

Scaling of Excitons in Carbon Nanotubes

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Light emission from carbon nanotubes is expected to be dominated by excitonic recombination. Here we calculate the properties of excitons in nanotubes embedded in a dielectric, for a wide range of tube radii and dielectric environments. We find that simple scaling relationships give a good description of the binding energy, exciton size, and oscillator strength.

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The optical properties of carbon nanotubes have received increasing experimental and theoretical attention. Optical absorption and emission spectra of carbon nanotubes have been studied by a number of groups [1–6], and electro-optical devices have already appeared [7,8]. Initial attempts to explain the experimental observations naturally took independent-electron theory as their starting point. However, theoretically it is now clear that emission is dominated by excitonic recombination [9–12].

A number of theoretical approaches have been used to describe these excitons. One approach involves variational calculations [10,11]. While valuable, these have been limited to an effective-mass approximation and do not address issues of spectral weight. The most accurate description is provided by an *ab initio* solution of the Bethe-Salpeter equation (BSE) using *GW*-corrected quasiparticle energies [12]. However, it is not currently feasible to apply this computationally intensive approach to a wide range of nanotube sizes or environments.

Here we use an intermediate level of theory to provide a broad overview of the exciton properties. We calculate the excitonic properties of nanotubes embedded in dielectric media for the range of tube radii and dielectric constants most relevant to potential applications. We find that the exciton size, binding energy, and oscillator strength all exhibit robust (though approximate) scaling relationships. The relationships obtained for the excitonic properties can be used to better understand and optimize the operation of nanotube optoelectronic devices.

The proper procedure for the calculation of excitons has been described in detail in Ref. [13]. It involves solving the Bethe-Salpeter equation,

$$\Delta_k A_k^S + \sum_{k'} \mathcal{K}_{k,k'} A_{k'}^S = \Omega_S A_k^S, \quad (1)$$

where the kernel $\mathcal{K}_{k,k'}$ describes the interaction between all possible electron-hole pairs of total momentum q_{exc} , and Δ_k is the quasiparticle energy for a noninteracting electron and hole with wave vector k and $q_{\text{exc}} - k$. The exciton momentum q_{exc} is equal to that of the exciting photon, and is hereafter approximated by $q_{\text{exc}} = 0$. We approximate the quasiparticle energies by eigenvalues of

the tight-binding Hamiltonian [14,15] ($t = 3.0$ eV), with any additional self-energy corrections restricted to the so-called “scissors operator,” in which the self-energy is approximated by a rigid shift of the conduction band relative to the valence band. Since the quasiparticle band structures are not well known for nanotubes of varying diameters and embedding media, we report only properties that are not affected by the magnitude of this shift.

For the optically active singlet excitons, the interaction has two contributions, direct (\mathcal{K}^d) and exchange (\mathcal{K}^x):

$$\mathcal{K}_{k,k'} = \mathcal{K}_{k,k'}^d + 2\mathcal{K}_{k,k'}^x, \quad (2)$$

where the direct (exchange) term is evaluated with the screened (bare) Coulomb interactions [13]. The unscreened Coulomb interaction between carbon p_z orbitals is modeled by the Ohno potential, which realistically describes organic polymer systems:

$$V(r_{ij}) = \frac{U}{\sqrt{\left(\frac{4\pi\epsilon_0}{e^2} U r_{ij}\right)^2 + 1}}, \quad (3)$$

where r_{ij} is the distance between sites i and j , and $U = 11.3$ eV is the energy cost to place two electrons on a single site ($r_{ij} = 0$). Our results are not sensitive to the value of U when the size of the exciton is large.

