Exciton scattering from impurities and acoustic phonons in carbon nanotubes

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Exciton scattering from impurities and acoustic phonons in semiconducting carbon nanotubes is theoretically studied in an effective-mass approximation. A selection rule for transitions resulting from the scattering is obtained, showing that the ground-state exciton for the lowest-exciton band is never scattered from long-range impurities and deformation potentials near the band edge. This arises from the symmetry of nanotubes for the successive transformations of the charge conjugation and parity and for the reflection of the coordinate along the nanotube axis. Agreement of numerical results with recent experiments supports the validity of this selection rule.

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I. INTRODUCTION

In optical excitation of semiconductors and insulators, pairs of an electron and hole are created. In many materials, the electrons and holes are not symmetric because of asymmetric conduction and valence bands. However, carbon nanotubes are one of the systems where the electrons and holes are approximately symmetric. Electronic states near the Fermi energy in carbon nanotubes are well described by an equation similar to the massless Dirac equation, i.e., the Weyl equation, with a boundary condition around the circumference of the nanotubes.¹ In this paper, we theoretically show that the symmetry of semiconducting carbon nanotubes can significantly reduce scattering of photoexcited electron-hole bound states called excitons from disorders and acoustic phonons.

In the optical response of carbon nanotubes, exciton effects are crucial because of strong effects of the Coulomb interaction in one dimension.^{2–11} The optical response of the nanotubes is anisotropic where light polarized in parallel to the nanotube axis strongly excites excitons as compared to perpendicular polarization.^{4,6,12–14} For the excitons excited for the parallel polarization, electrons and holes are well associated with specific symmetric conduction and valence subbands with respect to the Fermi energy. Such excitons consisting of electrons and holes in the i th-lowest conduction and the i th-highest valence subbands, respectively, are denoted as E_{ii} excitons. Photoluminescence, which is often used to study the optical response of nanotubes, is obtained from the ground-state E_{11} exciton with the lowest energy.⁹

Excitons in carbon nanotubes are mobile and scattered. At low-exciton densities, the interaction of excitons with disorders and phonons plays an important role in nonradiative processes. So far, many theoretical studies on this subject have been reported which include, for example, excitons trapped by impurity potentials,^{15,16} phonon side bands for exciton peaks in optical spectra,¹⁷ the interaction of excitons with acoustic and optical phonons in zigzag nanotubes,¹⁸ and the chirality dependence of the Raman scattering intensity for the breathing-mode phonons.^{19,20}

Experimentally, transition rates,^{21–24} the linewidth of exciton peaks,^{25–27} and diffusion constants and diffusion lengths^{28–35} have been intensively studied for excitons interacting with disorders and phonons in nanotubes. The results strongly depend on the experiments. Length scales associated

with exciton diffusion range from several tens of nanometers for nanotubes wrapped with surfactants²⁸ to several hundreds of nanometers for suspended individual nanotubes.³² One possible reason for this variation is that the exciton scattering is dominated by scattering from disorders, which can vary sample by sample in nature, depending on synthesis methods, surrounding environments, and so on.

On the other hand, exciton-phonon scattering in nanotubes is considered to be less dependent on samples than exciton-disorder scattering. The exciton-phonon scattering emerges as a temperature-dependent part of the transition rate and the energy broadening while the exciton-disorder scattering is independent of temperature. The temperature dependencies of the transition rate or energy broadening for excitons near band edges are monotonically increasing functions, which have been attributed to scattering from acoustic phonons around the Γ point and analyzed by using linear functions, sometimes plus the Bose-Einstein distribution with a constant phonon frequency.^{24–27} Recent experiments on the exciton-acoustic-phonon scattering using nanotubes with an almost unique chirality²⁴ or single isolated nanotubes^{25,26} are suitable to quantitative comparison between experiments and theories.

The exciton scattering from disorders and acoustic phonons around the Γ point, which is elastic and quasielastic, respectively, is expected to be the dominant origin for the energy broadening of the excitons. The purpose of this paper is to theoretically clarify the exciton scattering from these two kinds of scatterers in semiconducting carbon nanotubes in an effective-mass approximation. The paper is organized as follows: In Sec. II, a model and method are presented. Numerical results are presented in Sec. III and discussed in Sec. IV. Conclusions are given in Sec. V.

II. MODEL AND METHOD**A. Effective-mass approximation**

In this study, nanotubes are modeled as graphenes with periodic boundary conditions in the circumference direction of the nanotubes. The structure of the nanotubes is specified by chiral vector $\mathbf{L}$, which defines the circumference of the nanotubes on the graphenes. The Fermi energy of graphenes is located at the two valleys: K and K' points. Electrons around these points are well described by an equation similar to the

Weyl equation in an effective-mass approximation. For the K point, it is written as^{1,36}

$$\gamma(\vec{\sigma} \cdot \hat{\mathbf{k}})\mathbf{F}^K(\mathbf{r}) = \varepsilon^K \mathbf{F}^K(\mathbf{r}), \quad (1)$$

where γ is a band parameter, $\vec{\sigma}^T = (\sigma_x, \sigma_y)$ the Pauli spin matrices, $\hat{\mathbf{k}}^T = (\hat{k}_x, \hat{k}_y) = -i\vec{\nabla}^T$ the wave-vector operator, $\mathbf{F}^K(\mathbf{r})$ a two-component envelope function resulting from the A and B sublattices at position $\mathbf{r}^T = (x, y)$ with the x and y coordinates being in the circumference and axis directions, respectively, and ε^K an eigenenergy measured from the Fermi energy. The electronic states of the nanotubes are obtained by imposing the boundary conditions around the circumference direction with the effective magnetic flux $\nu/3$, where $\nu = 0, \pm 1$ which is determined by $\mathbf{L}$.¹ This leads to discretization of the wave vector in the circumference direction κ^K , which specifies the conduction and valence subbands.

The eigenfunction is written as

$$\mathbf{F}_{\pm}^K(\mathbf{r}) = \frac{1}{\sqrt{2AL}} \begin{pmatrix} b_k^K \\ \pm 1 \end{pmatrix} e^{i\kappa^K x + iky}, \quad (2)$$

with

$$\kappa^K = \frac{2\pi}{L} \left(n - \frac{\nu}{3} \right), \quad b_k^K = \frac{\kappa^K - ik}{|\kappa^K - ik|}, \quad (3)$$

where k is the wave vector in the axis direction, $L = |\mathbf{L}|$, A the nanotube length, $\pm$ denotes the conduction (+) and valence (−) bands, $n = 0, \pm 1, \dots$, and the origins of the wave vectors are chosen at the K point. The corresponding eigenenergy is given by

$$\varepsilon_{\pm, k}^K = \pm \gamma \sqrt{(\kappa^K)^2 + k^2}. \quad (4)$$

The nanotubes are metallic for $\nu = 0$ and semiconducting for $\nu = \pm 1$. The eigenenergy has reflection symmetries about the axes of $\varepsilon_{\pm, k}^K = 0$ and $k = 0$.

