave vector $\vec{k}$, and c and v label the conduction (electron) and valence (hole) bands. The coefficients $A^{S(Q)}_{vc\vec{k}}$, which describe the weight of electron-hole pairs in the coherent superposition, are obtained from the Bethe-Salpeter equation along with the excitation energy $\hbar\Omega_S(\vec{Q})$.

The radiative lifetime is calculated using Fermi's golden rule. We start with the usual Hamiltonian describing the interaction between electrons and photons,

$$H^{\text{int}} = -\frac{e}{mc}\int d\vec{r}\Psi(\vec{r})^\dagger \vec{A}(\vec{r})\cdot\vec{p}\Psi(\vec{r}), \tag{3}$$

where $\vec{p} = -i\hbar\vec{\nabla}$ and $\vec{A}(\vec{r})$ is the vector potential for the electromagnetic field in the Coulomb gauge. We decompose $\vec{A}(\vec{r})$ into plane wave modes [19]:

$$\vec{A}(\vec{r}) = \sum_{\vec{q}\lambda} \sqrt{\frac{2\pi\hbar c}{Vq}}\, \vec{\epsilon}_{\vec{q}\lambda} [a^{\dagger}_{\vec{q}\lambda} e^{-i\vec{q}\cdot\vec{r}} + \text{H.c.}], \tag{4}$$

with $a^{\dagger}_{\vec{q}\lambda}$ ($a_{\vec{q}\lambda}$) being the creation (annihilation) operators of photons with polarization vector $\vec{\epsilon}_{\vec{q}\lambda}$. The radiative decay rate for a system in an initial state with one exciton and no photon $|S(\vec{Q}), 0\rangle$ to the electronic ground state is given by

$$\gamma(\vec{Q}) = \frac{2\pi}{\hbar} \sum_{\vec{q}\lambda} |\langle G, 1_{\vec{q}\lambda} | H^{\text{int}} | S(\vec{Q}), 0\rangle|^2 \delta(\hbar\Omega(\vec{Q}) - \hbar c q). \tag{5}$$

with

$$\langle G, 1_{\vec{q}\lambda} | H^{\text{int}} | S(\vec{Q}), 0\rangle = -\frac{e}{mc} \sqrt{\frac{2\pi\hbar c}{Vq}} \vec{\epsilon}_{\vec{q}\lambda} \cdot \sum_{vc\vec{k}} A^{S(Q)}_{vc\vec{k}} \langle v\vec{k} | e^{-i\vec{q}\cdot\vec{r}} \vec{p} | c\vec{k} + \vec{Q}\rangle. \tag{6}$$

In a quasi-1D system like a SWCNT, momentum conservation requires the photon momentum along the tube axis $\hat{z}$ to equal the exciton momentum $\vec{Q} = Q\hat{z}$. And for optical photon energies, we may use the dipole approximation

$$\langle v\vec{k} | e^{-i\vec{q}\cdot\vec{r}} \vec{p} | c\vec{k} + \vec{Q}\rangle \approx \langle v\vec{k} | \vec{p} | c\vec{k}\rangle \delta_{q_z, Q}. \tag{7}$$

Moreover, SWCNTs have a negligible optical response for electric fields polarized perpendicular to the tube axis, due to the ''depolarization effect'' [20]. Thus,

$$\vec{\epsilon}_{\vec{q}\lambda} \cdot \langle G | \vec{p} | S(0)\rangle \approx \vec{\epsilon}_{\vec{q}\lambda} \cdot \hat{z} \langle G | p_z | S(0)\rangle, \tag{8}$$

where we have made use of the shorthand definition

$$\langle G | \vec{p} | S(0)\rangle = \sum_{vc\vec{k}} A^{S(0)}_{vc\vec{k}} \langle v\vec{k} | \vec{p} | c\vec{k}\rangle. \tag{9}$$

Summing over two arbitrary orthogonal polarizations of the electric field, and increasing the volume $V = L_x L_y L_z$ to ∞, the decay rate becomes

$$\gamma(Q) = \lim_{L_z\to\infty} \frac{|\langle G | p_z | S(0)\rangle|^2}{L_z} \frac{e^2}{m^2 c^2 \hbar} \times \int_{-\infty}^{\infty} dq_x \int_{-\infty}^{\infty} dq_y \left[\frac{q_x^2 + q_y^2}{(q_x^2 + q_y^2 + Q^2)^{3/2}}\right] \times \delta\left(\frac{\Omega(Q)}{c} - \sqrt{q_x^2 + q_y^2 + Q^2}\right). \tag{10}$$