An ideal calculation would include the nonlocal dielectric response of both the nanotube itself and the medium in which it is embedded. Here, for computational simplicity, we replace this complicated response function with a single dielectric constant ϵ [16]. This is most accurate for narrow tubes, and for embedding media with large dielectric constants. In this regime, the exciton length along the tube is large relative to the tube radius, and most of the dielectric screening occurs in the surrounding medium. The screening is then well described by the dielectric constant ϵ of the nanotube environment. For isolated nanotubes, or tubes in low- ϵ media, this treatment is not very accurate. Fortunately, it is most accurate in precisely the regime of greatest technological interest. Modulated electro-optical devices [7,8] are most practical for relatively narrow tubes embedded in SiO_2 ($\epsilon \sim 4$) or higher- ϵ materials.

To calculate the optical properties, we evaluate the imaginary part of the dielectric function for light polarized along the nanotube axis [17]:

$$\epsilon_2(\omega) = \frac{8\pi^2 e^2}{V_0 m_e^2} \sum_S \left| \sum_k A_k^S \frac{P_{cv}(k)}{\Delta_k} \right|^2 \delta(\hbar\omega - \Omega_S), \quad (4)$$

where P is the dipole matrix element [18]. The optical response Eq. (4) is the same as derived in the presence of the GW nonlocal potential [17]. $\epsilon_2(\omega)$ obeys a sum rule, where $\int \epsilon_2 d\omega \propto \sum_k P_{cv}^2(k)/\Delta_k^2$ is a constant independent of the strength of the screened interaction e^2/ϵ .

We solve the BSE equation (1) by direct diagonalization, choosing a k sample sufficient to converge the low-energy optical spectra (and *a fortiori* the binding energies). We calculate the binding energy, size, and spectral function for singlet excitons. The binding energy of the first optically active exciton versus ϵ is shown in Fig. 1(a) for four zigzag tubes with diameters $d = 1.0$ – 2.5 nm. (There is another singlet state 3–5 meV lower in energy, but it is optically silent by symmetry.)

The dependence of binding energy E_{b1} on ϵ in Fig. 1 can be fitted well with a power law, with the exponent being almost independent of the tube diameter. This suggests a more general power-law scaling, which we can motivate in an effective-mass approximation as follows. Given a variational wave function described by a single parameter L that scales the size along the tube axis, the exciton binding energy is

$$E_L \propto \frac{\hbar^2}{2mL^2} - \frac{e^2}{\epsilon R} f\left(\frac{L}{R}\right) = \frac{\hbar^2}{mR^2} g\left(\frac{L}{R}, \frac{mR}{\epsilon}\right). \quad (5)$$

Here the first term is the kinetic energy and m is the effective mass. The second term is the potential energy,

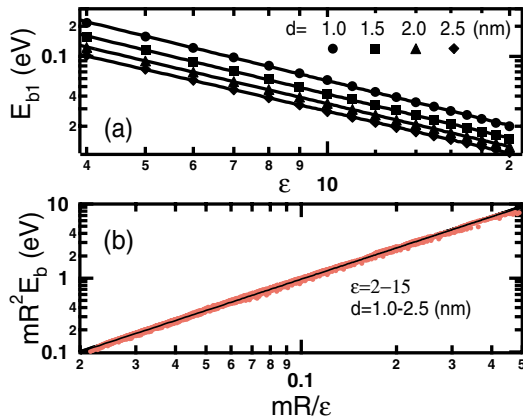


FIG. 1 (color online). (a) Binding energy of first optically active exciton, versus ϵ , in four semiconducting zigzag tubes: (13, 0), (19, 0), (25, 0), and (31, 0). (b) Scaling of binding energy of first and second exciton (red dots) in semiconducting tubes with all possible chirality (156 tubes with $d = 1.0$ – 2.5 nm, $\epsilon = 2$ – 15). Here R and m are in a.u. The black solid line is the best fit to Eq. (7) for $\epsilon = 4$ – 15 (3% rms error over this range), corresponding to $\alpha = 1.40$ and $A_b = 24.1$ eV.