For the K' point, the Hamiltonian is the complex conjugate of that for the K point and the sign of the effective magnetic flux for the boundary condition is inverted. The eigenfunctions and eigenenergies are given by those for the K point with the replacements of $\kappa^K \rightarrow \kappa^{K'}$ and $b_k^K \rightarrow b_k^{K'}$ where

$$\kappa^{K'} = \frac{2\pi}{L} \left(n + \frac{\nu}{3} \right), \quad b_k^{K'} = \frac{\kappa^{K'} + ik}{|\kappa^{K'} + ik|}. \quad (5)$$

Thus, the subband with $\kappa^{K'}$ at the K' point is degenerated with that with $\kappa^K = -\kappa^{K'}$ at the K point.

The Hamiltonian for each valley is invariant under the successive transformations of the charge conjugation and parity (CP) as is well known and also under the reflection $y \rightarrow -y$ with the exchange of the A and B sublattices. The CP transformation plus this reflection changes an electron state specified by $(\kappa^\zeta, k, \varepsilon^\zeta)$ to the hole state for the vacancy of the electron specified by $(\kappa^\zeta, -k, -\varepsilon^\zeta)$ where $\zeta = \{K, K'\}$. This symmetry is weakly broken in real systems, which can be included in the effective-mass approximation by higher-order corrections.³⁷

B. Interaction with impurities and acoustic phonons

Because of the two valleys and the two sublattices, interaction terms in the Hamiltonian for electrons take the

form of 4×4 matrices, whose elements are denoted as $V_{\sigma\tau}^{\zeta\xi}$ with $\zeta, \xi = \{K, K'\}$ and $\sigma, \tau = \{A, B\}$ where $V_{\tau\sigma}^{\xi\zeta} = V_{\sigma\tau}^{\zeta\xi*}$. All the 16 elements can appear in the interaction with disorders and/or that with phonons.

The interaction with disorders such as impurities and lattice vacancies can be introduced by local impurity potentials.^{38,39} In this case, the intersublattice elements vanish, $V_{AB}^{\zeta\xi} = 0$, because local potentials are diagonal with respect to positions. In the case of long-range impurities with extensions larger than the lattice constant, the intervalley elements vanish, $V_{\sigma\tau}^{KK'} = 0$, and all the intrasublattice elements are same between the A and B sublattices in the same unit cell, $V_{AA}^{KK} = V_{BB}^{KK} = V_{AA}^{K'K'} = V_{BB}^{K'K'}$, because they consist of Fourier transforms with long wavelengths only.

For the interaction with phonons, various theories have been reported.^{40–45} In this study, we use a continuum model of phonons.^{46,47} An important contribution arises from the change of the bond length between the nearest-neighboring carbon atoms on the A and B sublattices, leading to the finite intersublattice elements $V_{AB}^{\zeta\xi}$ and the vanishing intrasublattice ones $V_{\sigma\sigma}^{\zeta\xi} = 0$. In the case of acoustic phonons with much smaller wave vectors than the reciprocal lattice vectors, deformation potentials with long ranges are added, for which $V_{AA}^{KK} = V_{BB}^{KK} = V_{AA}^{K'K'} = V_{BB}^{K'K'}$ and $V_{AB}^{\zeta\xi} = 0$. The deformation potentials have the same form as that of the long-range impurities.

In the numerical calculations in Sec. III, we use impurities with sufficiently short ranges which are distributed on the A and B sublattices. These are written for the intravalley elements as³⁸

$$V_{\sigma\sigma}^{\zeta\xi} = \sum_{j=1}^{N_{i\sigma}} v_{\sigma j} \delta(\mathbf{r} - \mathbf{r}_{\sigma j}), \quad (6)$$

and for the intervalley ones $V_{AA}^{KK'} = e^{i\eta} V_{AA}^{KK}$ and $V_{BB}^{KK'} = e^{-i(\eta-\pi/3)} V_{BB}^{KK}$, where $v_{\sigma j}$ is the potential amplitude integrated over the nanotube surface for an impurity at the j th σ site at position $\mathbf{r}_{\sigma j}$ and $N_{i\sigma}$ the number of impurities at the σ sites. For the long-range impurities, we use³⁸

$$V_{\sigma\sigma}^{\zeta\xi} = \sum_{j=1}^{N_i} v_j \delta(\mathbf{r} - \mathbf{r}_j), \quad (7)$$

where v_j is the amplitude integrated over the nanotube surface of the j th impurity potential centered at position $\mathbf{r}_j$ and N_i the number of impurities.

We use impurity potentials whose positions and amplitudes are distributed at random where the short-range impurities are distributed on the A and B sublattices with an equal probability. For the short- and long-range impurities, we denote the average of the squared absolute value of the potential amplitude integrated over the nanotube surface as $\langle v^2 \rangle$ and the average number of impurities per unit area as $\langle n \rangle$, and the average amplitude of the potentials is set to zero.

The values of $\langle v^2 \rangle$ and $\langle n \rangle$ strongly depend on samples. For reference, we give an example for moderate doping by nitrogen substitutions where $\langle v^2 \rangle \sim (3 \text{ eV} \times S)^2$ with $S = \sqrt{3}a^2/4$ being the area for one carbon atom⁴⁸

and $\langle n \rangle = n_a/S \sim 0.001/S$ with n_a being the ratio between the numbers of impurities and carbon atoms which is set to be one order of magnitude smaller than that for heavy doping $n_a \sim 0.01$.^{49,50} It is marginal if the potential range for nitrogen substitutions is long or short since it is of the order of the lattice constant.⁴⁸ In the following, we will give results as realistic examples by using these values irrespective of the potential ranges for simplicity.

Since only elastic and quasielastic scattering of excitons is studied in the following, the intravalley interaction with the acoustic phonons with small wave vectors is considered.⁴⁶ Its intrasublattice elements, i.e., the deformation potentials, which are independent of the valleys and sublattices, are written as

$$V_{\sigma\sigma}^{\zeta\zeta} = g_1(u_{xx} + u_{yy}), \quad (8)$$

and its intersublattice elements due to the bond-length change are written as

$$V_{AB}^{KK} = g_2(u_{xx} - u_{yy} + 2iu_{xy})e^{3i\eta}, \quad (9)$$

and $V_{AB}^{K'K'} = -V_{AB}^{KK*}$ where g_1 and g_2 are coupling constants, u_{xx} , u_{yy} , and u_{xy} the elements of a strain tensor, and η the chiral angle,¹ which is determined by $\mathbf{L}$ and is 0 and $\pi/6$ for zigzag and armchair nanotubes, respectively. The elements of the strain tensor are given by

$$\begin{aligned} u_{xx} &= \frac{\partial u_x}{\partial x} + \frac{2\pi u_z}{L}, & u_{yy} &= \frac{\partial u_y}{\partial y}, \\ u_{xy} &= \frac{1}{2} \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right), \end{aligned} \quad (10)$$

where $(u_x, u_y, u_z) = \mathbf{u}^T$ is the displacement vector with the z axis being normal to the nanotube surface. It should be noted that Eq. (9) depends on the chiral angle η , although the electronic states in the lowest-order effective-mass approximation are independent of the chiral angle as shown in Eq. (1).

