# Excitons and Many-Electron Effects in the Optical Response of Single-Walled Boron Nitride Nanotubes

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We report first-principles calculations of the effects of quasiparticle self-energy and electron-hole interaction on the optical properties of single-walled boron nitride nanotubes. Excitonic effects are shown to be even more important in BN nanotubes than in carbon nanotubes. Electron-hole interactions give rise to complexes of bright (and dark) excitons, which qualitatively alter the optical response. Excitons with a binding energy larger than 2 eV are found in the (8, 0) BN nanotubes. Moreover, unlike the carbon nanotubes, theory predicts that these exciton states are comprised of coherent supposition of transitions from several different subband pairs, giving rise to novel behaviors.

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Boron nitride nanotubes (BNNTs) are isoelectronic to carbon nanotubes (CNTs); however, their electronic properties are quite different. Whereas carbon nanotubes are metals or semiconductors with different size band gaps depending on diameter and chirality [1], BN nanotubes are wide gap insulators [2,3]. Although BNNTs have been synthesized since 1995 [4], only recently optical measurement on single-walled (SW) BNNTs has been performed [5–7]. Theoretical calculations [8,9], as well as experiments [10–12], have shown that excitonic effects dramatically alter the behavior of the optical response of single-walled CNTs. For the BNNTs, these effects are expected to be even more important due to the wide band gap nature of BNNTs.

Experimentally it is found that BN nanotubes favor a zigzag structure in current synthesis processes [13]. Thus, we focus our study on the zigzag tubes. Our calculations on the (8, 0) single-walled BNNT show that, indeed, many-electron effects lead to the formation of strongly bound excitons of multiband character with extraordinarily large binding energies, which dramatically change its optical absorption spectrum.

To compute the optical response, we use the method of Rohlfing and Louie [14] in which electron-hole excitations and optical spectra are calculated from first principles in three steps. First, we treat the electronic ground state with *ab initio* pseudopotential density-functional theory in the local density approximation (LDA) [15]. Second, we obtain the quasiparticle energies $E_{n\mathbf{k}}$ within the *GW* approximation for the electron self-energy $\Sigma$ [16], with wave functions and screening obtained from the LDA calculation, by solving the Dyson equation:

$$\left[-\frac{\nabla^2}{2} + V_{\text{ion}} + V_{\text{Hartree}} + \Sigma(E_{n\mathbf{k}})\right]\psi_{n\mathbf{k}} = E_{n\mathbf{k}}\psi_{n\mathbf{k}}.$$

Finally, we calculate the coupled electron-hole excitation energies and optical spectrum by solving the Bethe-Salpeter (BS) equation of the two-particle Green's function [14,17]:

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A^S_{vc\mathbf{k}} + \sum_{\mathbf{k}'v'c'} \langle vc\mathbf{k}|K^{\text{eh}}|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega^S A^S_{vc\mathbf{k}},$$

where $A^S_{vc\mathbf{k}}$ is the exciton amplitude, $K^{\text{eh}}$ is the electron-hole interaction kernel, and $|c\mathbf{k}\rangle$ and $|v\mathbf{k}\rangle$ are the quasielectron and quasihole states, respectively.

The LDA calculations were carried out using a plane-wave basis [18] with an energy cutoff of 100 Ry. *Ab initio* Troullier-Martins pseudopotentials [19] in the Kleinman-Bylander form [20] were used. For convergent results to better than 0.05 eV, up to 32 $\mathbf{k}$ points in the one-dimensional Brillouin zone were used for the *GW* calculations and for solving the BS equation. All calculations were carried out in a supercell geometry with a wall-to-wall intertube separation of 9.5 Å to mimic isolated tubes, together with a truncated Coulomb interaction to eliminate unphysical interactions between periodic images on the different tubes. The Coulomb interaction was truncated with a cutoff of 8 Å in the radial direction and also a cutoff