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which depends on the exciton size via the dimensionless function $f(L/R)$. Then the exciton binding energy is

$$E_b = \min(E_L) = \frac{\hbar^2}{mR^2} h\left(\frac{mR}{\epsilon}\right), \quad (6)$$

$$E_b \approx A_b R^{\alpha-2} m^{\alpha-1} \epsilon^{-\alpha}, \quad (7)$$

where we approximate the function h by a power law over the range of interest, with empirical parameters α and A_b . The effective mass m depends on the tube indices [14] (i.e., on radius and chirality).

In 3D semiconductors, the potential energy is $\propto 1/L$, and the energy is minimized when the exciton size $L_S \propto \epsilon/m$, so the binding energy scales as $E_b \propto m/\epsilon^2$. This corresponds to true scaling, with a power law $\alpha = 2$ in Eq. (7). In the case of nanotubes, the power-law scaling is only an approximation. Nevertheless, for the most important range of tube sizes and dielectric constants, the behavior is rather well described by a power-law scaling in R and ϵ with a single value of α . Indeed, all the binding energies for the first and second excitons in semiconducting tubes, with all possible chiralities ($d = 1.0$ – 1.5 nm), collapse onto a single curve shown in Fig. 1(b). Similar energy scaling was reported by Pedersen [10] in a variational effective-mass model. In the range $\epsilon \gtrsim 4$, where our approach is most reliable, we obtain the best fit with $\alpha = 1.40$.

The second exciton that is optically active derives primarily from the second band of the nanotube. It falls within the continuum of the first band, and so becomes a resonance with a finite lifetime [12]. By artificially turning off the interband coupling, we determine that this coupling has very little effect on the exciton energy.

Considerable attention has been focused on the ratio E_{b2}/E_{b1} between the binding energies of the first and second excitons [11,12]. (E_{b2} is defined relative to the second-band quasiparticle gap. Note that the exciton formation energies involve also the quasiparticle band gaps.) The scaling relation of Eq. (7) predicts $E_{b2}/E_{b1} = (m_2/m_1)^{\alpha-1}$, where m_2 and m_1 are the effective masses of the first and second bands. In the case of zigzag tubes,

$$\begin{aligned} m_1 &= \frac{\hbar^2 \Delta_1}{3a^2 t^2} \left(1 + \sigma \frac{\Delta_1}{2t}\right)^{-1}, \\ m_2 &= \frac{\hbar^2 \Delta_2}{3a^2 t^2} \left(1 - \sigma \frac{\Delta_2}{2t}\right)^{-1}. \end{aligned} \quad (8)$$

Here Δ_1 and Δ_2 are the tight-binding band gaps, a is the graphene lattice constant, and for tube indices $(n, 0)$, $\sigma = 1$ if $\text{mod}(n, 3) = 1$ and $\sigma = -1$ if $\text{mod}(n, 3) = 2$.

It is common to treat the gap values in the infinite-radius limit, $\Delta_2^\infty = 2\Delta_1^\infty = 2ta/\sqrt{3}R$. This is rather accurate (within 5%) for tubes with $d = 1.0$ – 2.5 . On the other hand, for the same range of diameters, the effective-mass ratio m_2/m_1 varies from 3.4 to 1.3, approaching the infinite-radius limit $m_2/m_1 \rightarrow 2$ much more slowly than the gap ratio. Thus caution must be used in discussing

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available experimental data in terms of the $R \rightarrow \infty$ limit [11]. In particular, for the (8, 0) tube $m_2/m_1 = 0.96$, and according to Eq. (7) the binding energies of the first two excitons should be very similar. Indeed, the accurate first-principles calculations by Spataru *et al.* [12] find the binding energies of the first and second excitons (A'_1 and C'_1 in [12]) to be 0.99 and 1.00 eV. Using $\varepsilon = 1.93$ to best reproduce this, our calculations give $E_{b1} = 0.99$ eV and $E_{b2} = 1.05$ eV. In contrast, the (10, 0) tube has $m_2/m_1 = 4.14$, and for the same $\varepsilon = 1.93$ we find $E_{b2}/E_{b1} = 1.41$. (The simple $m^{\alpha-1}$ scaling is not accurate for such small ε .) It is important to note that effective-mass dependence similar to Eq. (8) holds also for chiralities other than zigzag tubes. Thus we expect exciton properties in tubes of index (m, n) to depend primarily on whether $\text{mod}(n - m, 3) = 1$ or 2, independent of the chiral angle.

