Multi-excitonic effects on optical spectra of semiconducting carbon nanotubes

Kouta Watanabe, Kenichi Asano and Tetsuo Ogawa
Department of Physics, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan
E-mail: watanabe@acty.phys.sci.osaka-u.ac.jp

Abstract. We calculated the wavefunction and the binding energy of the biexciton in semiconducting carbon nanotubes and studied the spectral weights of the photoluminescence spectra and the biexciton contribution to the two-photon absorption spectra. The wavefunction and the binding energy are calculated by means of the Lanczos method.

1. Introduction
Carbon nanotube, cylindrical molecule of carbon, is one of the most intensively studied material over the past 15 years. They are either metallic or semiconducting, depending on their diameters and helical arrangement [1]. Because of their one dimensionality, it is found both theoretically [2] and experimentally [3] that the excitons on the semiconducting carbon nanotubes (s-CNTs) have huge binding energies. Further, theoretical studies also predict stable biexcitons with large binding energies [4, 5]. However, they have never been observed in the photoluminescence (PL) measurements [6]. To clear up this mystery, we investigate the Auger decay of the biexciton [7], which is completely ignored in the previous theories. As a result, we find that the biexciton is still stable: the decay rate is smaller than the binding energy of biexcitons. However, the method of our calculation unfortunately lacks quantitative accuracy. We need more elaborate scheme to estimate the biexciton binding energies and wave functions.

2. Formulation
In monolayer graphite (graphene), the $\pi$-band has a massless dispersion near the K and K’ points. In s-CNTs, it splits into massive subbands due to the periodic boundary condition in the circumference direction. Their energy dispersions are given as $\epsilon_{\nu,n}(k) = \pm \gamma \sqrt{k^2 + (n - \nu/3)^2/R^2}$ in the effective mass approximation [1], where $R$ is the radius of the s-CNT, $\gamma$ is the band parameter, $k$ is the wave vector in the axis direction, the integer $n$ is the subband index, $\nu = \pm 1$ is a parameter determined by the chiral vector, and the positive and negative signs denote the conduction and valence bands, respectively [2]. In the present paper, we use the simplified model used in Ref. [4]: we consider the ground subband ($n = 0$) near the K point, only, and neglect its nonparabolicity, approximating the energy dispersion by $\epsilon_{\nu,n=0}(k) \sim \pm \left( E_g/2 + \hbar^2 k^2/2m \right)$ with the effective band mass $m = \hbar^2/3\gamma R$ and the bandgap energy $E_g = 2\gamma/3R$. The photoexcited electrons and holes interacts via the Coulomb potential $\pm (2e^2/\pi\kappa r) K(-4R^2/r^3)$, where $e$ is the electron charge, $\kappa$ is the dielectric constant, $K$ is the elliptic integral, $r$ is the inter-particle
separation along the CNT axis, and the sign is positive for the electron-electron (e-e) and hole-hole (h-h) interactions and negative for the electron-hole (e-h) interaction, respectively. The electron-hole exchange and Auger processes are ignored. In the following, we measure the length in units of the radius $R$, and the energy in units of $\gamma/R$. Then, this model is characterized by only one dimensionless coupling constant $v_c = e^2/\kappa \gamma$, which we fix to 0.6 in our calculation [5].

We apply the finite difference method to our model: the one dimensional system is discretized on a grid with interval $\Delta \approx 0.1$ under the periodic boundary condition, where the distance between the $i$th and $j$th grid points is defined as $r_{ij} = \Delta \min(|i-j|, M-|i-j|)$ with the number of grid points, $M$. Defining $E_n^{(N)}$ and $|n; N\rangle$ as the $n$th eigenenergy and eigenstate for the systems consisting of $N$ electrons and $N$ holes, respectively, we numerically compute all eigenpairs, $E^{(1)}_0$ and $|0; 1\rangle$, for $N = 2$ systems. It is noteworthy that our discretization scheme in the real space is quite suitable for the Lanczos algorithm, because the Hamiltonian is represented by a sparse matrix.