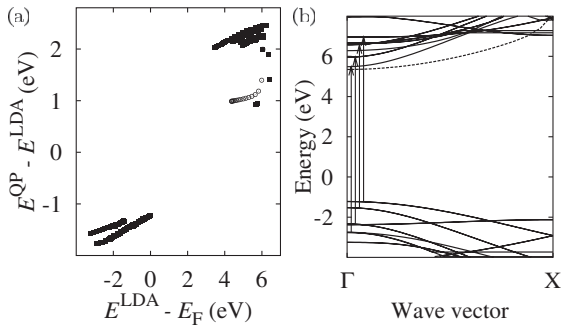


FIG. 1. Difference between the *GW* quasiparticle energy and the LDA Kohn-Sham eigenvalue (a) and quasiparticle band structure (b) for the (8, 0) SWBNNT. Empty circles in (a) and the dashed line in (b) show the nearly free-electron tubule states.

 

of 70 Å in the tube axis direction. As shown in Ref. [21], it is important to truncate the Coulomb interaction because, if not, the unphysical intertube interactions would increase the effective screening in the system and hence reduce both the self-energy correction and the exciton binding energy. Because of depolarization effects in nanotubes [22], strong optical response is only observed for light polarized along the tube axis ($\hat{z}$). We consider only this polarization.

Figure 1(a) shows the quasiparticle energy corrections to the LDA energy eigenvalues. These corrections are quite large, in comparison to those for bulk hexagonal BN (h-BN) and SWCNTs. The quasiparticle corrections open the LDA gap of bulk h-BN by ≈1.58 eV near zone center or the $\Gamma$ point [23], while the gap opening in the (8, 0) SWBNNT near the $\Gamma$ point is ≈3.25 eV. This is a consequence of enhanced Coulomb interaction in reduced dimension [9]. Also, due to its larger gap, the quasiparticle corrections to the gap in the (8, 0) SWBNNT are larger than those for a similar SWCNT [which are ≈1.15 eV near the $\Gamma$ point [9] ]. The quasiparticle corrections also have a complex band and energy dependence, so for accurate results they cannot be obtained by a simple scissor shift operation. The corrections depend on the character of the wave function. For example, states of the fourth lowest conduction band in the LDA band structure are nearly-free-electron (NFE) states localized inside the tube. These tubule states form a separate branch in the quasiparticle correction diagram with significantly smaller corrections. Figure 1(b) depicts the quasiparticle band structure of the (8, 0) SWBNNT. The arrows indicate the optically allowed interband transitions between four pairs of bands which give rise to the lowest-energy peak structures in the non-interacting optical spectrum in Fig. 2.

Figure 2 depicts the optical absorption spectrum calculated with and without electron-hole interaction effects. The plotted quantity is the imaginary part of the calculated dielectric susceptibility, $\chi = (\epsilon - 1)/4\pi$, multiplied by the cross-sectional area of the supercell perpendicular to the tube axis. This quantity $\alpha$, as defined above, gives the

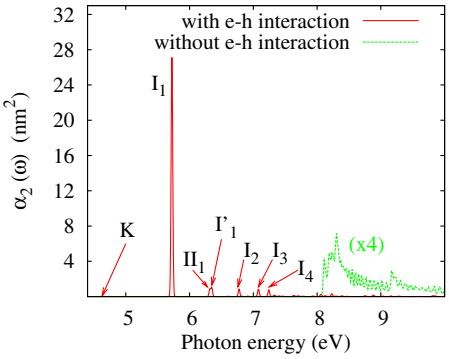


FIG. 2 (color online). Absorption spectra of the (8, 0) SWBNNTs. The imaginary part of the polarizability per tube $\alpha_2(\omega)$ is given in unit of nm$^2$. (See text.) The spectra are broadened with a Gaussian of 0.0125 eV.