The displacement vector is written in the second quantization form as

$$\mathbf{u} = \sum_g \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2N_u M_c \omega_{g,\mathbf{q}}}} (b_{g,\mathbf{q}} + b_{g,-\mathbf{q}}^\dagger) \mathbf{e}_{g,\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (11)$$

where $b_{g,\mathbf{q}}$ and $b_{g,\mathbf{q}}^\dagger$ are, respectively, annihilation and creation operators of the phonon with mode g and wave vector $\mathbf{q}^T = (q_x, q_y)$, N_u the number of unit cells in the nanotube, M_c the mass of the carbon atom, $\mathbf{e}_{g,\mathbf{q}}$ the unit vector along the displacement vector for the phonon with g and $\mathbf{q}$. When quasielastic scattering is considered, only phonons with low energies, i.e., with the zero circumferential wave vector $q_x = 0$, and the small wave vectors in the axis direction q_y with $q_y L/2\pi \ll 1$ can be important. There are three modes in the low-energy region which are denoted as twisting ($g = 1$), stretching ($g = 2$), and breathing ($g = 3$) modes. For these

three modes, $\mathbf{e}_{g,\mathbf{q}}$ is given by

$$\begin{pmatrix} e_{1x} \\ e_{1y} \\ e_{1z} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad (12)$$

$$\begin{pmatrix} e_{2x} \\ e_{2y} \\ e_{2z} \end{pmatrix} = C_2 \begin{pmatrix} 0 \\ 1 \\ (M\omega_-^2 - A_{yy})/A_{yz} \end{pmatrix}, \quad (13)$$

$$\begin{pmatrix} e_{3x} \\ e_{3y} \\ e_{3z} \end{pmatrix} = C_3 \begin{pmatrix} 0 \\ (M\omega_+^2 - A_{zz})/A_{yz}^* \\ 1 \end{pmatrix}, \quad (14)$$

with the subscript $\mathbf{q}$ of $\mathbf{e}_{g,\mathbf{q}}$ being eliminated for simplicity, C_2 and C_3 being the normalization factors, M being the carbon mass per unit area, and

$$A_{yy} = (B + \mu)q_y^2, \quad A_{zz} = \frac{4\pi^2(B + \mu)}{L^2}, \quad (15)$$

$$A_{yz} = -\frac{2\pi i(B - \mu)q_y}{L},$$

$$\omega_{\pm}^2 = \frac{1}{2M} [A_{yy} + A_{zz} \pm \sqrt{(A_{yy} - A_{zz})^2 + 4|A_{yz}|^2}], \quad (16)$$

where A_{yy} , A_{zz} , and A_{yz} are the elements of the dynamical matrix and B and μ the bulk and shear moduli, respectively. The eigenfrequencies of the three modes are given by

$$\omega_{1,\mathbf{q}} = \sqrt{\frac{\mu}{M}} |q_y|, \quad \omega_{2,\mathbf{q}} = |\omega_-|, \quad \omega_{3,\mathbf{q}} = |\omega_+|. \quad (17)$$

The deformation potential vanishes for the twisting mode because $u_{xx} = u_{yy} = 0$.

In the following, we use $B/M = 2.90 \times 10^8 \text{ m}^2/\text{s}^2$ and $\mu/M = 1.51 \times 10^8 \text{ m}^2/\text{s}^2$.^{46,47} In the limit of $q_y \rightarrow 0$, the frequencies of the twisting and stretching modes are linear in $|q_y|$ whose group velocities are two orders of magnitude smaller than those for the linear dispersion of the graphenes $\gamma/\hbar$, while the frequency for the breathing mode becomes a constant, which is inversely proportional to the tube diameter and typically a few tens of meV. The constants g_1 and g_2 , are considered to be ~ 20 – 30 eV and ~ 1.5 eV, respectively.^{46,47} A recent study⁵¹ reported the smaller value $g_1 \approx 14$ eV, which is still one order of magnitude larger than g_2 .

C. Excitons

An exciton specified by a center-of-mass wave vector in the axis direction k_c and $u = (\zeta, \xi, j)$ where ζ and ξ denote the valleys for the electron and hole, respectively, and j is the index for the other degrees of freedom, is written by a superposition of electron-hole pair states as^{2,12}

$$|uk_c\rangle = \sum_k \psi_{k+k_c,k}^u c_{+,\kappa^\zeta,k}^\dagger c_{-,\kappa^\xi,k}^\dagger |g\rangle, \quad (18)$$

where $\psi_{k+k_c,k}^u$ is the expansion coefficient, $c_{+,\kappa^\zeta,k}^\dagger$ ($c_{-,\kappa^\xi,k}^\dagger$) the creation (annihilation) operator for the electron in the conduction (valence) band with wave vectors κ^ζ and k at valley ζ , and $|g\rangle$ the ground state. There are two types of excitons such as intravalley excitons for $\zeta = \xi$ and intervalley ones for $\zeta \neq \xi$. Since each exciton is well associated with specific

subbands, κ^ζ and κ^ξ can be fixed to these subbands. However, the following results do not depend on this simplification. We restrict ourselves to the excitons where the electron and hole belong to symmetric subbands about the Fermi energy, i.e., $\kappa^\zeta = \pm\kappa^\xi$ for the intravalley (+) and intervalley (−) excitons. For each κ^ξ , there exists a series of excitons such as the ground-state exciton, the first-excited exciton, etc. Only singlet spin states are considered. Details of the calculations of the excitons are presented in previous studies^{2,12} and in the Appendix.

The electron-hole pair state of the basis for $\psi_{k+k_c, k}^u$, which has the center-of-mass wave vector k_c , is transformed to that for $\psi_{-k, -k-k_c}^u$ with the same center-of-mass wave vector by the CP transformation plus the reflection of the y coordinate mentioned in Sec. II A. In the absence of the Coulomb interaction, these two states are degenerated. The Coulomb interaction does not break the symmetry for these two transformations, but the excitons are not degenerated because of mixing the electron-hole pair states with different energies. Since the excitons are eigenstates of the successive operations of the two transformations, we have

$$\psi_{-k, -k-k_c}^u = \pm \psi_{k+k_c, k}^u, \quad (19)$$

where even (+) and odd (−) symmetries are uniquely determined by u and independent of k_c . For a given κ^ξ in Eq. (18), the ground-state exciton, the second-excited exciton, . . . have the even symmetry while the first-excited exciton, the third-excited exciton, . . . have the odd symmetry.

In calculations of the self-energy for the Coulomb interaction, a cutoff energy of the order of the π band width $\varepsilon_c \approx 3\gamma_0$ is introduced² where γ_0 is the resonance integral between π orbitals at the nearest-neighboring atoms which is related to γ as $\gamma = \sqrt{3}\gamma_0 a/2$ with $a = 2.46$ Å being the lattice constant. In the following, $\varepsilon_c(2\pi\gamma/L)^{-1} = (\sqrt{3}/\pi)(L/a) = 10$ is used as a typical nanotube with a diameter of 1.4 nm unless otherwise specified, where $2\pi\gamma/L$ is a typical kinetic energy and $\varepsilon_c(2\pi\gamma/L)^{-1}$ determines L/a . The strength of the Coulomb interaction is characterized by a background dielectric constant κ . According to previous studies,^{52,53} we use $(e^2/\kappa L)(2\pi\gamma/L)^{-1} = 1.5$ for $\kappa \approx 2.6$ with $\gamma = 5.8$ eV Å ($\gamma_0 = 2.7$ eV).