In our calculations, finite sampling of N k points for the above equations is equivalent to having a supercell along the tube axis with $L_z = Na$, where a is the physical unit cell size along the tube axis. Using the relation of momentum and velocity, $p_z = m v_z = m \frac{i}{\hbar}[H, z]$,

$$\lim_{L_z\to\infty} \frac{|\langle G | p_z | S(0)\rangle|^2}{L_z} = m^2 \Omega(0)^2 \lim_{N\to\infty} \frac{|\langle G | z | S(0)\rangle|^2}{Na} \equiv m^2 \Omega(0)^2 \frac{\mu_a^2}{a}, \tag{11}$$

where μ_a^2/a is the squared exciton transition dipole matrix element per unit tube length. Performing the integral in Eq. (10), the decay rate can finally be written as

$$\gamma(Q) = \begin{cases} \frac{2\pi e^2 \Omega(0)^2}{\hbar c^2} \frac{\mu_a^2}{a} \frac{\Omega^2(Q) - c^2 Q^2}{\Omega^2(Q)} & \text{if } |Q| \le Q_0 \\ 0 & \text{if } |Q| \ge Q_0 \end{cases}, \tag{12}$$

where Q_0 is defined by the condition $\hbar\Omega(Q_0) = \hbar c Q_0$ and is the maximum momentum a decaying exciton can have. The decay of excitons with momentum $Q > Q_0$ is forbidden by momentum conservation: such a decay would have the photon momentum along $\hat{z}$ be smaller than the exciton momentum. For optical exciton energies where the photon momentum is small compared to the scale of Brillouin zone, $Q_0 \approx \frac{\Omega(0)}{c}$. Thus the intrinsic radiative lifetime τ of an exciton is shortest for an exciton with $Q = 0$ and increases as a function of momentum until it becomes infinite for $Q = Q_0$ [21].

The above expression for the radiative decay rate of a zero-momentum exciton in a SWCNT, $\gamma(0) = 2\pi e^2 \Omega(0)^2/\hbar c^2 (\mu_a^2/a)$, may be compared to that of a molecule of size l, $\gamma = 4e^2\Omega^3/3\hbar c^3 (\mu^2)$. Assuming similar excitation energies $\hbar\Omega(0) \sim \hbar\Omega$ and squared dipole moments per unit length $\mu_a^2/a \sim \mu^2/l$ for excitons in SWCNT and molecule, comparison of the two expressions indicates that $\gamma(0)$ is enhanced with respect to γ by a factor $\frac{\lambda}{l}$. Thus we expect the intrinsic radiative lifetime of zero-momentum excitons in a SWCNT to be about 3 orders of magnitude shorter than the radiative lifetime of excitons in small molecules, which is typically on the order of a few ns. Table I shows our *ab initio* results for μ_a^2/a and the intrinsic radiative lifetime of the lowest bright exciton $\tau(0)$ for the four semiconducting SWCNTs we considered: (7, 0), (8, 0), (10, 0), and (11, 0). While μ_a^2/a is indeed of the order of a few a.u., $\tau(0)$ is much shorter than the typical radiative lifetime in small molecules. We find $\tau(0)$ between 8 and 19 ps for zigzag tubes with diameters between 5.5 and 8.7 Å. We see well-defined diameter and chirality trends in the results of Table I: for any given ν family of tubes [where $\nu = (n - m) \bmod 3$], $\tau(0)$ increases with diameter and shows a ν-family oscillation. Such oscillations usually reveal chirality dependences in the form of $(-1)^{\nu} \cos(3\theta)$ [22], where θ is the chiral angle.

Because the intrinsic radiative lifetime of bright excitons ranges from ~10 ps to ∞ depending on their momentum

TABLE I. The squared dipole matrix element per unit length, excitation energy, and intrinsic radiative lifetime of the lowest bright exciton ($Q = 0$) for several zigzag SWCNTs.