Then, we obtain the binding energy of the ground exciton and biexciton via $E_{XX} = |E^{(2)}_0 - 2E^{(1)}_0|$, respectively. Further, the photoluminescence (PL) spectra from the exciton and the biexciton are calculated as

$$P_X(\omega) \propto |\langle \text{vac.}|d|X\rangle|^2 \delta \left( \hbar \omega - E^{(1)}_0 \right),$$

$$P_{XX}(\omega) \propto \sum_n |\langle n; 1|d|XX\rangle|^2 \delta \left( \hbar \omega - E^{(2)}_0 + E^{(1)}_n \right),$$

respectively, and the biexciton contribution to the two-photon absorption spectra (TPA) is given as

$$I_{XX}^{TPA}(\omega) \propto \sum_n \frac{|\langle \text{vac.}|d|n; 1\rangle \langle n; 1|d|XX\rangle|^2}{\hbar \omega - E^{(1)}_n} \delta \left( 2\hbar \omega - E^{(2)}_0 \right),$$

where $d$ is the dipole operator in the CNT axis direction, $\hbar \omega$ is the photon energy, $|\text{vac.}\rangle$ is the vacuum state. In this study, we assume that two photons have the same energy. The ground exciton and biexciton states, $|0; 1\rangle$ and $|0; 2\rangle$, are abbreviated to $|X\rangle$ and $|XX\rangle$, respectively.

**Figure 1.** Cutoff dependence of $E_{XX}$. Here, $y_c$ is half the length of the $s$-CNT.

**Figure 2.** Biexciton two-photon absorption spectrum. Here, $\delta$ is the linewidth of exciton, units of $E_{XX}$ and $E_g = 2/3$ is the bandgap energy.
3. Results and Discussion
Our calculation estimates the exciton binding energy as \(E_X = 0.236\). It is about 2 percent smaller than that obtained with the diffusion Monte Carlo (DMC) method [5], in which not only the ground but excited subbands are considered. We also find that the nonparabolicity effects reduce the exciton binding energy only by 5 percent. On the other hand, our value of \(E_X\) is about 20 percent larger than that evaluated by means of the screened Hartree-Fock approximation [2]. The effects of the excited subbands and nonparabolicity are negligible, but the inter-subband screening and self-energy gives a considerable correction to the exciton binding energy.

Now, let us discuss the biexciton binding energy. In Fig. 1, exhibits its dependence on the system size, \(2y_c\), and the discretization parameter, \(\Delta\). The binding energy shows a fast convergence for the increase of \(y_c\). On the other hand, it slowly increases and saturates as \(\Delta\) decreases, and we can extrapolate \(E_{XX}\) as 0.031. This value is slightly larger than that obtained by the variational method [4], and about 30 percent smaller than that obtained by DMC method [5]. These results shows that the short-wavelength components are relatively important in the biexciton wavefunction, and give a considerable correction to the value of \(E_{XX}\).

The calculated PL spectra from the biexciton are almost dominated only by a single peak, which corresponds to the transition from the biexciton state \(|XX\rangle\) to the ground exciton state \(|X\rangle\). In other words, the dipole matrix element \(|\langle n;1|d|XX\rangle|\) is negligible compared with \(|\langle X|d|XX\rangle|\) for \(n \neq 0\). The intensity ratio of the dominant peak in the biexciton PL to that in the exciton PL is estimated as \(|\langle X|d|XX\rangle|^2/|\langle \text{vac},d|X\rangle|^2 = 0.28\). This shows that the biexciton peak is observable, if the ground biexciton is formed in the initial state.

Figure 2 shows the biexciton contribution to the two-photon absorption spectra. In this calculation, we introduce a phenomenological linewidth \(\delta\). The spectra consist of two peaks, which are the high-energy exciton peak at \(\hbar \omega = E_0^{(1)}\) and the low-energy biexciton peak at \(\hbar \omega = E_0^{(2)}/2 = E_0^{(1)} - E_{XX}/2\). Because of \(|\langle n;1|d|XX\rangle| \ll |\langle X|d|XX\rangle|\) for \(n \neq 0\), only the ground exciton state \(|X\rangle\) gives the dominant contribution among the intermediate states. We can identify the biexciton signal from the two-peak structure of the TPA spectra only when \(\delta \leq 0.2E_{XX}\).

4. Summary
We numerically calculated the wavefunction and the binding energy of the exciton and biexciton, and evaluated the PL and TPA spectra in s-CNT. We found that the PL spectra should show the biexciton peak as long as the biexciton is formed in the initial state, and the biexciton signal can be observed by TPA spectra only when the peak broadening is much smaller than \(E_{XX}\).

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