To quantify the exciton size, we use the root mean square (rms) distance between electron and hole, L_S . The size L_1 of the first exciton is shown in Fig. 2(a) as a function of ε , for four different tube diameters. The size is approximately linear in ε . From Eq. (5), L_S/R is expected to be a function of mR/ε . Combining this with the observed linear dependence on ε , we anticipate that the exciton size will obey the scaling relationship

$$\frac{L_1}{R} = A_L + B_L \frac{\varepsilon}{Rm_1}, \quad (9)$$

This is confirmed in Fig. 2(b), which shows a linear

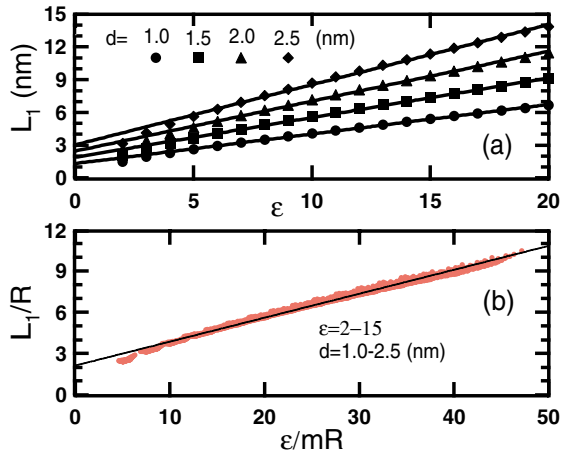


FIG. 2 (color online). (a) First exciton rms e - h separation L_1 in four zigzag tubes (13, 0), (19, 0), (25, 0), and (31, 0). The solid lines are the best linear fits. The slope k scales approximately as m^{-1} , the product km_1 (in a.u.) equals 0.167, 0.160, 0.157, and 0.155 for tubes with diameter 1.0, 1.5, 2.0, and 2.5 nm, respectively. (b) The linear scaling of L_1/R with ε/mR in semiconducting tubes of all possible chirality with $d = 1.0$ –2.5 nm, and $\varepsilon = 2$ –15. The solid line is the best fit to Eq. (9) to the results in the range $\varepsilon \geq 4$, giving $A_L = 2.13$ and $B_L = 0.174$ (for m and R in a.u.). The rms discrepancy between the fit and the full calculations is 2% for the subset of data having $\varepsilon \geq 4$ or $\varepsilon/mR^2 \geq 9.5$.

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dependence of L_1/R on ε/m_1R in all semiconducting tubes with $d = 1.0$ –2.5 nm, for all chiralities.

The exciton size directly affects observable quantities such as the exciton oscillator strength and the radiative lifetime. The exciton oscillator strength is proportional to the probability to find an electron and a hole at the same position [19]. In 3D semiconductors this is inversely proportional to the exciton volume $1/L^3$. In the case of nanotubes the electron and hole wave functions are confined in two dimensions and therefore the oscillator strength should be inversely proportional to the exciton size L_1 .

Typical optical absorption spectra are shown in Figs. 3(a)–3(c), calculated for a (19, 0) tube in different dielectric media. As ε increases, the spectral function converges to the noninteracting limit. For $\varepsilon = 10$, the spectral weight transfer to the first and second excitons, as a fraction of the total spectral weights for first and second bands in the noninteracting limit, is 71% and 55%, respectively. The second exciton resonance is more bound than the first, by 63 versus 43 meV. The higher spectral weight transfer to the first exciton is due not to stronger binding, but rather to the smaller band gap Δ_1 .

