Optical Absorption in Collapsed Carbon Nanotubes

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The optical absorption spectra are calculated in collapsed carbon nanotubes, described by dynamical conductivity \( \sigma_{yy}(\omega) \) for the polarization of electric field parallel to the axis, and \( \tilde{\sigma}_{xx}(\omega) \) and \( \tilde{\sigma}_{yy}(\omega) \) perpendicular to the axis and parallel and perpendicular, respectively, to the flattened region. For \( \sigma_{yy}(\omega) \), clear interband peaks appear corresponding to band gaps between allowed bands. Inter-wall interaction due to collapsing causes splitting and shift of the peaks from uncollapsed tubes. Such effects are largest in nonchiral zigzag and armchair tubes, for which the spectra depends on the relative displacement in the flattened region, and rapidly decrease for tubes with chiral structure. Depolarization effect suppresses interband absorption in \( \tilde{\sigma}_{xx}(\omega) \) and \( \tilde{\sigma}_{yy}(\omega) \). For \( \tilde{\sigma}_{xx}(\omega) \), the rapid spatial variation of the effective electric field tends to reduce the absorption in the low energy region and shifts the threshold to higher energy than for \( \tilde{\sigma}_{yy}(\omega) \).

I. INTRODUCTION

Single-wall carbon nanotubes were synthesized\(^{1,2} \) a few years after the first discovery of nanotubes in a form of multi-wall cylinders.\(^{3,4} \) A single-wall nanotube changes from metallic to semiconducting depending on its tubular circumferential vector. The unique feature was first predicted in tight-binding models\(^{5-14} \) and was described also in an effective-mass scheme.\(^{15-17} \) When a diameter becomes sufficiently large, it has an additional stable structure with a partially flattened region. This collapsing has been demonstrated both experimentally\(^{18-32} \) and theoretically.\(^{33-54} \) The purpose of this work is to study optical absorption spectra of collapsed nanotubes within the effective-mass approximation.

The band structure of various collapsed nanotubes was previously studied within the effective-mass scheme.\(^{55} \) The results show that effects of collapse are small and almost negligible in chiral nanotubes, but cause strong modification depending on the relative displacement of flattened layers in nonchiral tubes such as zigzag and armchair. Strong effects on nonchiral tubes were further studied in a model of bilayer ribbons with closed edges.\(^{56} \) The orbital magnetic susceptibility of collapsed tubes was also studied.\(^{57} \)

The optical spectra, absorption and luminescence, have played decisive roles in understanding electronic states as well as the tube structure itself in cylindrical nanotubes.\(^{58-62} \) It is expected that the same is true of collapsed tubes. This paper is organized as follows: In Sect. II the method of calculations of the absorption spectra is discussed, after a brief review on effective-mass description of electronic states. Some examples of numerical results are shown in Sect. III. Results are discussed and summarized in Sect. IV.

II. FORMULATION

In graphene, a unit cell contains two carbon atoms denoted by A and B, and the conduction and valence bands consisting of \( \pi \) orbitals cross at K and K’ points of the Brillouin zone, where the Fermi level is located.\(^{63,64} \) Figure 1 shows the lattice structure and the first Brillouin zone of graphene. A unit cell contains two carbon atoms, denoted by A and B. The nanotube is specified by circumference vector \( \mathbf{L} \) or \((n_a, n_b)\), corresponding to the circumference. The shortest translational vector perpendicular to \( \mathbf{L} \) is denoted by \( \mathbf{T} \) or \((m_a, m_b)\). A rectangle formed by \( \mathbf{L} \) and \( \mathbf{T} \) is a unit cell of the nanotube and \( f \) is the family index.

![FIG. 1: (Color online) The lattice structure and the first Brillouin zone of graphene. The structure of a nanotube is specified by chiral vector \( \mathbf{L} \) or \((n_a, n_b)\), corresponding to the circumference. The shortest translational vector perpendicular to \( \mathbf{L} \) is denoted by \( \mathbf{T} \) or \((m_a, m_b)\). A rectangle formed by \( \mathbf{L} \) and \( \mathbf{T} \) is a unit cell of the nanotube and \( f \) is the family index.](image)