polarizability per single tube in units of nm$^2$; so the susceptibility of an experimental sample containing a density of $n$ infinitely long tubes per unit area may be obtained directly as $\chi = n\alpha$ if intertube interaction is neglected. The absorption profile changes dramatically when the electron-hole interaction is taken into account. We use the labels $I$, $I'$, and $II$ to denote distinct series of bright excitons. Subscripts 1, 2, 3, and 4 refer to the ground, first-excited, second-excited, and third-excited states of a particular bright exciton series, respectively. $K$ refers to the lowest-energy exciton, which is dark. The first absorption peak at 5.72 eV corresponds to a bound exciton ($I_1$) with a binding energy of 2.3 eV. The area under this peak is 0.87 nm$^2$ eV. Excitons $I_1$ and $I_1'$ are different states, made up of transitions from the same set of four pairs of valence and conduction subbands of the (8, 0) BNNT, all of which have similar quasiparticle transition energies from 8.1 eV to 8.3 eV [see arrows in Fig. 1(b)]. These transitions are coupled strongly to each other by the electron-hole interaction to form the lowest optically active states (the singly degenerate $I_1$ and doubly degenerate $I_1'$). This behavior is very different from the (8, 0) SWCNT in which the exciton states are composed mainly of transitions between a single pair of quasiparticle bands.

The mixing of transitions of different subbands alters the electron-hole wave function, localizing further the electron amplitude with respect to the hole position in real space and making it deviate from a 1D behavior with spatial variations in directions perpendicular to the tube axis. Figure 3(a) shows the isosurface plots of the electron distribution $|\Phi(\mathbf{r}_e, \mathbf{r}_h)|^2$ with the hole position $\mathbf{r}_h$ fixed (the black star in the figure) for the first bound exciton ($I_1$). Figure 3(b) quantifies the electron-hole correlation for this state by plotting $|\Phi|^2$ along the tube axis after integrating out the electron coordinates in the perpendicular plane (the hole position is set at zero). The position of the peaks in Fig. 3(b) corresponds to the position of plane of boron atoms; i.e., the photoexcited electron is localized on the boron atoms near the hole. Thus, as expected, the photoexcitation process corresponds to a transfer of electron from nitrogen atoms to nearby boron atoms; but the resulting electron and hole amplitudes are strongly correlated with an extent of only a few interatomic distances. Figure 3(c) shows the excited electron probability distribution in a plane perpendicular to the tube axis and containing the hole as well as other nitrogen atoms.

As a comparison to carbon nanotubes, Figs. 3(d)–3(f) show similar quantities as in Figs. 3(a)–3(c) but for the first bright bound exciton in the (8, 0) SWCNT [9]. In the figure, the hole is fixed slightly above a carbon atom. The exciton in the (8, 0) SWBNNT is significantly more tightly bound than that in the (8, 0) SWCNT and cannot really be viewed as a 1D object. The root-mean-square size of the exciton along the tube axis is 3.67 Å for the (8, 0) SWBNNT and 8.59 Å for the (8, 0) SWCNT, and their