D. Transition matrix elements and a selection rule

Matrix elements of the interaction with impurities or phonons V between the exciton with the wave vector k_c and $u = (\zeta, \xi, j)$ and that with k'_c and $u' = (\zeta', \xi', j')$ are given by

$$\begin{aligned} & \langle u'k'_c | V | uk_c \rangle \\ &= \sum_{i=1}^2 \sum_k [\delta_{\xi'\xi} \psi_{k+k'_c, k}^{u'*} \psi_{k+k_c, k}^u V_{i+}^{\zeta'\zeta}(k+k'_c, k+k_c) \\ & \quad - \delta_{\zeta'\zeta} \psi_{-k, -k-k'_c}^{u'*} \psi_{-k, -k-k_c}^u V_{i-}^{\zeta'\zeta}(-k-k'_c, -k-k_c)], \end{aligned} \quad (20)$$

where $V_{i\pm}^{\zeta'\zeta}(k', k)$ denotes the transition matrix elements of the intrasublattice ($i = 1$) and intersublattice ($i = 2$) elements of the interaction between one-particle states with k at valley ζ and with k' at valley ζ' in the conduction (+) and valence (−)

bands, which is given by

$$\begin{aligned} V_{1+}^{\zeta'\zeta}(k', k) &= V_{1-}^{\zeta'\zeta}(k', k) \\ &= \frac{1}{2} [b_{k'}^{\zeta'*} b_k^{\zeta} V_{AA}^{\zeta'\zeta}(k' - k) + V_{BB}^{\zeta'\zeta}(k' - k)], \end{aligned} \quad (21)$$

$$V_{2\pm}^{\zeta'\zeta}(k', k) = \pm \frac{1}{2} [b_{k'}^{\zeta'*} V_{AB}^{\zeta'\zeta}(k' - k) + b_k^{\zeta} V_{BA}^{\zeta'\zeta}(k' - k)], \quad (22)$$

with

$$V_{\sigma'\sigma}^{\zeta'\zeta}(k) = \frac{1}{AL} \int_0^L dx \int_0^A dy V_{\sigma'\sigma}^{\zeta'\zeta} e^{-i(\kappa^{\zeta'} - \kappa^\zeta)x -iky}. \quad (23)$$

The following relations are satisfied:

$$V_{1-}^{\zeta'\zeta}(-k', -k) = V_{1-}^{\bar{\zeta}\bar{\zeta}}(-k', -k) = V_{1+}^{\zeta'\zeta}(k, k'), \quad (24)$$

where $\bar{\zeta}$ denotes the valley other than that denoted by ζ and $b_{-k}^{\zeta} = b_k^{\zeta*} = -b_{-k}^{\bar{\zeta}}$ for $\kappa^{\bar{\zeta}} = -\kappa^\zeta$ is used. The first and second terms on the right-hand side of Eq. (20) describe scattering of the electron and hole, respectively, where the different signs reflect the different charges of the electron and hole.

Intravalley scattering is considered for the intravalley and intervalley excitons, where the valleys for the electrons and holes of the excitons are the same between the initial and final states, i.e., $\zeta' = \zeta$ and $\xi' = \xi$ in Eq. (20). In this case, the electron and hole scattering processes coexist to interfere with each other. Because of Eq. (19), the absolute value of the product of the expansion coefficients in the electron scattering term in Eq. (20) is the same as that of the hole scattering term, while the signs of the two products are the same or different, depending on whether the symmetries of the initial and final states are the same or different. Thus, because of Eq. (24), scattering due to the intrasublattice elements of the interaction vanishes between the excitons with the same symmetry both for the intravalley and intervalley excitons.

This selection rule especially shows that both the lowest intravalley and intervalley ground-state excitons are not scattered from the intravalley intrasublattice elements such as the long-range impurities and the deformation potentials far below the band bottom of the first-excited exciton. This is because final states with the different symmetry from that of the ground-state exciton do not exist in this energy regime.

E. Energy broadening

Transition rates associated with scattering of the exciton denoted by $|uk_c\rangle$ from the impurities and phonons $1/\tau_i$ and $1/\tau_p$, respectively, are given by using Fermi's golden rule as

$$\frac{1}{\tau_i} = \frac{2\pi}{\hbar} \sum_{u'k'_c} |\langle u'k'_c | V | uk_c \rangle|^2 \delta(E_{uk_c} - E_{u'k'_c}), \quad (25)$$

$$\begin{aligned} \frac{1}{\tau_p} &= \frac{2\pi}{\hbar} \sum_g \sum_{u'k'_c} |\langle u'k'_c | V | uk_c \rangle|^2 \{ \delta(E_{uk_c} - E_{u'k'_c} + \hbar\omega_g) \\ & \quad \times n(\omega_g) + \delta(E_{uk_c} - E_{u'k'_c} - \hbar\omega_g) [n(\omega_g) + 1] \}, \end{aligned} \quad (26)$$

where $\langle \dots \rangle_{en}$ denotes the average over the impurity positions, and for the phonon scattering, g runs over the three phonon modes and the first and second terms in the curly brackets indicate phonon absorption and emission processes, respectively, with ω_g and $n(\omega_g)$ being the frequency of the phonons and the Bose-Einstein distribution function, respectively. The

corresponding energy broadening is given by $\Gamma_i = \hbar/\tau_i$ and $\Gamma_p = \hbar/\tau_p$.

The energy conservation described by the delta functions in Eqs. (25) and (26) is smeared by the finite lifetime of the excitons. The effect of the lifetime which arises from a dominant scattering mechanism can be phenomenologically introduced by the imaginary part of the exciton energy $-i\Gamma_l/2$, with Γ_l being the energy broadening associated with the lifetime, leading to replacements, for example, in Eq. (26),

$$\delta(E_{uk_c} - E_{u'k'_c} \pm \hbar\omega_g) \rightarrow \frac{\Gamma_l}{\pi[(E_{uk_c} - E_{u'k'_c} \pm \hbar\omega_g)^2 + \Gamma_l^2]}, \quad (27)$$

where it is assumed that the initial and final states have the same lifetime. This suppresses the divergence of the exciton-phonon joint density of states associated with the one-dimensional band edges with the width of Γ_l .

The temperature dependence of the energy broadening is considered. The total energy broadening at low-exciton densities is approximately given by $\Gamma = \Gamma_i + \Gamma_p$ where its temperature dependence arises from the energy broadening due to the phonon scattering Γ_p . We consider the two limiting cases of $\Gamma_p \ll \Gamma_i$ and $\Gamma_p \gg \Gamma_i$. For $\Gamma_p \ll \Gamma_i$, effects of the impurity scattering on Γ_p can be taken into account by introducing the imaginary part of the exciton energy of $-i\Gamma_i/2$, i.e., by setting $\Gamma_l = \Gamma_i$ in Eq. (27). The observable energy broadening of the exciton peaks corresponds to the energy broadening at the band edges for $k_c \approx 0$ since the wave vectors of light are negligibly small as compared to the reciprocal lattice vectors.