The optical absorption spectra are calculated in collapsed carbon nanotubes, described by dynamical conductivity \( \sigma_{yy}(\omega) \) for the polarization of electric field parallel to the axis, and \( \tilde{\sigma}_{xx}(\omega) \) and \( \tilde{\sigma}_{yy}(\omega) \) perpendicular to the axis and parallel and perpendicular, respectively, to the flattened region. For \( \sigma_{yy}(\omega) \), clear interband peaks appear corresponding to band gaps between allowed bands. Inter-wall interaction due to collapsing causes splitting and shift of the peaks from uncollapsed tubes. Such effects are largest in nonchiral zigzag and armchair tubes, for which the spectra depends on the relative displacement in the flattened region, and rapidly decrease for tubes with chiral structure. Depolarization effect suppresses interband absorption in \( \tilde{\sigma}_{xx}(\omega) \) and \( \tilde{\sigma}_{yy}(\omega) \). For \( \tilde{\sigma}_{xx}(\omega) \), the rapid spatial variation of the effective electric field tends to reduce the absorption in the low energy region and shifts the threshold to higher energy than for \( \tilde{\sigma}_{yy}(\omega) \).

We consider a nanotube partially flattened as illustrated in Fig. 2.\(^{55} \) The width of the flattened region is denoted by \( L_F \) and that of the curved region by \( L_C \). We have

\[
L_F + L_C = L.
\]
Curved Region  
(Monolayer)  
Flattened Region  
(Bilayer)  
Curved Region  
(Monolayer)  

FIG. 2: (Color online) A schematic illustration of a collapsed carbon nanotube and three configurations of electric field associated with incident light and corresponding dynamical conductivity.

We choose the x axis in the direction of \( \mathbf{L} \) and the y axis in the direction of \( \mathbf{T} \). The origin of the x coordinate in graphene is shifted from a B site by \( \zeta \). Then, the left hand side of the line \( x = 0 \) is folded down to form the lower half of the flattened nanotube \(-L/2 < x < 0\). The right hand side \( 0 < x < L/2 \) forms the upper half. The relative displacement between the top and bottom layers in the flattened region is characterized by \( \zeta \).

The effective-mass equation in a collapsed nanotube has been obtained as\(^5\)\(^5\)

\[
\mathcal{H}(\mathbf{k})\mathbf{F}(\mathbf{r}) + \int d\mathbf{r}' \mathcal{V}(\mathbf{r}, \mathbf{r}') \mathbf{F}(\mathbf{r}') = \varepsilon \mathbf{F}(\mathbf{r}),
\]

with

\[
\mathcal{H}(\mathbf{k}) = \begin{pmatrix} \mathcal{H}^K(\mathbf{k}) & 0 \\ 0 & \mathcal{H}^{K'}(\mathbf{k}) \end{pmatrix},
\]

\[
\mathcal{H}^K(\mathbf{k}) = \gamma(\sigma \cdot \mathbf{k}),
\]

\[
\mathcal{H}^{K'}(\mathbf{k}) = \gamma(\sigma^* \cdot \mathbf{k}),
\]

\[
\mathbf{F}(\mathbf{r}) = \begin{pmatrix} \mathbf{F}^K(\mathbf{r}) \\ \mathbf{F}^{K'}(\mathbf{r}) \end{pmatrix},
\]

with \( \mathbf{k} \equiv -i \nabla \) and Pauli matrices \( \sigma = (\sigma_x, \sigma_y) \). In the above, \( \gamma \) is a band parameter defined by \( \gamma \equiv \sqrt{3} \gamma_{0}/2 \) with \( \gamma_0 \) the lattice constant (0.246 nm) and the nearest-neighbor hopping integral \( \gamma_0 \) (\( \approx 2.7 \) eV), and \( \mathbf{F}^K(\mathbf{r}) \) and \( \mathbf{F}^{K'}(\mathbf{r}) \) are the two-component envelope wave functions for the K and K' points, respectively, satisfying

\[
\mathbf{F}^K(\mathbf{r} + \mathbf{L}) = e^{-2\pi i \nu/3} \mathbf{F}^K(\mathbf{r}),
\]

\[
\mathbf{F}^{K'}(\mathbf{r} + \mathbf{L}) = e^{+2\pi i \nu/3} \mathbf{F}^{K'}(\mathbf{r}),
\]

where \( \nu = 0 \) or \( \pm 1 \), determined by

\[
u_a + \nu_b = 3N + \nu,
\]

with integer \( N \).

