Breakdown of exchange approximation for cross-polarized excitons in carbon nanotubes

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Abstract. Cross-polarized excitons in carbon nanotubes where polarization is perpendicular to the tube axis are calculated in a Tamm-Dancoff-type approximation and the results are compared with those obtained in the self-consistent-field method. For the lowest exciton, the oscillator strength for the optical absorption peak is considerably reduced and the energy is overestimated.

1. Introduction
Carbon nanotubes are quasi-one-dimensional systems of rolled up graphenes. For optical absorption, there are two possible polarizations, parallel and perpendicular to the tube axis. For perpendicular (cross) polarization, an excited electron-hole pair is separated into opposite sides of the circular cross-section and a depolarization field is induced. It was shown that this depolarization effect considerably reduces band-to-band optical absorption \cite{1, 2}, but distinct peaks can appear in absorption spectra due to strong exciton effects even in its presence \cite{3–7}. The depolarization effect should be considered in the self-consistent-field method where an optically induced current and electric field which electrons feel are determined self-consistently \cite{1, 2, 5}. It is sometimes treated within a Tamm-Dancoff-type approximation where the effect is included in the form of a so-called electron-hole exchange interaction for excitonic Bethe-Salpeter-type equation \cite{3, 4, 8–10}. In this paper we show that the latter approximation does not appropriately describe this depolarization effect in carbon nanotubes.

2. Model and method
In carbon nanotubes, electrons near the Fermi energy exist around two valleys, \( K \) and \( K' \) points at the corners of the first Brillouin zone. In an effective-mass approximation \cite{11, 12}, states can be specified by a set of indices \( \alpha = (\pm, n, k, v) \) where \( + \) and \( - \) denote the conduction and valence band, respectively, \( n \) is the band index indicating the wave vector in the circumference direction, \( k \) is the wave vector in the axis direction, and \( v = K \) and \( K' \).

An exciton wave function at valley \( v \) with momentum \( 2\pi hl/L \) in the circumference direction, where \( L \) is the circumference length, is written as \cite{5, 13, 14}

\[
|u, l, v\rangle = \sum_{n,k} \psi_{n,v}(k) c_{u,l,v,k,v}^\dagger c_{-u,n,k,v,}^\dagger |g\rangle,
\]  

(1)
where $c^\dagger_\alpha$ and $c_\alpha$ are the creation and annihilation operators, respectively, and $|g\rangle$ is the ground state. The coefficients $\psi^l_{n,v}(k)$ and energy eigenvalues for the corresponding states, $\varepsilon_{n,v}$, are obtained by solving an equation of motion for an electron and hole under attractive interaction, i.e.,

$$\varepsilon_u\psi^l_{n,v}(k) = \Delta\varepsilon_{n,v}(k)\psi^l_{n,v}(k) - \sum_{m,q} V(+,n+l,k,v;+,m+l,k+q,v)(-,m,k+q,v;-,n,k,v)\psi^l_{m,v}(k + q),$$

(2)

where $\Delta\varepsilon_{n,v}(k)$ is the one-particle transition energy between states with $(+, n + l, k, v)$ and $(-, n, k, v)$ and $V(\alpha,\alpha')(\beta,\beta')$ is a matrix element of the screened Coulomb interaction between a two-particle state with $\alpha$ and $\beta$ and that with $\alpha'$ and $\beta'$. For perpendicular polarization, $l = \pm 1$, and the dynamical conductivity without the depolarization effect, $\sigma_{xx}(\omega)$, is obtained from solutions of this equation, for example, with the use of the Kubo formula.

For perpendicular polarization, the depolarization effect must be considered. The effect is included in the self-consistent-field method [1, 2, 5] and the dynamical conductivity $\tilde{\sigma}_{xx}(\omega)$ characterizing the optical absorption is given by

$$\tilde{\sigma}_{xx}(\omega) = \frac{1}{2} \sum_{l=\pm 1} \tilde{\sigma}^l_{xx}(\omega), \quad \tilde{\sigma}^l_{xx}(\omega) = \frac{\sigma^l_{xx}(\omega)}{\varepsilon^l_{xx}(\omega)}, \quad \varepsilon^l_{xx}(\omega) = 1 + \frac{4\pi^2 i}{\kappa L\omega} \sigma^l_{xx}(\omega),$$

(3)

where $\kappa$ is an effective dielectric constant describing screening by electrons in $\sigma$ bands, core states, and the $\pi$ bands away from the $K$ and $K'$ points.