The probability argument [19] along with Eq. (4) suggest the following scaling relation for the exciton oscillator strength:

$$\frac{I_1}{I_0} = \frac{A_I}{\Delta^2 L_1 R} \left(1 - \frac{B_I R}{L_1} \right), \quad (10)$$

where I_0 is the spectral weight of the first band for noninteracting particles. The second term is a higher order

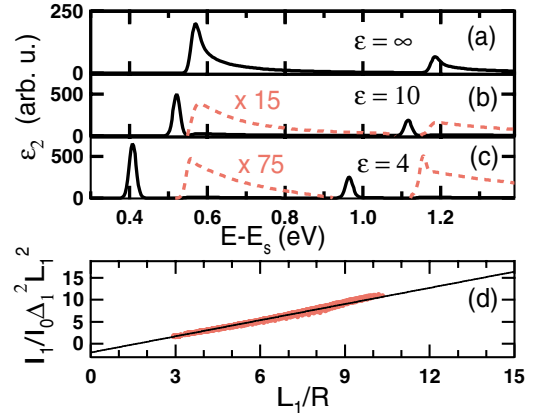


FIG. 3 (color online). Absorption spectra ε_2 of (19, 0) tube in dielectric environment (a) $\varepsilon = \infty$ (equivalent to no e - h interaction), (b) $\varepsilon = 10$, (c) $\varepsilon = 4$. (E_s is the unknown self-energy shift.) Note expanded scales for dotted lines in continuum region in (b) and (c). The fractional spectral weight transfer to the first exciton is $I_1/I_0 = 0, 0.71$, and 0.95 , respectively. Spectra are broadened with a Gaussian width of 0.0125 eV. (d) The scaling of spectral weight transfer to the first exciton, I_1 , in all semiconducting tubes with $d = 1.0$ –2.5 nm and $\varepsilon = 2$ –15 and all possible chiralities. The best fit to Eq. (10) (rms difference 3.5%) is obtained with $A_I = 1.22$ eV² nm² and $B_I = 1.61$.

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correction due to the band mixing and the nonconstant band-to-band optical density. Figure 3(d) confirms this scaling. While L_1 is not directly observable, the figure is virtually unchanged whether we use the actual calculated L_1 values or the scaling expression Eq. (9) for L_1 . Thus I_1/I_0 obeys rather well an explicit scaling relationship with ε/Rm .

The radiative lifetime of the excitons in carbon nanotubes is a key factor for possible applications in photonics and optoelectronics. The radiative lifetime of an exciton is inversely proportional to its oscillator strength [20]. In the regime of large binding ($\varepsilon \lesssim 3$), $I_1 \approx I_0$. Then the oscillator strength per atom is almost independent of tube diameter and chirality, and is equal to $f_0 \approx (0.014 \text{ eV}^{-1})E_{\text{exc}}$.

We emphasize however that the radiative lifetime and luminescence efficiency of nanotubes involve other factors as well. In principle, a single exciton coherently captures spectral weight from a macroscopic region [21], so the lifetime of an exciton actually depends on the coherence length in the nanotube, which in turn depends on environment and temperature. (If the coherence length is sufficiently large, other length scales such as tube length or photon wavelength can become important.) Another important factor is that electrons and holes are relatively unlikely to form optically active excitons, because there are far more excitons that are optically inactive. These include triplet and other dipole-forbidden excitons at *lower energy* than the optically active exciton. Most importantly, only a tiny fraction of excitons have a total momentum compatible with photon emission, so phonon scattering plays an important role [22].

In conclusion, we have calculated optical spectra of carbon nanotubes including the electron-hole Coulomb interaction by solving the Bethe-Salpeter equation (1) in a tight-binding wave function basis set. We find scaling relations with respect to the tube radius and dielectric constant ε , for the binding energy [Eq. (7)], exciton size [Eq. (9)], and oscillator strength [Eq. (10)]. Thus the absorption and emission properties depend on the dielectric media in which the nanotube is placed. We find a strong dependence on tube index (chirality), but only via the effective mass. This depends strongly on whether $\text{mod}(n - m, 3) = 1$ or 2 , but is otherwise insensitive to the chiral angle.

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