Thus, in the absence of inter-wall interaction, the wave vector in the circumference direction for the K and K' points is quantized into

\[
k^K(\mathbf{r}) = \frac{2\pi}{L}(n - \nu),
\]

\[
k^{K'}(\mathbf{r}) = \frac{2\pi}{L}(n + \nu),
\]

with integer \( n \), and the energy bands become

\[
\varepsilon^K_n(k) = \pm \gamma \sqrt{n^2 + k^2},
\]

\[
\varepsilon^{K'}_n(k) = \pm \gamma \sqrt{n^2 + k^2},
\]

where \( k \) is measured from the K or K' point. This immediately leads to the conclusion that the nanotube before collapsing is a metal for \( \nu = 0 \) and a semiconductor for \( \nu = \pm 1 \). This property can also be specified by family index \( f \), defined by \( f = 2n_b - n_a \). The horizontal component of the chiral vector is \( \mathbf{L} \cdot \mathbf{a} = (1/2)fa \) as shown in Fig. 1. Because \( n_a + n_b = 3n_a - f \), tubes with a given value of \( f \) have the same value of \( \nu \), i.e., semiconducting or metallic independent of individual values of \( n_a \) and \( n_b \).

In general, the K and K' points are mixed with each other in the presence of inter-wall interaction in collapsed tubes. The \((4,4)\) matrix inter-wall potential is given by \( \mathcal{V}(\mathbf{r}, \mathbf{r'}) = V(\mathbf{r})\delta(\mathbf{r'} - \mathbf{r}) \), where \( \mathbf{r} \) is the mirror reflection of \( \mathbf{r} \) with respect to the line \( x = 0 \). These inter-wall potentials have been obtained in the previous work based on a tight-binding model. Typically, we have \( |V(\mathbf{r})| \lesssim \gamma_1 \), where \( \gamma_1 \) is the hopping integral between nearest-neighbor sites of neighboring layers in graphite (\( \gamma_1 = 0.4 \) eV).

In the following, we shall consider the dynamical conductivity describing interband optical absorption, extending the procedure developed in a previous work for uncollapsed tubes. There are various configurations in the polarization of incident light, as illustrated in Fig. 2. We shall neglect exciton effects, for which a brief discussion will be made in Sect. IV.

For the electric field parallel to the axis (the y polarization), the field \( E_y \) is uniform in the circumference direction and therefore the relevant conductivity is denoted as \( \sigma_{yy}(\omega) \), which represents induced current in the y direction. Using the Kubo formula,\(^5\)\(^5\) it is given by

\[
\sigma_{yy}(\omega) = \frac{g_e e^2 \gamma^2}{i \hbar A L} \sum_{\alpha \alpha'} (f_{\alpha} - f_{\alpha'}) |\langle \alpha' | \Sigma_y | \alpha \rangle|^2,
\]

with spin degeneracy \( g_s = 2 \), positive infinitesimal \( \delta \), and

\[
\Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & -\sigma_y \end{pmatrix},
\]

where \( A \) is the length of the tube, \( \alpha \) and \( \alpha' \) specify eigen states, \( \varepsilon_\alpha \) and \( \varepsilon_\alpha' \) are their energies, \( \varepsilon_\alpha - \varepsilon_\alpha' \), and \( f_\alpha \equiv f(\varepsilon_\alpha) \) is the Fermi distribution function.
For the field perpendicular to the axis, effective field $E_x(x, t)$ and therefore induced current $j_x(x, t)$ vary as a function of $x$ along the circumference. The resulting spatial charges and induced electric field strongly modify the optical spectra. This depolarization effect is known to play important roles in nanotubes.\textsuperscript{58} We shall define the Fourier series:

$$j_x(x, t) = \sum_{l} j_x(l) e^{-i\omega t} e^{2\pi i l x/L}, \quad E_x(x, t) = \sum_{l} E_x(l) e^{-i\omega t} e^{2\pi i l x/L}. \quad (16)$$

Then, we have

$$j_x(l) = \sum_{l'} \sigma_{xx}(l'; \omega) E_x(l'), \quad (18)$$

where the conductivity is given by

$$\sigma_{xx}(ll'; \omega) = \frac{q^2 e^2 \kappa^2}{ih} \frac{1}{\Delta l} \sum_{\alpha \alpha'} (f_\alpha - f_{\alpha'}) \times \langle \alpha | \Sigma_x e^{-2\pi i l x/L} | \alpha' \rangle \langle \alpha' | \Sigma_x e^{2\pi i l' x/L} | \alpha \rangle \frac{\varepsilon_{\alpha \alpha'}(\varepsilon_{\alpha \alpha'} + h\omega + i\delta)}{(\varepsilon_{\alpha \alpha'} + h\omega + i\delta)}, \quad (19)$$

with

$$\Sigma_x = \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix}. \quad (20)$$

