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Large electron-hole exchange interaction of carbon nanotubes

Hiroshi Ajiki
Photon Pioneers Center, Osaka University, 2-1 Yamadaoka, Suita 565-087, Japan
E-mail: ajiki@ppc.osaka-u.ac.jp

Abstract. Effect of electron-hole (e-h) exchange interaction of exciton in a single-walled carbon nanotube is studied. Large e-h exchange interaction for light field perpendicular to the tube axis drastically changes absorption spectra predicted from a band structure.

1. Introduction
A single walled carbon nanotube (SWCNT) is a quasi-one-dimensional (1D) graphite material with cylindrical structure. The electronic states near the Fermi energy can be described by massless Dirac Fermion in conjunction with the boundary condition in the circumference direction. Because of the topological structure and characteristic electronic states, a SWCNT shows various fascinating properties [1]. In this paper, I present another interesting property on exciton states excited by polarized light perpendicular to the tube axis. It is known that an exciton level exhibits large blue shift due to the depolarization effect [2]. This effect can be interpreted as the electron-hole (e-h) exchange interaction. I calculate absorption spectra in terms of the e-h exchange interaction, in which bright and dark states of exciton can be obtained directly. It has been theoretically reported that two absorption peaks appear for perpendicular polarization due to the asymmetry of conduction and valence bands [3]. However, the large e-h exchange interaction causes essential change of the absorption spectra.

2. Electronic states and overlap integral
The electronic states of a SWCNT are understood from those of graphene. The conduction and valence bands of the graphene touch at the K and K’ points. The width of the conduction band is larger than that of the valence band. This asymmetry comes from a nonzero overlap integral s. Near the Fermi energy, the electronic states of graphene are well described by a $\mathbf{k} \cdot \mathbf{p}$ equation. The $\mathbf{k} \cdot \mathbf{p}$ equation with overlap integral near the K point is given by

$$
\gamma (\sigma_x \hat{k}_x + \sigma_y \hat{k}_y) \mathbf{F}^K(\mathbf{r}) = \varepsilon \left[ 1 - s (\sigma_x \hat{k}_x + \sigma_y \hat{k}_y) \right] \mathbf{F}^K(\mathbf{r}),
$$

(1)

where $\gamma$ is a band parameter, $\sigma_x$ and $\sigma_y$ are the Pauli spin matrices, $\hat{k} \equiv -i\nabla$ is the wave-vector operator, and $\varepsilon$ is the eigenenergy. The band parameter $\gamma$ is related to the hopping integral $\gamma_0$ as $\gamma = (\sqrt{3}/2)a\gamma_0$ with lattice constant $a = 2.46 \text{ Å}$. $\mathbf{F}^K(\mathbf{r})$ is the envelope function with two components representing the amplitude at two carbon atoms in a unit cell. By imposing the boundary condition around the circumference with length $L$, we obtain electronic states of the
Figure 1. (a) The lattice structure of a 2D graphite. (b) Schematic illustration of a SWCNT and applied field with perpendicular polarization. (c) Allowed transitions are indicated for parallel ($l = 0$, dotted arrows) and perpendicular ($l = 1$, solid arrows) polarizations.

SWCNT: $\varepsilon^{K}_{\pm n,l} = \pm \gamma \sqrt{\kappa_{\nu \varphi}(n)^2 + k^2} \left( 1 \mp s \sqrt{\kappa_{\nu \varphi}(n)^2 + k^2} \right)$ with $\kappa_{\nu \varphi}(n) = (2\pi/L)(n + \varphi - \nu/3)$ where upper and lower signs correspond to conduction and valence states, respectively. $\kappa_{\nu \varphi}(n)$ is a discrete wave number, where we generalize it in the presence of an Aharonov-Bohm (AB) magnetic flux $\varphi = \phi/\phi_0$ with magnetic flux quantum $\phi_0 = ch/e$. The AB flux changes the band gap in the period of $\phi_0$ [4]. The integer $\nu$ takes 0, +1, or −1 depending on the chiral structure of SWCNT. The SWCNT is metallic for $\nu = 0$ and is semiconducting for $\nu = \pm 1$. Finite overlap integral enhances conduction-band width and reduces valence-band width.

3. Exciton states and electron-hole exchange interaction
An excited conduction electron and a valence hole form an exciton state. Because of two valleys at the K and K’ points and two-fold spin degeneracy, the exciton states exhibits fine structure having 16 states [5]. Among the states, I focus on spin singlet exciton consisting of electron and hole in the same valley (K or K’ point). The exciton states around the K point are represented as

$$|u, l; K\rangle = \sqrt{2} \sum_{n,k} \psi_{u,l}(n,k) c_{n+l,k,\sigma}^{K\dagger} c_{-n,k,\sigma}^{K\dagger} |g\rangle,$$

where $c_{\pm n,l,k,\sigma}^{K}$ is the annihilation operator for an electron with spin $\sigma$ near the K point with energy $\varepsilon_{\pm n,l}^{K}$, $l$ denotes the quantum number for wave vector $2\pi l/L$ around the tube axis, and $u$ denotes the exciton levels. The selection rules of optical excitations depend on the light polarization. Transitions with $l = 0$ are allowed for polarized light parallel to the tube axis, while transitions with $l = \pm 1$ are allowed for perpendicular polarization.

For parallel polarization, electron excitations around the K and K’ points are degenerate regardless of the overlap integral [see dotted arrows in Fig 1 (c)], and thus, there exists just one optically allowed state or bright state [5]. The bright state is represented by a bonding state between $|u, l; K\rangle$ and $|u, l; K'\rangle$. In addition to the bright state, there is an anti-bonding dark state. The level splitting between the bright and dark states is a few meV. The degeneracy around the K and K’ points can be removed by an AB flux, and consequently, the initial dark state becomes optically allowed with increase of the AB flux. This behavior in conjunction with the level splitting proportional to the AB flux has been observed in luminescence spectra [6, 7].