SWCNTs	μ_a^2/a (a.u.)	$\hbar\Omega(0)$ (eV)	$\tau(0)$ (ps)
(7, 0)	2.8	1.20	12.8
(8, 0)	2.8	1.55	8.1
(10, 0)	2.8	1.00	19.1
(11, 0)	2.5	1.21	14.3

Q, we use an exciton distribution function to estimate an effective radiative lifetime $\tau^b_{\rm eff}$. Experimentally, $\tau_{\rm eff}$ has been deduced from time-resolved fluorescence data taken over a time range of several tens of ps [14,15]. We assume that much more rapid relaxation processes exist in SWCNTs and make the excitons assume a thermal (Boltzman) distribution. We employ an effective mass approximation for the exciton energy dispersion: $\hbar\Omega(Q) = \hbar\Omega(0) + \hbar^2Q^2/2M$, with $M = m^*_e + m^*_h$ being simply the sum of the effective electron and hole masses of the conduction and valence bands which comprise the exciton. The effective masses m^*_e and m^*_h are taken from density functional theory (DFT) band-structure calculations. We are thus neglecting two different effects which tend to cancel each other: the quasiparticle self-energy effects which would give electron and hole masses smaller than the values predicted by DFT (over the range in k space for states forming the excitons), and the electron-hole interaction effects which would give an exciton mass larger than the sum of the electron and hole masses [23,24]. With these assumptions, the effective decay rate of bright excitons $\gamma^b_{\rm eff}$ can be estimated by performing a simple statistical average [25]:

$$\gamma^b_{\rm eff} = \gamma(0)\frac{\int_0^\Delta dE\,\frac{1}{\sqrt{E}}e^{-(E/k_BT)}\{[\hbar\Omega(0)+E]^2 - 2Mc^2E\}/[\hbar\Omega(0)+E]^2}{\int_0^\infty dE\,\frac{1}{\sqrt{E}}e^{-(E/k_BT)}} \tag{13}$$

where $E = \hbar^2Q^2/2M$ is the energy of an exciton measured from the bottom of the exciton band and Δ is the maximum energy E that a radiatively decaying exciton can have. Given the smallness of the photon momentum, one has $\Delta = \hbar^2Q_0^2/2M \approx \hbar^2\Omega^2(0)/2Mc^2 \ll k_BT$. Evaluation of Eq. (13) at finite temperature gives

$$\gamma^b_{\rm eff} \approx \frac{4}{3}\frac{1}{\sqrt{\pi}}\sqrt{\frac{\Delta}{k_BT}}\gamma(0). \tag{14}$$

Thus, the effective radiative lifetime $\tau^b_{\rm eff}$ gets enhanced with respect to the intrinsic radiative lifetime of a bright exciton $\tau(0)$ by a factor of approximately $\sqrt{\frac{k_BT}{\Delta}}$. At room temperature this factor is ≈ 100, reflecting the fact that $\Delta \ll k_BT$: only a small fraction of thermalized excitons are in the allowed radiative region. In Table II we present our *ab initio* results for the effective mass M and the effective radiative lifetime $\tau^b_{\rm eff}$ of the lowest bright exciton at $T = 300$ K for four semiconducting SWCNTs considering only the intra-exciton-band distribution effect. At this level of analysis we see that $\tau^b_{\rm eff}$ is of the order of about 1 ns at room temperature for the SWCNTs we studied, with larger values for the larger diameters.

Until now we considered only bright excitons when evaluating the effective radiative lifetime. However, a more accurate description of $\tau_{\rm eff}$ should take into account the complete electronic structure of the lowest energy complex of spin-singlet excitonic states, which includes dark states as well [8,9,13]. Figure 1 shows our calculated electronic structure of the lowest excitonic states in the $(10, 0)$ tube [a similar picture holds for $(11, 0)$] [26]. The states are labeled according to the irreducible representation of the symmetry group to which they belong [27]. We see that the lowest singlet exciton (${}_0B_0^-$) is actually a dark one, followed by a bright (${}_0A_0^-$) and then two other (${}_0E_6^-$) degenerate dark excitons. The key observation is that both the optical transition matrix element and the exciton exchange energy depend on the exciton amplitude $\chi(\vec{r},\vec{r})$ evaluated for electron and hole at the same position. Excitons of ${}_0B_0^-$ are odd under σ_v (vertical planes) reflections and therefore have $\chi(\vec{r},\vec{r}) = 0$ on these planes [28]. These nodes and concomitant oscillations in sign of χ lead to a vanishingly small exchange energy. Figure 1 shows that the exchange interaction shifts up all other singlet excitons states with respect to their triplet counterparts and the ${}_0B_0^-$ then becomes the lowest singlet state. A similar analysis can be made for chiral tubes. In fact, our *ab initio* results, in combination with a symmetry analysis based on group theory, show, in general, that the lowest exciton state is dark for any zigzag and chiral semiconducting SWCNT [28]. Therefore, optical darkness and small exchange energies have the same physical origin, a