The charge density, $\rho(x, t)$, corresponding to current density, $j_x(x, t)$, is determined by the equation of continuity:

$$\frac{\partial \rho(x, t)}{\partial t} + \frac{\partial}{\partial x} j_x(x, t) = 0, \quad (21)$$

and the corresponding potential $\phi(x, t)$ and electric field $E_{\text{ind}}(x, t)$ are given by

$$\phi(x, t) = \frac{2}{\kappa} \int_{x'} dx' \rho(x', t) \ln[R(x, x')], \quad (22)$$

$$E_{\text{ind}}(x, t) = -\frac{\partial \phi(x, t)}{\partial x}, \quad (23)$$

where $R(x, x')$ is the distance between $x$ and $x'$ and $\kappa$ is an effective dielectric constant. In bulk graphite we have $\kappa \approx 2.4,\text{66}$ and a comparison with two-photon absorption experiments places $\kappa$ should be close to this value.\textsuperscript{67} In the following, therefore, we shall use $\kappa = 2.5$ in explicit calculations as in previous works on excitons in uncollapsed nanotubes.\textsuperscript{67-70}

In the Fourier space, we have

$$E_{\text{ind}}^l(l) = -\frac{i}{2\pi} \frac{2\pi l}{L} \sum_{l', l''} V(ll') \frac{2\pi l''}{L} \sigma_{xx}(ll''; \omega) E_x(l''), \quad (24)$$

with Coulomb potential

$$V(ll') = -\frac{2L}{\kappa} \int dx' \int dx e^{-2\pi i(l-l')x/L} \ln[R(x, x')]. \quad (25)$$

In terms of $E_x^\text{ext}$ applied externally, we have

$$E_x(l) - E_x^\text{ext}(l) = \sum_{l'} \Pi(ll'; \omega) E_x(l'), \quad (26)$$

$$\Pi(ll'; \omega) = -\frac{i}{\omega} \frac{2\pi l''}{L} \sum_{l''} V(ll'') \frac{2\pi l''}{L} \sigma_{xx}(l''l', \omega). \quad (27)$$

The above is formally solved as

$$\hat{E}_x = \hat{\Xi}(\omega) \hat{E}_x^\text{ext}, \quad (28)$$

$$\hat{\Xi}(\omega) = [1 - \Pi(\omega)]^{-1}, \quad (29)$$

where $\hat{E}_x$ is the vector consisting of $E_x(l)$, and $\hat{\Pi}(\omega)$ and $\hat{\Xi}(\omega)$ are matrices consisting of $\Pi(ll'; \omega)$ and $\Xi(ll'; \omega)$, respectively. The induced current is written as

$$j_x(l) = \sum_{l'} \sigma_{xx}(ll'; \omega) E_x^\text{ext}(l'), \quad (30)$$

Then, the absorption intensity is proportional to

$$P = \int dx \text{Re} \left[ j_x(x, t) E_x^\text{ext}(x, t)^* \right] = \text{Re} \sum_{ll'} E_x^\text{ext}(l)^* \sigma_{xx}(ll'; \omega) E_x^\text{ext}(l'), \quad (31)$$

where we have used the fact that the induced electric field is completely out of phase with the induced current.

As shown in Fig. 2, we have two configurations, $E_\parallel$ and $E_\perp$, parallel and perpendicular to the flattened bilayer region, respectively. For the structure shown in Fig. 2, the effective field, given by the field component parallel to the circumference direction, is

$$E_\parallel(x) = \begin{cases} E_\parallel \sin \frac{4\varphi}{L_C} x & (0 < x < \frac{1}{2} L_C); \\ E_\parallel & (\frac{1}{2} L_C < x < \frac{1}{2} L - \frac{1}{2} L_C); \\ E_\parallel \sin \frac{4\varphi}{L_C} \left( \frac{L}{2} - x \right) & (\frac{1}{2} L - \frac{1}{2} L_C < x < \frac{1}{2} L), \end{cases} \quad (32)$$

and

$$E_\perp(x) = \begin{cases} E_\perp \cos \frac{4\varphi}{L_C} x & (0 < x < \frac{1}{4} L_C); \\ 0 & (\frac{1}{4} L_C < x < \frac{1}{2} L - \frac{1}{4} L_C); \\ -E_\perp \cos \frac{4\varphi}{L_C} \left( \frac{L}{2} - x \right) & (\frac{1}{2} L - \frac{1}{4} L_C < x < \frac{1}{4} L), \end{cases} \quad (33)$$