For perpendicular polarization, optical transitions with $l = 1$ and $l = -1$ are allowed, which are illustrated by solid arrows in Fig. 1 (c) for $l = 1$. The transition energies at the K and K’ points are intrinsically different due to the anti-symmetry of conduction and valence bands.
Because of the removal of the degeneracy, the anti-bonding state is slightly modified, and as a result, the dark state acquire small but finite oscillator strength [8]. So far, the dark and bright excitons for perpendicular polarization have been discussed in the absence of the overlap integral, where the exciton states around the K and K’ points are treated independently [2]. Then, the level splitting between bright and dark states is estimated by comparing the exciton levels with and without the depolarization field. The depolarization effect originates from the electron-hole (e-h) exchange interaction. In order to discuss the optical activity of exciton states in the presence of the finite overlap integral, I calculate absorption spectra based on an optical response theory [9, 10] that explicitly treats the e-h exchange interaction. We have calculated radiation force exerted on a SWCNT by using this method [11, 12].

In this method, current density of exciton and light field are obtained self-consistently because they drive each other. Then, the resulting self-consistent equations contain matrix elements $A_{uu',l}^{KK'}$ of self-energy between excitons $|u, l; K\rangle$ and $|u', l; K'\rangle$:

$$A_{uu',l}^{KK'} = \frac{-\hbar}{i E_{uu',l}^{KK'}} \int dr \int dr' \langle u, l; K | \hat{J}^K(r) | g \rangle \cdot G(r, r') \cdot \langle g | \hat{J}^{K'}(r') | u', l; K' \rangle,$$

where $E_{uu',l}^{KK'}$ is an exciton energy, $\hat{J}^K(r)$ is a current density operator, $G$ is a dyadic Green’s function for Maxwell equations, and $|g\rangle$ represents the ground state. $A_{uu',l}^{KK'}$ has real and imaginary parts. The imaginary part corresponds to a radiative lifetime of exciton, which is a few tens of $\mu$eV for both parallel and perpendicular polarizations [12]. The real part contains a radiative shift for transverse component of exciton and e-h exchange interaction for longitudinal component. For parallel polarization with $l = 0$, the order of Re[$A_{uu',0}^{KK'}$] is determined by $[\gamma/(\hbar c)]^2 \approx 10^{-5}$ in units of a band gap about 1 eV. For perpendicular polarization with $l = \pm 1$, however, the order of Re[$A_{uu',\pm1}^{KK'}$] is much larger than that for parallel polarization by a factor of $16\pi/(qL)^2 = (4/\pi^3)(\lambda/d)^2 \approx 10^4$ with $\lambda$ being wavelength of light and $d$ being a diameter of SWCNT. This Re[$A_{uu',\pm1}^{KK'}$] comes from the long-range e-h exchange interaction, and the magnitude reaches a few hundred of meV. The e-h exchange interaction can be understood from the depolarization field arisen due to the cylindrical shape of a SWCNT [13].

4. Numerical Results

Figure 2 shows absorption spectra of a SWCNT with diameter of 1 nm for perpendicular polarization. In this calculation, the overlap integral is $s = 0.18$, the hopping parameter is

![Figure 2. Absorption spectra with (solid line) and without (dotted line) e-h exchange interaction.](image1)

![Figure 3. Energy levels of bright (solid line) and quasi-dark (dotted line) states.](image2)
\( \gamma_0 = 2.7 \) eV, and the phenomenological damping constant is \( \Gamma = 10 \) meV at room temperature. Exciton states are calculated by using the screened Hartree-Fock approximation in terms of the effective-mass approximation [14]. In this method, the strength of the effective Coulomb interaction is characterized by \( \bar{v} = (e^2/\kappa_c L)/(2\pi \gamma/L) \) independent of \( L \) where \( \kappa_c \) is the effective static dielectric constant of the SWCNT, and the value is set to be \( \bar{v} = 0.15 \). The dotted line shows absorption spectrum of exciton without e-h exchange interaction, where two prominent peaks correspond to the optical transitions indicated by solid arrows in Fig. 1 (c). When the overlap integral is zero, these transitions are degenerate. The spectral shape is drastically changed by taking account of the e-h exchange interaction indicated by solid line. It is known that the spectral peak is suppressed and shifted to the higher energy side due to the depolarization effect [2]. In addition to the characteristic features, the number of prominent peaks reduces from two to one. Therefore, the signature of the two allowed transitions with different energy cannot be observed due to the large e-h exchange interaction. A tiny peak at 1.53 eV originates from a quasi-dark state.

Figure 2 shows the energy levels of the bright (solid line) and quasi-dark (dotted line) states for perpendicular polarization as a function of effective Coulomb interaction \( \bar{v} \). The effective Coulomb interaction between 0.1 and 0.2 well describes the experimental results. In this range, the level splitting of quasi-dark and bright states, which comes from the e-h exchange interaction, ranges from 100 to 200 meV.

5. Summary
I have studied absorption spectra of a SWCNT for perpendicular polarization in terms of the e-h exchange interaction. Because of (i) large oscillator strength of exciton due to the quasi 1D structure and (ii) characteristic cylindrical structure, a SWCNT exhibits quite large e-h exchange interaction in this configuration. It has been predicted that two absorption peaks for perpendicular polarization would be observed because of the asymmetry of conduction and valence bands [3]. However, the calculated result taking account of the e-h exchange interaction shows just one prominent peak. This drastic change comes from the large e-h exchange interaction of exciton in a SWCNT excited by a perpendicular polarization.

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