In the case of $\Gamma_p \gg \Gamma_i$, the impurity scattering can be neglected for the temperature dependence of Γ . However, the observable energy broadening is not considered to simply correspond to Γ_p for $k_c \approx 0$ in Eq. (26) because the divergence of the exciton-phonon joint density of states associated with the band edges is expected to be smeared with Γ_p itself. Thus, we obtain a phenomenological self-consistent equation for calculations of Γ_p , i.e., Eq. (26) with Eq. (27) where $\Gamma_l = \Gamma_p$, which is essentially same as that obtained previously.⁵⁴ In this case, the energy broadening at the one-dimensional band edges becomes proportional to $T^{2/3}$ instead of T for $\hbar\omega_g/k_B T \ll 1$ where T and k_B are temperature and the Boltzmann constant, respectively.⁵⁴ It should be noted that when the impurity scattering is dominant, the energy broadening at the band edges due to the impurity scattering is also given by a similar self-consistent equation (25) where the delta function is replaced similarly to Eq. (27) with $\Gamma_l = \Gamma_i$.

III. NUMERICAL RESULTS

A. Scattering from impurities

In this section, numerical results are shown for optically allowed intravalley E_{11} excitons. Figures 1(a) and 1(b) show the typical energy broadening due to the impurity scattering as a function of the exciton energy E_j , where j denotes the ground-state exciton ($j = 0$), the first-excited exciton ($j = 1$), etc., for (a) the long-range and (b) the short-range impurities. Solid lines denote the results of the ground-state exciton and the dashed and dotted lines denote those of the first- and second-

excited excitons, respectively. Arrows with integers i show the edges of the energy bands of the i th-excited excitons where $i = 0$ denotes the ground-state exciton.

In Fig. 1(a), the result denoted by the solid line shows the absence of scattering below the band edge for the first-excited exciton $E_0(2\pi\gamma/L)^{-1} \leq 1.091$, and also shows divergences at the band edges of the first- and third-excited excitons but not at the band edge for the second-excited exciton. This is due to the selection rule that scattering from the long-range impurities vanishes and appears between the excitons with the same and different symmetries, respectively. Actually, the ground-state and second-excited excitons have the even symmetry while the first-excited exciton has the odd symmetry. The divergences arise from the van Hove singularities of the density of states of the final states, which are proportional to $(E_j - E_{j'}^{(0)})^{-1/2}$ where $E_{j'}^{(0)}$ is the band edge for the exciton denoted by j' . The results denoted by the dashed and dotted lines can also be understood by this selection rule, where the energy broadening does not vanish because the final state with the different symmetry from that of the initial state always exists. It should be noted that the divergences of the energy broadening are smeared in real systems because those of the density of states of the excitons are cut off by the finite lifetime of the excitons.

In the case of the short-range impurities in Fig. 1(b), all the results diverge at the band edges because of the existence of the intervalley scattering. The energy broadening diverges at the band edges as $(E_j - E_{j'}^{(0)})^{-1/2}$.

The mean-free path for the excitons is defined by $l_i = v_e \tau_i$ where v_e is the group velocity of the excitons. In Figs. 1(c) and 1(d), the inverse of the mean-free path is shown as a function of the exciton energy for the ground-state (solid lines), the first-excited (dashed lines), and the second-excited (dotted lines) excitons for (c) the long-range and (d) the short-range impurities. The group velocity of each exciton vanishes at its band edge as $v_e \propto (E_j - E_j^{(0)})^{1/2}$. Thus, in Fig. 1(c), l_i^{-1} of the first- and second-excited excitons diverges at their own band edges as $l_i^{-1} \propto (E_j - E_j^{(0)})^{-1/2}$ while that of the ground-state exciton vanishes below the band edge for the first-excited exciton because of the vanishing scattering. In Fig. 1(d), l_i^{-1} of the exciton denoted by j diverges at its band edge as $l_i^{-1} \propto (E_j - E_j^{(0)})^{-1}$ and at the other band edges as $l_i^{-1} \propto (E_j - E_{j'}^{(0)})^{-1/2}$ for $j' \neq j$.

In order to investigate effects of the symmetry breaking on the absence of the long-range-impurity scattering of the ground-state exciton in Fig. 1(a), a (15, 5) nanotube with $\varepsilon_c(2\pi\gamma/L)^{-1} \approx 10$ is calculated as a typical example in the effective-mass approximation with the higher-order corrections.³⁷ Figure 2 shows the results of the energy broadening (solid lines) and the inverse of the mean-free path (dashed line) of the ground-state exciton as a function of the exciton energy measured from the lowest band edge corresponding to the arrow with 0 in Fig. 1(a). Near the lowest band edge, both the results are not exactly zero but sufficiently small and vanish at the band edge. The energy dependence of the energy broadening near the band edge is $\Gamma_i \propto (E_0 - E_0^{(0)})^{3/2}$ because the transition matrix element is quadratic in k_c near the band edge, leading to

FIG. 1. (Color online) Energy dependence of the energy broadening [(a) and (b)] and the inverse of the mean-free path [(c) and (d)] of E_{11} excitons due to scattering from the long-range [(a) and (c)] and the short-range [(b) and (d)] impurities. Lines denote the ground-state (solid lines), the first-excited (dashed lines), and the second-excited (dotted lines) excitons. Arrows with integers i show the edges of the energy bands of the i th-excited excitons. The cutoff energy is chosen as $\varepsilon_c(2\pi\gamma/L)^{-1} = 10$. Scales of the right vertical axes are those for $\langle v^2 \rangle = (3 \text{ eV} \times S)^2$ and $\langle n \rangle = 0.001/S$.

$|\langle u, -k_c | V | uk_c \rangle|^2 \propto k_c^4 \propto (E_0 - E_0^{(0)})^2$, where it is noted that $\langle uk_c | V | uk_c \rangle = 0$. Thus, the energy dependence of the inverse of the mean-free path near the band edge is $l_i^{-1} \propto E_0 - E_0^{(0)}$.

B. Scattering from acoustic phonons

Figures 3(a) and 3(b) show the energy broadening for the ground-state exciton due to scattering from the acoustic phonons at temperatures of $T = 10, 100$, and 300 K for (a) zigzag and (b) armchair nanotubes with $g_1 = 25 \text{ eV}$ and $g_2 = 2 \text{ eV}$. In Fig. 3(a), two divergences due to those of the exciton-phonon joint density of states appear at $E_0(2\pi\gamma/L)^{-1} \approx 0.890$ and 0.925 . The divergence at the former energy is slightly above the band edge for the ground-state exciton because of the finite-energy dispersions of the phonons. The scattering in this energy regime originates from the intersublattice elements of the interaction due to the bond-length change because scattering from the intrasublattice elements, i.e., the deformation potentials, is absent for the same reason as that for the absence of the long-range-impurity scattering. Near and above the band edge for the first-excited exciton $E_0(2\pi\gamma/L)^{-1} = 1.091$, the energy broadening

suddenly increases to become one order of magnitude larger than that near the lowest band edge because of the appearance of scattering from the deformation potentials between the ground-state and first-excited excitons.