with $E_{\parallel}(x) = -E_{\perp}(x)$ and $E_{\perp}(x) = E_{\parallel}(x)$, where $\varphi$ is defined in Fig. 2. The corresponding Fourier coefficients are

$$E_{\parallel}(l) = \int dx \left[ E_\parallel \left\{ \frac{L_C}{4L} \left( \frac{\pi L_C}{2L} + \varphi \right)^{-1} \sin \left( \frac{\pi l L_C}{2L} + \varphi \right) - \left( \frac{\pi L_C}{2L} - \varphi \right)^{-1} \sin \left( \frac{\pi l L_C}{2L} - \varphi \right) \right] - \frac{1}{\pi} \cos \frac{\pi l L_C}{2L} \right], \quad (34)$$
For a uniform field perpendicular to the axis, we have $E(x) = E \cos(2\pi x/L)$ and therefore

$$\tilde{\sigma}_{xx}(\omega) = \sigma_{xx}(\omega) \left[ 1 + i \frac{(2\pi)^2}{\kappa \omega L} \sigma_{xx}(\omega) \right]^{-1},$$

with $\sigma_{xx}(\omega) \equiv \sigma_{xx}(l; \omega)$ for $l = \pm 1$, in agreement with the previous result.\(^5\)

Actually, the effective electric field in a collapsed nanotube varies in a way much smoother than that given by Eqs. (32) and (33), which are discontinuous at the boundaries between the flattened region and the curved region. This fact may be partially included by limiting the number of the Fourier coefficients for $E_x(l)$ and $E_x(l')$ to a small $l_{\text{max}}$, which will be chosen as $l_{\text{max}} = 10$ in following numerical calculations. Figure 3 shows some examples of the field distribution for $l_{\text{max}} = 10$, $\varphi = 5\pi/6$, and $L_F/L = 1/4$. It shows that discrete jumps in the field distribution are reasonably smoothed out by the present procedure. We can certainly perform more elaborate calculations once the exact form of the cross section is known.

Figure 4 shows the absolute value of the Fourier coefficient of $E_x(l)$ and $E_x(l')$ for $L_F/L = 1/4$, and the cross section of the nanotube in the inset. The dominant component is given by $l = \pm 1$ for the parallel configuration and by $l = \pm 3$ for the perpendicular configuration. As a result, dominant transitions contributing to $\tilde{\sigma}_{xx}(\omega)$ and $\tilde{\sigma}_{xx}(\omega)$ become different. This fact is demonstrated by absorption spectra of a nanotube with a collapsed form but without inter-wall interaction.

Figure 5 shows some examples of the absorption spectra in (a) semiconducting and (b) metallic carbon nanotubes with a collapsed form of $L_F/L = 1/4$ in the absence of inter-wall interaction. A phenomenological broadening $\Gamma = 0.07 \times (2\pi\gamma/L)$ has been introduced. The corre-
FIG. 5: (Color online) Some examples of the absorption spectra in (a) semiconducting and (b) metallic carbon nanotubes with a collapsed form of \( L_F/L = 1/4 \) in the absence of inter-wall interaction, and (c) cylindrical nanotubes. \( \Gamma (2\pi \gamma /L)^{-1} = 0.07 \). The band structure and dominant interband transitions for \( \sigma_{yy}(\omega) \), \( \sigma_{yx}(\omega) \), and \( \sigma_{xy}(\omega) \) are denoted by arrows in the top panel.

The corresponding band structure is shown in the top panel together with dominant interband transitions for \( \sigma_{yy}(\omega) \), \( \sigma_{xx}^{\parallel}(\omega) \), and \( \sigma_{xx}^{\perp}(\omega) \) being denoted by arrows. The results in nanotubes with cylindrical cross section are shown in Fig. 5(c). For the light polarization with electric field in the axis \( y \) direction, the absorption spectra given by \( \sigma_{yy}(\omega) \) are exactly the same as in cylindrical nanotubes.

For the polarization corresponding to \( \sigma_{xx}^{\parallel}(\omega) \) and \( \sigma_{xx}^{\perp}(\omega) \), the dominant transitions are given by \(|\Delta n|=1\) the same as in cylindrical tubes. For the polarization corresponding to \( \sigma_{xy}^{\parallel}(\omega) \) and \( \sigma_{xy}^{\perp}(\omega) \), the dominant transitions are given by \(|\Delta n|=3\) as has been shown in Fig. 4. In comparison with spectra in cylindrical tubes, \( \sigma_{xx}^{\parallel}(\omega) \) is enhanced and \( \sigma_{xx}^{\perp}(\omega) \) is reduced. The origin of this behavior is attributed mainly to the change in the effective electric field and partly to slight reduction in the depolarization effect due to the collapsed form.