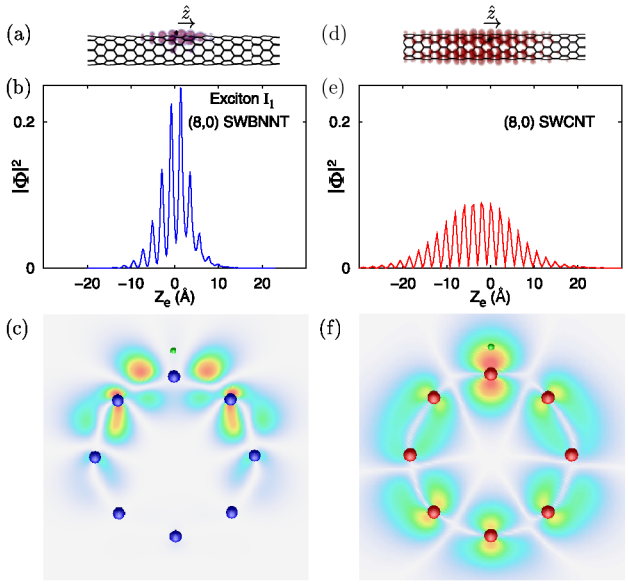


FIG. 3 (color online). (a)–(c) Wave function of the lowest-energy bright exciton of the (8, 0) SWBNNT. (a) Isosurface plot of electron probability distribution $|\Phi(\mathbf{r}_e, \mathbf{r}_h)|^2$ with the hole fixed at the position indicated by black star. (b) $|\Phi(\mathbf{r}_e, \mathbf{r}_h)|^2$ averaged over tube cross section. Hole position is set at zero. (c) $|\Phi(\mathbf{r}_e, \mathbf{r}_h)|^2$ evaluated on a cross-sectional plane of the tube. (d)–(f) Wave function of the lowest-energy bright exciton of the (8, 0) SWCNT. Plotted quantities are similar to those in (a)–(c).

binding energies are 2.3 eV and 1.0 eV, respectively. This difference in behavior is due to the wide band gap and weaker screening in SWBNNT. Also, we note that while the binding energy of the excitons in the bulk h-BN is only 0.7 eV [24,25], the binding energy in the (8, 0) SWBNNT is more than 3 times larger.

Figures 4(a) and 4(b) show similar quantities as in Fig. 3(b) for the excitons $I_1'$ and $I_2$. For exciton $I_1'$, the electron is less tightly bound to the hole than in exciton $I_1$. The state $I_2$, which is an excited state of exciton $I_1$, is also more diffuse than $I_1$ and the electron amplitude is not at a maximum near the hole which is the case for $I_1$ [Fig. 3(b)]. We also note that, for the (8, 0) SWBNNT, there are numerous dark excitons distributed rather uniformly in energy below and among the bright excitons shown in Fig. 2. The energy of the lowest doubly degenerate bound dark exciton ($K$) is at 4.63 eV. This dark exciton is made up

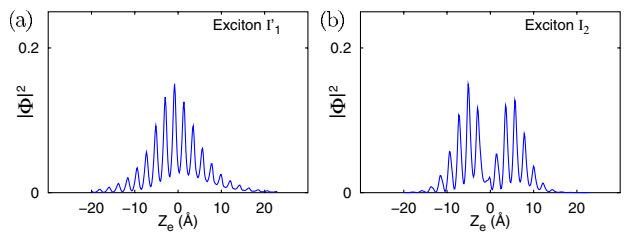


FIG. 4 (color online). Wave functions of excitons of the (8, 0) SWBNNT. Plotted quantities are similar to those in Fig. 3(b).

of transitions from the highest valence band to the lowest conduction band (the NFE tubule state) in the quasiparticle band structure, and has a binding energy of 1.94 eV with respect to these interband transition energies.

The various lowest-energy exciton states (for both bright and dark excitons) derived from the various different sets of interband transitions, on the average, have a large binding energy of about 1.9 eV. However, the binding energy of the first bright exciton is 2.3 eV. We ascribe this extra binding energy of about 0.4 eV to the fact that four different sets of interband transitions are strongly coupled in forming the first bright exciton ($I_1$). This strong coupling mixes states from the different transitions, splits the excitation energy levels, and increases the binding energy of the final lowest-energy exciton.

Arenal *et al.* [6] and Aloni *et al.* [7] have recently done EELS measurements of the optical gaps of SW and multiwalled BNNTs. The optical gaps measured in both experiments are $5.8 \pm 0.2$ eV, independent of the geometry of nanotubes, which is in very good agreement with our calculation (5.72 eV).