In Fig. 3(b), the results at $E_0(2\pi\gamma/L)^{-1} \gtrsim 1.06$ are similar to those in Fig. 3(a), while the results near the lowest band edge are different in that the divergence at $E_0(2\pi\gamma/L)^{-1} = 0.925$ disappears. The chiral-angle dependence of the results near the lowest band edge is due to that of the intersublattice elements of the interaction in Eq. (9).

Components for the energy broadening at $T = 300 \text{ K}$ in Figs. 3(a) and 3(b) are plotted as a function of the exciton energy in Figs. 3(c) and 3(d), respectively. They are phonon absorption (solid lines) and emission (dashed lines) processes, each of which is associated with the twisting, stretching, and breathing modes. In Fig. 3(c), the dominant contribution near the lowest band edge arises from the emission and absorption for the stretching mode and the emission for the breathing mode becomes dominant for $E_0(2\pi\gamma/L)^{-1} \geq 0.925$ where the components for the twisting mode are absent, which is consistent with a previous study.¹⁸ In Fig. 3(d), the dominant contribution near the lowest band edge is due to the emission

FIG. 2. (Color online) Energy dependence of the energy broadening (solid line) and the inverse of the mean-free path (dashed lines) of the ground-state E_{11} exciton due to scattering from the long-range impurities for a (15, 5) nanotube. The energy for the horizontal axis is measured from the band edge for the ground-state E_{11} exciton. Higher-order corrections are included where dimensionless parameters are $\beta = 1.5$ for the trigonal warping, $S = 0.2$ for the electron-hole asymmetry, and $p = -0.2$ for the curvature and resulting lattice distortion (Ref. 37). Dotted lines denote the energy dependencies proportional to $E_0 - E_0^{(0)}$ and $(E_0 - E_0^{(0)})^{3/2}$ for reference. Scales of the right vertical axes are those for $\langle v^2 \rangle = (3 \text{ eV} \times S)^2$ and $\langle n \rangle = 0.001/S$.

and absorption for the twisting mode and the processes for the stretching and breathing modes are absent, where the result for the breathing mode is consistent with previous studies.^{19,20}

The absence of the scattering from the specific phonon modes in zigzag and armchair nanotubes is due to special forms of the intrasublattice elements of the interaction. For the twisting mode in zigzag nanotubes, $V_{AB}^{\zeta\zeta} = 2ig_2u_{xy}$ because of $\eta = 0$ and $u_{xx} = u_{yy} = 0$ while for the stretching and breathing modes in armchair nanotubes, $V_{AB}^{\zeta\zeta} = ig_2(u_{xx} - u_{yy})$ because of $\eta = \pi/6$ and $u_{xy} = 0$. Since $V_{BA}^{\zeta\zeta} = -V_{AB}^{\zeta\zeta}$ in both the nanotubes, we have $V_{2-}^{\zeta\zeta}(-k', -k) = V_{2+}^{\zeta\zeta}(k, k')$ for Eq. (22). Thus, cancellation between the electron and hole scattering processes occurs similarly to that for the deformation potentials resulting from Eq. (24). For chiral nanotubes, all the three phonon modes contribute to the energy broadening. The components for the twisting mode are much smaller than the others at the energy above the band edge for the first-excited exciton in Figs. 3(c) and 3(d) because the deformation potential for the twisting mode is zero.

C. Temperature dependence

In Fig. 4, the temperature dependence of the observable energy broadening of the ground-state exciton due to scattering from the acoustic phonons is shown for calculations with the use of Eq. (27) by setting (a) $\Gamma_l = \Gamma_i$ and (b) $\Gamma_l = \Gamma_p$. The coupling constants are chosen as $g_1 = 25 \text{ eV}$ and $g_2 = 1, 2$, and 3 eV . Lines and symbols denote calculated and experimental results, respectively. Chiral indices of the used nanotubes are (9, 8) (solid lines and triangles²⁶), (10, 3) (dashed lines and squares²⁵), and (6, 5) (dotted lines and crosses²⁴) and those

for the circles²⁷ are not assigned where the theoretical results are calculated in the lowest-order effective-mass scheme with the corresponding tube diameters and chiral angles. For the experiments, the originally estimated values of Γ_i are chosen as the origins of the energy broadening, which are 2.5 (triangles), 1.4 (squares), 2.45 (crosses), and 6.9 (circles) meV.

In the calculations for Fig. 4(a), Γ_i is chosen as 2.5 meV for the solid and dotted lines and 1.4 meV for the dashed lines according to the experimental values. Since the divergence of the energy broadening near the lowest band edge slightly deviates from the band edge as mentioned for Figs. 3(a) and 3(b), the calculated energy broadening remains finite even for $\Gamma_i = 0$. When Γ_i is of the order of 1 meV, Γ_p decreases with the increase of Γ_i because of effects of averaging. The results indicated by the solid and dashed lines for $g_2 = 2 \text{ eV}$ at $\Gamma_p \lesssim 2 \text{ meV}$ are in agreement with the experimental results for the triangles and squares, respectively. For the dotted lines, the result for $g_2 = 1 \text{ eV}$ well agrees with that denoted by the crosses. These calculated results are considered to be valid for $\Gamma_p \ll \Gamma_i$ as mentioned in Sec. II E.

For $\Gamma_p \gg \Gamma_i$, the energy broadening is expected to cross over to those given by the self-consistent calculations in Fig. 4(b). In Fig. 4(b), with the increase of temperature, the energy broadening denoted by the solid and dashed lines for $g_2 = 2 \text{ eV}$ increases beyond 2.5 and 1.4 meV, which are Γ_i used in Fig. 4(a) for the solid and dashed lines, respectively, where the results for the solid and dashed lines agree with those for the triangles and squares, respectively, again. For the result denoted by the dotted line for $g_2 = 1 \text{ eV}$, the values are less than 2.5 meV, which is Γ_i in Fig. 4(a) for the dotted lines, except for those at $T \sim 300 \text{ K}$. More details of the crossover between the two kinds of the temperature dependencies of the energy broadening can not be discussed because of the fluctuations and error bars of the experimental data.

The experimental results denoted by the circles are similar to those for the triangles and squares for $T \lesssim 100 \text{ K}$ in spite of that Γ_i of 6.9 meV for the circles is a few times as large as those of 2.5 and 1.4 meV for the triangles and squares, respectively. For typical nanotubes, Γ_p calculated by using the method for Fig. 4(a) with $\Gamma_i \sim 6.9 \text{ meV}$ becomes much smaller than Γ_p for $\Gamma_i = 2.5$ and 1.4 meV (results not shown). This might mean that a much larger value of g_2 than 2 eV is needed to reproduce the experimental results for the circles. However, it is more likely that Γ_i for the circles includes the additional contributions of inhomogeneity resulting from the use of the ensembles of nanotubes with various structures. Actually, it is considered that such contributions do not exist or are less important in the experiments for the triangles, squares, and crosses since single nanotubes or nanotubes with an almost unique chirality were used.