In principle, small induced charges may appear varying in the axis direction with period \( 2\pi/T \) because of nonzero inter-wall potential. In armchair and zigzag nanotubes, these charges have a period of the order of lattice constant \( a \) and therefore can safely be neglected because \( L/a \gg 1 \). In chiral nanotubes, \( T \) can become as large as circumference \( L \). As has been shown in previous calculations, \( \Gamma \) however, effects of inter-wall interactions remain quite small in chiral nanotubes. Therefore, such effects will be neglected in this paper.

### III. NUMERICAL RESULTS

In following numerical calculations, we shall expand the wave functions in terms of those in uncollapsed tubes as has been made in previous works, \( \text{55,57} \). As has previously been shown, \( \text{55,57} \), the band structure depends on displacement \( \zeta \) only in nonchiral nanotubes such as zigzag and armchair. The same is true of optical spectra and \( \zeta \) is relevant only in zigzag and armchair nanotubes.

Figure 6 shows examples of the absorption spectra and corresponding band structure in the semiconducting case \( \nu = -1 \) with \( f = 142 \) in the vicinity of the zigzag and armchair structure. Here, we assume \( \zeta/a = 0 \) and have introduced a phenomenological broadening \( \Gamma = 0.05 \times \gamma_1 \). Obviously, no exact armchair structure is possible.

When a zigzag nanotube with \( (n_s,n_h) = (71,0) \) is collapsed as in (a), the band structure is strongly modified due to the inter-wall coupling in such a way that the tube becomes metallic because of the overlapping of the conduction and valence bands. In absorption spectra, the fundamental peak with the lowest energy \( (\hbar \omega/\gamma_1 \sim 0.44) \) in \( \sigma_{yy}(\omega) \) is considerably reduced, while other higher-energy peaks remain at the same energy with some broadening corresponding to energy splitting of relevant transitions shown in the upper panel. The disappearance of the fundamental peak is due to the crossing of the band edge.
with the Fermi level corresponding to the change from a semiconductor to a metal. This change is responsible to the appearance of a small low-energy peak ($\hbar\omega/\gamma_1 \sim 0.03$) in $\sigma_{yy}(\omega)$.

In Fig. 6(b) for $(n_a, n_b) = (72, 2)$, slightly away from the zigzag structure, the tube is semiconducting with band structure slightly modified from that in the uncollapsed tube. Accordingly, the two low-energy absorption peaks in $\sigma_{yy}(\omega)$ ($\hbar\omega/\gamma_1 \sim 0.4$ and 0.7) are slightly shifted to the lower energy side from those in the uncollapsed tube.
Effects of collapsing on the absorption in the high-energy region \(1.5 \lesssim \hbar \omega / \gamma_1 \lesssim 2.3\) are much stronger, and the two peaks of \(\sigma_{yy}(\omega)\) around \(\hbar \omega / \gamma_1 \approx 1.7\) and 2.2 in the uncollapsed tube are split into many smaller peaks. With the further increase of \(n_b\) or \(\eta\) as shown in (c), the features of the absorption characteristic of the uncollapsed semiconducting nanotube are quickly recovered except the slight increase in the broadening. The same behavior appears also in \(\sigma_{xx}(\omega)\) and \(\sigma_{zz}(\omega)\), i.e., they quickly become closer to the results of the tube with flattened form but without inter-wall interaction with the increase of \(\eta\).

In the vicinity of the armchair structure as shown in Figs. 6 (d), (e), and (f), all the tubes shown here remain semiconducting. Correspondingly, the absorption spectra in \(\sigma_{yy}(\omega)\) have a pair of low energy peaks common to those in uncollapsed semiconducting tubes, although their positions are considerably shifted to the low energy side in (f) closest to the armchair structure. This shift becomes smaller as the structure moves away from the armchair, i.e., (f) \(\rightarrow\) (e) \(\rightarrow\) (d), although the approach toward the uncollapsed tube is slower than in the vicinity of the zigzag nanotube. Essentially similar features can be seen in \(\sigma_{xx}(\omega)\) and \(\sigma_{zz}(\omega)\), although they remain not so clear because of the suppression of the peak structure due to the depolarization effect.