Lauret *et al.* [5] measured directly the optical properties of SWBNNTs and observed three absorption peaks at 4.45, 5.5, and 6.15 eV, respectively. The calculated first peak position for the (8, 0) tube is rather close to the observed 5.5 eV peak. Also, the difference between the second and the third observed absorption peak position in the experiment is 0.65 eV, very close to the difference between the first and the second absorption peaks in our calculation which is 0.62 eV, while the difference between the first and the second observed peak position is 1.05 eV. We thus suspect that the observed second peak at 5.5 eV in Ref. [5] is likely due to an exciton, corresponding in nature to our first absorption peak. Moreover, theory predicts that, for the (8, 0) BNNT, there are many dark excitons whose excitation energies are 4.63 eV and higher. The excitation energy difference between the first dark exciton ($K$) and the first bright exciton ($I_1$) in our calculation is 1.1 eV. This suggests that the 4.45 eV peak in the experiment may be due to some dark excitons with low excitation energies activated by external perturbations. Another possibility is that this extra low-energy feature may arise from impurities. Small differences between calculated excitation energies and measured values are unavoidable due to environmental effects. The theory is for a perfectly isolated tube, whereas experimentally the tubes are surrounded by a dielectric medium which can modify the excitation energies. For SWCNTs, the effect of the surrounding dielectric medium on the optical spectrum is expected to be small (even though it can be important for the exciton binding energy) due to an almost cancellation between the quasiparticle self-energy correction and the binding energy of excitons [9]. For SWBNNTs, screening by external medium may be more important because intrinsic screening of the BNNT is much weaker. In particular, for the isolated

(8, 0) SWBNNT, we find that the energy difference between the quasiparticle self-energy correction and the binding energy of the exciton is large (about 0.9 eV). In the presence of a dielectric medium, we expect this to decrease, which would likely result in a redshift in the excitation energies.

Although the average diameter of the tubes measured in the experiments [5–7] ( $\gtrsim 1.4$ nm) is greater than the diameter of the relaxed (8, 0) SWBNNT in our work (0.65 nm), we expect the comparison to be reasonable because the binding energy of SWBNNTs is found to be an insensitive function of its diameter. For example, the exciton binding energy (2.1 eV) of an isolated BN sheet [26], which is equivalent to an infinitely large diameter SWBNNT, is only smaller than that of our (8, 0) SWBNNT by 0.2 eV. Since the exciton binding energy is expected to increase with decreasing diameter, the exciton binding energies for the SWBNNTs in the experiments would be smaller than our calculated value by at most about 0.1–0.2 eV.

Among previous theories of the optical properties of BNNTs, Guo and Lin [27] carried out LDA calculations without considering many-electron effects. Their optical absorption spectra are qualitatively different from the present final results. From their results for the (6, 0) and (9, 0) tubes, we can deduce an LDA-RPA peak position for the (8, 0) tube to be near 4.9 eV, as we find in our LDA-RPA level calculation. The first peak position in Fig. 2 with electron-hole interaction included is blue shifted by about 0.9 eV from that of the LDA-RPA calculation.

In summary, we have done calculations on the (8, 0) SWBNNT to study the effects of many-electron interactions on its optical response. The *GW* corrections to the quasiparticle excitation energies of the SWBNNTs are significantly larger than those for SWCNTs or bulk h-BN. Also, the quasiparticle energy corrections are found to be complicated so that interpolation by a simple scissor shift operation is not a good scheme for accurate calculation. Theory predicts that, unlike the noninteracting case, the absorption spectrum of the (8, 0) SWBNNT is dominated by a huge peak at 5.72 eV, due to an exciton with a large binding energy of 2.3 eV. This exciton state is made up of optically allowed transitions between four different pairs of subbands. Moreover, an intricate set of dark excitons is found to exist. Self-energy and electron-hole interaction effects therefore are even more important in the optical response of the SWBNNTs than in the SWCNTs.

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*Note added.*—After the submission of this Letter, we became aware of a recent theoretical work by Wirtz, Marini, and Rubio [26] showing also very large excitonic effects in the optical response of the BNNTs.

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