The depolarization effect may approximately be included based on the Bethe-Salpeter equation for the exciton in terms of an exchange term under the condition that only a single electron-hole pair can be excited [3, 4, 8], corresponding to a Tamm-Dancoff-type approximation [9, 10]. In this scheme, the equation is given by (2) with the following term on the right-hand side:

$$2 \sum_{\alpha} \sum_{m,q} V^0_{(\alpha,\alpha')(\beta,\beta')}(+,n+l,k,v;-,n,k,v)(-,m,k+q,v;+,m+l,k+q,v)\psi^l_{m,v}(k + q),$$

(4)

where $V^0_{(\alpha,\alpha')(\beta,\beta')}$ is a matrix element of the unscreened Coulomb interaction and factor two is due to the electron spin. The dynamical conductivity with the depolarization effect is directly given from the eigenstates and eigenenergies of Eq. (2) with term (4) by using the Kubo formula. It should be noted that term (4) vanishes for the parallel polarization because of the zero center-of-mass momentum of excitons and the charge neutrality.

The Tamm-Dancoff-type approximation is certainly valid when the spectrum is dominated by a single resonance peak well separated from others. In nanotubes in the cross-polarized geometry, however, various resonances such as excitons and interband continuum coexist and strongly interact with each other, and the approximate method can give results significantly different from exact results. In the following, we show that the approximation is actually very poor in describing the absorption intensity in comparison with the absorption energies, using the lowest order effective-mass approximation [11–14].

3. Numerical results

In the effective-mass scheme, the energy is scaled by a typical kinetic energy $2\pi\gamma/L$ where $\gamma$ is a band parameter describing the slope of the linear dispersion of graphene. Thus, a typical Coulomb interaction is given by $(e^2/\kappa L)(2\pi\gamma/L)^{-1} \approx 0.35/\kappa$. Because $\kappa$ is considered to be of the order of unity ($\kappa = 2.4$ for graphite, for example), the typical strength of the Coulomb interaction is of the order of 0.1–0.2. We should introduce a cutoff energy which corresponds to the half of the $\pi$-band width $3\gamma_0$, where $\gamma_0$ is the resonance integral between nearest neighbor
\[ \varepsilon_c(2\pi\gamma/L)^{-1} \approx (\sqrt{3}/\pi)(L/a) = \sqrt{3}d/a, \] with \( d \) being the diameter of the nanotube. In the following, \( \varepsilon_c(2\pi\gamma/L)^{-1} = 10 \) is used, corresponding to a diameter \( \sim 1.4 \) nm.

Figure 1 shows the calculated dynamical conductivity near the lowest band edge when the Coulomb interaction parameter is (a) 0.1 and (b) 0.15. Solid and dashed lines denote results in the self-consistent-field method and the Tamm-Dancoff-type approximation, respectively. For the solid lines, sharp peaks appear due to the lowest exciton. For the dashed lines, the conductivity is considerably suppressed in comparison with the solid lines and the peak positions are shifted to the higher energy side.

In Fig. 2 the lowest exciton energy is shown as a function of the Coulomb interaction. Solid and dashed lines are results for the self-consistent-field method and the Tamm-Dancoff-type approximation, respectively, and the dotted line is the band gap. The exciton energy obtained in the Tamm-Dancoff-type approximation is higher than that obtained in the self-consistent-field method. The difference may not look so important in the absolute value, but is significant in the scale of the exciton binding energy, i.e., the difference between the band gap and the exciton level. In Fig. 3 the oscillator strength for the exciton peak is shown. The dashed line obtained in the Tamm-Dancoff-type approximation becomes vanishingly small at \( (e^2/\kappa L)(2\pi\gamma/L)^{-1} \approx 0.25 \), showing that the approximation becomes invalid in the important parameter region of 0.1 \( \lesssim (e^2/\kappa L)(2\pi\gamma/L)^{-1} \lesssim 0.2 \).

Equation (3) shows that the exciton energy is determined by a zero of \( \varepsilon_{\pm 1}^{xx}(\omega) \), where \( \sigma_{\pm 1}^{xx}(\omega) \) becomes a pure imaginary. The imaginary part of \( \sigma_{\pm 1}^{xx}(\omega) \) vanishes at a point lying between adjacent two discrete energy levels corresponding to poles of \( \sigma_{\pm 1}^{xx}(\omega) \). In the Tamm-Dancoff-type approximation, \( \sigma_{\pm 1}^{xx}(\omega) \) in \( \varepsilon_{\pm 1}^{xx}(\omega) \) is replaced by an approximate expression because all excitations are assumed to have nearly same energy. Thus, \( \sigma_{\pm 1}^{xx}(\omega) \) in the numerator and in the denominator of \( \tilde{\sigma}_{xx}(\omega) \) effectively become different from each other, leading to vanishingly small imaginary part of \( \sigma_{\pm 1}^{xx}(\omega) \) in the numerator at an approximate zero of the denominator. This is the origin of the breakdown of the approximation scheme, particularly, for the oscillator strength, although such severe problems do not manifest themselves in the exciton energy.

In conclusion, cross-polarized excitons have been calculated in the Tamm-Dancoff-type approximation.
approximation and the results have been compared with those in the exact self-consistent field method in semiconducting carbon nanotubes. For the lowest exciton, the oscillator strength for the optical absorption peak can be considerably reduced and sometimes vanishingly small, and the excitation energies are overestimated.

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