Figure 7 shows results for semiconducting zigzag nanotubes \((n_a, n_b) = (71, 0)\) and \(\nu = -1\) for \(\zeta/a = 1/4\) and \(1/\sqrt{3}\). The inset shows the lattice structure in the flattened bilayer region. The absorption spectra in \(\sigma_{yy}(\omega)\) for \(\zeta/a = 1/4\) (half-period) are quite different from those in the uncollapsed tube, corresponding to the fact that the band structure itself is different. On the other hand, those for \(\zeta/a = 1/\sqrt{3}\) look similar to those of the semiconducting tube with \(\zeta = 0\), except for a low-energy peak at \(\hbar \omega / \gamma_1 \approx 0.05\) in \(\sigma_{yy}(\omega)\), corresponding to the transition across a narrow gap at zero energy. Because of the suppression of peaks due to the depolarization effect, \(\sigma_{xx}(\omega)\) and \(\sigma_{zz}(\omega)\) do not show prominent features varying strongly as a function of \(\zeta/a\).

Figure 8 shows examples of the absorption spectra and corresponding band structure in the metallic case with \(f = 144\) and \(\nu = 0\) in the vicinity of the zigzag and armchair structure. Here, we again assume \(\zeta/a = 0\). The lattice structure in the bilayer region is shown in the inset for the zigzag and armchair structure. When a zigzag nanotube \((n_a, n_b) = (72, 0)\) is collapsed in (a), the band structure is strongly modified due to the inter-wall coupling, although the tube remains metallic because of the presence of linear bands at the Fermi level. However, effects of collapsing on the absorption spectra in \(\sigma_{yy}(\omega)\) are
FIG. 8: (Color online) Some examples of optical absorption spectra in collapsed metallic nanotubes with $f = 144$ and $\zeta/a = 0$, having near-zigzag and near-armchair structures. The solid and dashed lines represent the results in collapsed and uncollapsed tubes. The top panels show the band structure and dominant transitions denoted by $y$ and $x$, corresponding to $\sigma_{yy}(\omega)$ and $\sigma_{xx}(\omega)$, respectively. The insets show the lattice structure in the flattened bilayer region. (a) $(n_a, n_b) = (72, 0)$ and $\eta(\pi/6)^{-1} = 0.046$. (b) $(73, 2)$ and 0.092. (d) $(94, 44)$ and 0.930. (e) $(95, 46)$ and 0.965. (f) $(96, 48)$ and 1. $\Gamma/\gamma_1 = 0.05$. The insets in the top panel of (a) and (f) show the lattice structure in the flattened bilayer region.

not strong and just cause small downward shift of peaks in $\sigma_{yy}(\omega)$

With the increase of $\eta$, i.e., (a) $\rightarrow$ (b) $\rightarrow$ (c), the band structure quickly becomes close to that of uncollapsed nanotubes. Correspondingly, the fundamental absorption peak in $\sigma_{yy}(\omega)$ approaches that of the uncollapsed tube except that noticeable splitting appears for $(n_a, n_b) = (73, 2)$ shown in (b). Similar splitting also for a higher-energy peak in $\sigma_{yy}(\omega)$ and disappears more slowly than for the fundamental peak with the ini-
crease of $n_b$ or $\eta$. In fact, clear splitting appears in the second peak for $(n_a, n_b) = (74, 4)$ shown in (c).

In the armchair nanotube shown in (f), the absorption spectra given by $\sigma_{yy}(\omega)$ are strongly modified by collapsing and peaks appear corresponding to each band edge like in an uncollapsed semiconducting nanotube, although their distance is somewhat irregular corresponding to the feature of the band structure. When the structure moves away from the armchair to chiral, i.e., (f) $\rightarrow$ (e) $\rightarrow$ (d), effects of inter-wall interactions are rapidly reduced, although the reduction rate is somewhat smaller in the vicinity of the zigzag structure.

In fact, the splitting in the fundamental peak at $\hbar\omega/\gamma_1 \sim 1.3$ in (e) is more prominent than in (b) and the shift of the fundamental peak in (d) is larger than in (c). Furthermore, a low-energy absorption similar to the Drude conductivity appears in (e) and (f) quite in contrast to (b) and (c). This low-energy absorption becomes smaller and disappears away from the armchair structure.