TABLE II. The exciton mass, effective lifetime at room temperature neglecting dark excitons $\tau^b_{\rm eff}$, dark-bright exciton splitting parameters δ_1 and δ_2, and the effective radiative lifetime at room temperature including dark excitons $\tau_{\rm eff}$ [26]. (See text.)

SWCNTs	M(m_e)	$\tau^b_{\rm eff}$ (ns)	δ_1 (meV)	δ_2 (meV)	$\tau_{\rm eff}$ (ns)
(7, 0)	0.21	1.1	···	···	···
(8, 0)	0.71	1.0	···	···	···
(10, 0)	0.19	1.8	29	33	10.4
(11, 0)	0.44	1.7	29	44	8.8

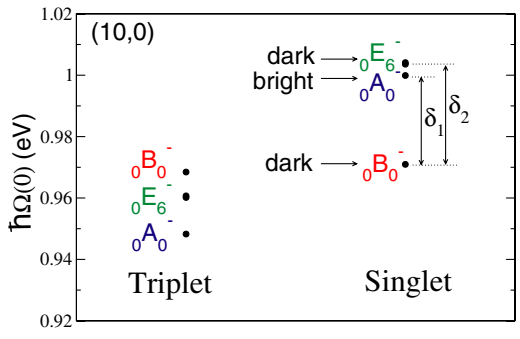

FIG. 1 (color online). Excitation energies of the lowest spin-triplet and spin-singlet excitons with zero momentum for the $(10, 0)$ SWCNT.

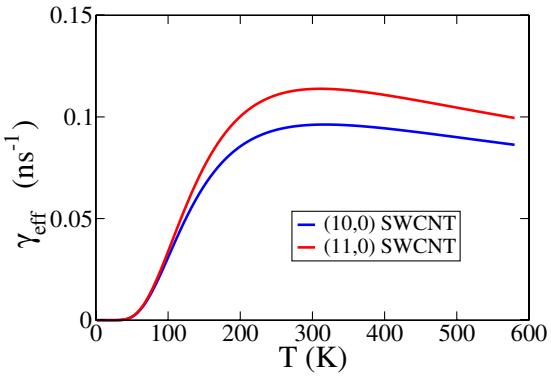

FIG. 2 (color online). Temperature dependence of the inverse effective radiative lifetime γ_{eff} for the excited nanotubes $(10, 0)$ and $(11, 0)$, taking into account thermal occupation of dark and bright exciton states.

fundamental result for the understanding of the low efficiency of light emission in SWCNTs.

Now, let us assume that there is perfect thermalization between dark and bright excitonic bands, given the fact that their energy separation is $\sim k_B T$ at room temperature. Then, it is easy to see that the statistical average will result in an effective radiative decay rate γ_{eff}:

$$\gamma_{\text{eff}} = \frac{e^{-\delta_1/k_B T}}{1 + e^{-\delta_1/k_B T} + 2e^{-\delta 2/k_B T}} \gamma^b_{\text{eff}}, \qquad (15)$$

where the parameters δ_1 and δ_2 are defined in Fig. 1. The dark excitons further enhance the effective radiative lifetime of excited SWCNTs. Our *ab initio* results for δ_1, δ_2, and τ_{eff} in the $(10, 0)$ and $(11, 0)$ tubes, shown in Table II, indicate that this enhancement factor is ~ 5 at room temperature, bringing the effective radiative lifetime to an order of magnitude of ~ 10 ns, in good agreement with experimental results. The overall temperature dependence of the effective radiative lifetime within this framework is illustrated in Fig. 2.

In summary, we have presented a theory and calculation, based on *ab initio* results, of the intrinsic radiative lifetime of bright excitons in several semiconducting single-walled carbon nanotubes. Taking account of dark excitons and assuming fast thermalization processes among both bright and dark excitons, our results provide an explanation for the effective radiative lifetime of excited nanotubes measured at room temperature.

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