The values $g_2 \sim 1$ and 2 eV , for which the calculated results are in agreement with those of the experiments, are consistent with the value estimated previously, $g_2 \sim 1.5 \text{ eV}$.⁴⁶ This indicates that in real systems, the deformation potentials do not scatter the ground-state E_{11} exciton because scattering from the deformation potentials, whose coupling constant g_1 is considered to be one order of magnitude larger than g_2 , should give the energy broadening one or two orders of magnitude larger than those resulting from g_2 as shown for $E_0(2\pi\gamma/L)^{-1} \gtrsim 1.06$ in Figs. 3(a) and 3(b). Thus, this con-

FIG. 3. (Color online) Energy dependence of the energy broadening [(a) and (b)] and its components [(c) and (d)] of the ground-state E_{11} exciton due to scattering from the acoustic phonons for zigzag [(a) and (c)] and armchair [(b) and (d)] nanotubes. Arrows indicate the bottoms of energy dispersions of excitons. The cutoff energy is chosen as $\epsilon_c(2\pi\gamma/L)^{-1} = 10$. The coupling constants are $g_1 = 25$ eV and $g_2 = 2$ eV. In (a) and (b), temperature is chosen as $T = 10$ (solid lines), 100 (dashed lines), and 300 (dotted lines) K. In (c) and (d), solid and dashed lines denote absorption and emission processes, respectively, each of which consists of processes associated with the twisting, stretching, and breathing modes.

sistency supports the validity of the selection rule mentioned in Sec. III D.

IV. DISCUSSIONS

Effects of the energy broadening of one-particle states are not taken into account in the present calculations. The energy broadening is considered to be dominated by that of the one-particle states if the effect of the electron-impurity or electron-phonon interaction is stronger than that of the electron-hole interaction. This is unlikely in realistic systems because the mean distance between an electron and hole of the excitons, which is of the order of the nanotube diameter,^{3,4,52} is much smaller than the mean-free path due to electron-impurity and electron-phonon scattering, which is typically of the order of hundreds of nanometers to a few micrometers.⁵⁵ However, there would be modulation of the energy bands such as the effective mass due to the electron-impurity and electron-phonon interactions, leading to small corrections to

the present results. Calculations of the corrections remain as future issues.

A previous study⁴³ shows that when the energy of one-particle states in the lowest conduction band is far above the band edge, the relaxation time for the states due to acoustic-phonon scattering is several tens of femtoseconds because of large deformation potentials, which must be considerably decreased near the band edge owing to the drastic increase of the joint density of states. These relaxation times are much shorter than those for the experiments in Fig. 4, which are a few hundreds of femtoseconds. This indicates that the energy broadening of the excitons is mainly determined not by that of the one-particle states, but by that of the correlated electron-hole pair states.

The deformation potential for electrons is possible to be different from that for holes. In this case, only the difference can contribute to the energy broadening. The results in Sec. III C suggest that the difference is at most of the order of g_2 , i.e., ~ 1 eV, because the much larger value of the

FIG. 4. (Color online) Temperature dependence of the energy broadening of the ground-state E_{11} exciton due to scattering from the acoustic phonons Γ_p , where $g_1 = 25$ eV and $g_2 = 1, 2$, and 3 eV. Lines denote the energy broadening calculated by setting (a) $\Gamma_l = \Gamma_i$ and (b) $\Gamma_l = \Gamma_p$ in Eq. (27). Symbols are experimental results of the temperature-dependent part of the energy broadening. Chiral indices are $(9, 8)$ [solid lines and triangles (Ref. 26)], $(10, 3)$ [dashed lines and squares (Ref. 25)], and $(6, 5)$ [dotted lines and crosses (Ref. 24)] and those for the circles (Ref. 27) are not assigned. For the experimental results, the values of the originally estimated temperature-independent part Γ_i , which are chosen as the origins of the experimental results, are 2.5 (triangles), 1.4 (squares), 2.45 (crosses), and 6.9 (circles) meV. Correspondingly, Γ_i for the calculations in (a) is set to 2.5 meV for the solid and dotted lines and 1.4 meV for the dashed lines.

difference than g_2 must give the substantially large energy broadening which can not reproduce the experimental results. The larger values of the difference of ~ 10 eV were reported in a study with first-principles calculations.⁵⁶ The reason for this discrepancy is not clear.

Effects of the short-range Coulomb interaction neglected in the present calculations are briefly discussed. When this interaction is considered, the degenerated ground states for the intravalley E_{11} excitons at the K and K' points in this study turn into optically allowed (bright) and optically forbidden (dark) excitons. The dark exciton exists below the bright exciton with a separation of a few meV in energy for typical nanotubes.⁵⁷ The bright and dark exciton states are written as⁵⁸

$$|\pm, k_c\rangle = \frac{1}{\sqrt{2}}(|K k_c\rangle \pm |K' k_c\rangle), \quad (28)$$

where $|\pm, k_c\rangle$ denotes the bright (+) and dark (−) excitons with the longitudinal wave vector k_c , and $|K k_c\rangle$ and $|K' k_c\rangle$ denote the ground-state intravalley E_{11} excitons with k_c at the K and K' points, respectively, which are the excitons studied in the previous sections. The matrix elements of the intravalley interaction between $|+, k_c\rangle$ and $|\pm, k'_c\rangle$ are given by

$$\langle \pm, k'_c | V | +, k_c \rangle = \frac{1}{2} (\langle K k'_c | V | K k_c \rangle \pm \langle K' k'_c | V | K' k_c \rangle), \quad (29)$$

where the interaction V consists of the intrasublattice elements such as the long-range impurities and the deformation potentials for the acoustic phonons V_1 , and the intersublattice elements due to the bond-length change for the acoustic phonons V_2 . For the intrasublattice elements, the matrix elements vanish because $\langle K k'_c | V_1 | K k_c \rangle = \langle K' k'_c | V_1 | K' k_c \rangle = 0$. For the intersublattice elements, because of $\langle K k'_c | V_2 | K k_c \rangle = \langle K' k'_c | V_2 | K' k_c \rangle$ as shown in the Appendix, we have

$$\langle +, k'_c | V_2 | +, k_c \rangle = \langle K k'_c | V_2 | K k_c \rangle = \langle K' k'_c | V_2 | K' k_c \rangle, \quad (30)$$

$$\langle -, k'_c | V_2 | +, k_c \rangle = 0, \quad (31)$$

where Eq. (31) was indicated before.⁵⁹ Thus, the short-range Coulomb interaction can be safely neglected in this study.

V. CONCLUSION

Exciton scattering from impurities and acoustic phonons has been theoretically studied in the lowest-order effective-mass approximation. It has been shown that scattering from the intravalley intrasublattice elements of the interaction such as the long-range impurities and the deformation potentials of the acoustic phonons vanishes between the excitons with the same symmetry because of cancellation between scattering processes of the electrons and holes. This selection rule leads to the absence of scattering of the ground-state excitons for the lowest bands from the long-range impurities and the deformation potentials near the band edges. The validity of this selection rule is supported by the agreement of numerical results with recent experimental results.