In the armchair nanotube shown (f), the absorption in $\sigma_{xx}^\parallel(\omega)$ and $\sigma_{yy}^\perp(\omega)$ starts at lower energy than in uncollapsed nanotubes. This low-energy threshold is slowly shifted to higher energy side with the increase in the deviation from the armchair structure, i.e., (f) $\rightarrow$ (e) $\rightarrow$ (d), and slowly disappears. In general, for $\sigma_{xx}^\parallel(\omega)$ and $\sigma_{yy}^\perp(\omega)$, the most prominent feature of collapsing appears in the change in the shape of the cross section because of the suppression of peaks due to the depolarization effect. This feature is exactly the same as in the case of semiconducting nanotubes.

IV. DISCUSSION AND SUMMARY

The optical absorption spectra have been calculated in collapsed nanotubes for different electric-field configurations of incident light, corresponding to $\sigma_{yy}(\omega)$ for the field parallel to the axis, $\sigma_{xx}^\parallel(\omega)$ and $\sigma_{yy}^\perp(\omega)$ for the field perpendicular to the axis and parallel and perpendicular, respectively, to the flattened bilayer region. For $\sigma_{xx}^\parallel(\omega)$, the rapid spatial variation of the effective electric field tends to reduce the absorption in the low energy region and shift the threshold to the higher energy than for $\sigma_{xx}^\perp(\omega)$.

In chiral nanotubes, calculated results show small and almost negligible effects of collapsing except for the modification of the effective electric field due to the change in the cross section when the electric field of light is perpendicular to the axis. This fact is well correlated with the band structure itself. In chiral nanotubes, inter-wall hopping becomes negligibly small due to cancellation caused by rapid and quasi-periodic variation of its phase for states in the vicinity of the K and K’ points except in some special cases.\footnote{S. Iijima and T. Ichihashi, Nature (London) 363, 603}

For zigzag and armchair nanotubes, such cancellation does not take place and the band structure and associated optical spectra are strongly modified by collapsing, depending on relative displacement of two layers in the flattened region.\footnote{S. Iijima and T. Ichihashi, Nature (London) 363, 603}

The top panel of Fig. 8(a) shows that two sets of linear bands crossing at zero energy in the collapsed nanotube lie outside the linear bands in the uncollapsed nanotube. A similar behavior can be seen in Figs. 6(a) and 7(b). Furthermore, this feature is partly true of the lowest conduction bands in Figs. 7(a) and 8(f). These results show that the corresponding wave vector in the circumference direction becomes imaginary in the curved monolayer region. [See ref. 56 for more details.]

This means that the wave function exponentially decays in the monolayer region and tends to have large amplitude in the flattened bilayer region, i.e., states in the vicinity of the Fermi level in collapsed zigzag and armchair nanotubes have characters originating from those in a bilayer region rather than those in a monolayer region. This is the reason that the electronic states are strongly affected by inter-wall interaction and dependent on relative displacement $\zeta$ in the bilayer region in nonchiral nanotubes.

Theoretical calculations based on various models and first-principles\footnote{S. Iijima and T. Ichihashi, Nature (London) 363, 603} seem to suggest that the cross section of a collapsed nanotube looks somewhat flatter in the curved monolayer region than that shown in Fig. 2 and the inset of Fig. 4. This difference in the actual form of the cross section is likely to enhance and reduce the effective electric field in the perpendicular and parallel configurations, respectively, and therefore tends to increase the anisotropy between $\sigma_{xx}^\parallel(\omega)$ and $\sigma_{yy}^\perp(\omega)$.

One of the most prominent features of optical properties of nanotubes appears in the large binding energy of excitons due to the one-dimensional nature of the electron motion.\footnote{S. Iijima and T. Ichihashi, Nature (London) 363, 603} The electron-hole interaction responsible to the exciton formation is known to be strongly modified by the screening. It is expected that the absorption spectra are strongly modified when the tube turns into metallic or semiconducting due to collapsing, although the exciton with small binding energy is known to survive in metallic nanotubes.\footnote{S. Iijima and T. Ichihashi, Nature (London) 363, 603} Furthermore, the exciton leads to a sharp absorption peak in the geometry with electric field perpendicular to the axis and parallel and perpendicular configurations, respectively, and therefore tends to increase the anisotropy between $\sigma_{xx}^\parallel(\omega)$ and $\sigma_{yy}^\perp(\omega)$.

Unfortunately, theoretical calculations of spectra with exciton effects are quite tedious and time-consuming, but certainly possible when the actual structure of a collapsed nanotube is given. This problem is left for a future study.

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