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APPENDIX: MATRIX ELEMENTS OF ELECTRON-PHONON INTERACTIONS BETWEEN BRIGHT AND DARK EXCITONS

An equation of motion for the intravalley exciton with a center-of-mass wave vector k_c and $u = (\zeta, \zeta, j)$ where $\zeta = \{K, K'\}$ is written as^{2,12}

$$\begin{aligned} E_{uk_c} \psi_{k+k_c, k}^u &= (\varepsilon_{+, k+k_c}^\zeta - \varepsilon_{-, k}^\zeta + \Sigma_{+, k+k_c}^\zeta - \Sigma_{-, k}^\zeta) \psi_{k+k_c, k}^u \\ &\quad - \sum_{k'} V_{(+, k+k_c; +, k'+k_c)(-, k'; -, k)}^{\zeta \zeta} \psi_{k'+k_c, k'}^u, \end{aligned} \quad (A1)$$

with

$$V_{(s_2,k+q;s_1,k)(s_4,k';s_3,k'+q)}^{\zeta\zeta} = \frac{2e^2}{A\kappa\epsilon_0(|q|)} I_0\left(\frac{L|q|}{2\pi}\right) K_0\left(\frac{L|q|}{2\pi}\right) \times (\mathbf{F}_{s_2,k+q}^{\zeta\dagger} \mathbf{F}_{s_1,k}^{\zeta}) (\mathbf{F}_{s_4,k'}^{\zeta\dagger} \mathbf{F}_{s_3,k'+q}^{\zeta}) \quad (\text{A2})$$

and

$$\Sigma_{\pm,k}^{\zeta} = - \sum_{k'} V_{(\pm,k;-k')(-k';\pm,k)}^{\zeta\zeta} g(\varepsilon_{\pm,k}^{\zeta}, \varepsilon_c). \quad (\text{A3})$$

Equation (A2) denotes the transition matrix element of the long-range Coulomb interaction from two one-particle states at valley ζ denoted by (s_1, k) and $(s_3, k' + q)$ to those denoted by $(s_2, k + q)$ and (s_4, k') , respectively, where $s_1 = \pm$, etc., with $+$ and $-$ being the conduction and valence bands, respectively, k , etc., are the wave vectors along the nanotube axis, the wave vectors in the circumference direction are fixed to those associated with the considered excitons, $I_0(t)$ and $K_0(t)$ are the modified Bessel functions of the first and second kinds of the zeroth order, respectively, and $\epsilon_0(|q|)$ is a dielectric function due to π electrons for the longitudinal wave vector q and the zero circumferential wave vector. Equation (A3) is the self-energy of the state at valley ζ denoted by $(\pm, k)$ where $g(\varepsilon, \varepsilon_c)$ is a cutoff function which is a unity for $|\varepsilon| \lesssim \varepsilon_c$ and vanishes for $|\varepsilon| \gtrsim \varepsilon_c$. In Eq. (A1), the electron-hole exchange term is neglected because the excitons with small k_c are considered where the term is small and vanishes for $k_c = 0$.

Since the relation

$$\mathbf{F}_{s_1,k}^{K'\dagger} \mathbf{F}_{s_2,k'}^{K'} = \mathbf{F}_{s_1,k}^{K\dagger} \mathbf{F}_{s_2,k'}^K \quad (\text{A4})$$

leads to

$$V_{(s_2,k+q;s_1,k)(s_4,k';s_3,k'+q)}^{K'K'} = V_{(s_2,k+q;s_1,k)(s_4,k';s_3,k'+q)}^{KK} \quad (\text{A5})$$

and $\Sigma_{\pm,k}^{K'} = \Sigma_{\pm,k}^K$, the eigenenergies and wave functions in Eq. (A1) are the same between the K and K' points. Therefore, we choose the expansion coefficients of the ground-state E_{11} exciton for the K and K' points as

$$\psi_{k+k_c,k}^{(K',K',0)} = \psi_{k+k_c,k}^{(K,K,0)}. \quad (\text{A6})$$

When the weak short-range Coulomb interaction is considered, the degeneracy between the K and K' points is

lifted. Since the ground-state E_{11} exciton is sufficiently apart from the other excited excitons in energy as compared to the short-range Coulomb interaction, effects of the short-range Coulomb interaction on the ground-state excitons with k_c at the K and K' points, $|Kk_c\rangle$ and $|K'k_c\rangle$, respectively, can be calculated on the basis of these two states. The effective Hamiltonian becomes⁵⁸

$$V_{KK,K'K'} = \frac{\sqrt{3}a^2}{2L^2} \begin{pmatrix} v_{KK} & v_{KK'} \\ v_{K'K} & v_{K'K'} \end{pmatrix}, \quad (\text{A7})$$

with

$$\begin{aligned} v_{KK} &= -w_1 p_{(KK)(KK)} + 2w_1 q_{KK}, \\ v_{KK'} &= -w_2 r_{(KK)(K'K')} + 2w_1 q_{KK'}, \\ v_{K'K} &= -w_2 r_{(K'K')(KK)} + 2w_1 q_{K'K}, \\ v_{K'K'} &= -w_1 p_{(K'K')(K'K')} + 2w_1 q_{K'K'}, \end{aligned} \quad (\text{A8})$$

where w_1 and w_2 are real parameters characterizing the strength of the short-range Coulomb interaction and

$$\begin{aligned} p_{(\zeta_1\zeta_2)(\zeta_3\zeta_4)} &= \text{Tr}(\sigma_z G_{\zeta_1\zeta_2}^{\dagger} \sigma_z G_{\zeta_3\zeta_4}), \\ q_{\zeta_1\zeta_2} &= (\text{Tr} \sigma_z G_{\zeta_1\zeta_1}^{\dagger})(\text{Tr} \sigma_z G_{\zeta_2\zeta_2}), \\ r_{(\zeta_1\zeta_2)(\zeta_3\zeta_4)} &= \text{Tr}(G_{\zeta_1\zeta_2}^{d\dagger} G_{\zeta_3\zeta_4}^d), \end{aligned} \quad (\text{A9})$$

with $G_{\zeta_1\zeta_2}$ being the 2×2 matrix defined as

$$G_{\zeta_1\zeta_2} = \frac{L}{A} \sum_k \mathbf{F}_{+,k+k_c}^{\zeta_1} \psi_{k+k_c,k}^{(\zeta_1,\zeta_2,0)} \mathbf{F}_{-,k}^{\zeta_2\dagger}, \quad (\text{A10})$$

and $G_{\zeta_1\zeta_2}^d$ being the matrix with only diagonal elements of $G_{\zeta_1\zeta_2}$. Using Eq. (A6), it is shown that all the elements of $V_{KK,K'K'}$ are real numbers and the diagonal elements are the same. Thus, the bright and dark excitons are written as the bonding and antibonding states, respectively, of $|Kk_c\rangle$ and $|K'k_c\rangle$ as shown in Eq. (28).

The matrix elements of the electron-phonon interaction due to the bond-length change V_2 between the bright excitons and between the bright and dark excitons are considered. For Eq. (22), the following relation is satisfied:

$$V_{2\pm}^{K'K'}(k', k) = -V_{2\mp}^{KK}(-k, -k'). \quad (\text{A11})$$

From Eqs. (20), (A6), and (A11), $\langle K'k'_c|V_2|K'k_c\rangle = \langle Kk'_c|V_2|Kk_c\rangle$ is obtained, thus leading to Eqs. (30) and (31).

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