

This is the accepted manuscript made available via CHORUS. The article has been published as:

Fine structure of exciton levels in carbon nanotubes: A semianalytical approach

S. V. Goupalov

Phys. Rev. B **84**, 125407 — Published 6 September 2011

DOI: [10.1103/PhysRevB.84.125407](https://doi.org/10.1103/PhysRevB.84.125407)

Fine Structure of Exciton Levels in Carbon Nanotubes: a Semi-analytical Approach

S.V. Goupalov

Department of Physics, Jackson State University, Jackson, MS 39217 USA

and A.F. Ioffe Physico-Technical Institute, 26 Polytechnicheskaya, 194021 St. Petersburg, Russia

We propose a new approach toward excitons in carbon nanotubes whereby the matrix elements of the electron-hole Coulomb interaction are expanded into a series over the nanotube's one-dimensional reciprocal lattice vectors. We show that only a few terms of this expansion give a non-vanishing contribution to the Coulomb matrix elements. The proposed approach allows one to single out Fourier components of the Coulomb potential responsible for the intervalley coupling and formation of the exciton fine structure for each particular nanotube chirality.

PACS numbers: 78.67.Ch, 78.67.-n, 71.35.Cc

Optical properties of single-walled carbon nanotubes (CNTs) are known to be dominated by the excitonic effects^{1–10}. The high spin and subband (valley) degeneracy of the electron-hole (e-h) pair ground state in the absence of the Coulomb interaction leads to a fine structure of excitonic levels when this interaction is taken into account. It has been realized¹ that both the long-range and the short-range parts of the e-h Coulomb interaction are essential for a description of the exciton fine structure in CNTs. It is believed^{4–6} that the best way to account for the short-range part of the Coulomb interaction in CNTs within the tight-binding method is to replace the Coulomb potential between the π -electrons of CNTs by the phenomenological Ohno potential of the form $V(r) = \frac{U}{\sqrt{(rU/e^2)^2 + 1}}$, where U is the energy cost to place two electrons on a single site. However, approaches based on the Ohno potential^{4–6} systematically over-estimate the experimentally measured energy splittings between the exciton singlet dark and bright states^{7–10}.

In this paper we show that the e-h Coulomb interaction in CNTs can be treated *per se* thus allowing one to avoid uncontrollable approximations. We present an approach whereby the matrix elements of the Coulomb potential are expanded into a series over CNT's one-dimensional reciprocal lattice vectors, $g_n = 2\pi n/|\mathbf{T}|$, where \mathbf{T} is the CNT translational vector¹¹. In this formulation the long-range part of the Coulomb potential is accounted for by the term with $n = 0$ while the rest of the expansion corresponds to the short-range part of the Coulomb interaction. We show that, in order to make a non-vanishing contribution to this expansion, the reciprocal lattice vector g_n must satisfy the condition $|n| < \mathcal{N}/\mathcal{M}$, where \mathcal{N} and \mathcal{M} are the chirality-specific integers relating the chiral, \mathbf{C}_h , symmetry, \mathbf{R} , and translational, \mathbf{T} , vectors of the CNT [shown in Fig. 1 for a (4,2) CNT] by $\mathcal{N}\mathbf{R} = \mathbf{C}_h + \mathcal{M}\mathbf{T}$ ¹¹ (\mathcal{N} has the meaning of the number of hexagons within the CNT unit cell). We obtain analytical expressions for the Coulomb matrix elements which provide an insight into exciton physics which cannot be gained using a formalism based upon the phenomenological Ohno potential. In particular, for each CNT chirality it is possible to single out Fourier components of the e-h Coulomb interaction responsible for the intervalley coupling and lifting of the subband degeneracy leading to the formation of the exciton fine structure.

While the formalism based on the Ohno potential originates from the description of organic π -conjugated polymer systems⁴, here we put the problem of the exciton in CNTs into the context of the solid state physics and adopt the

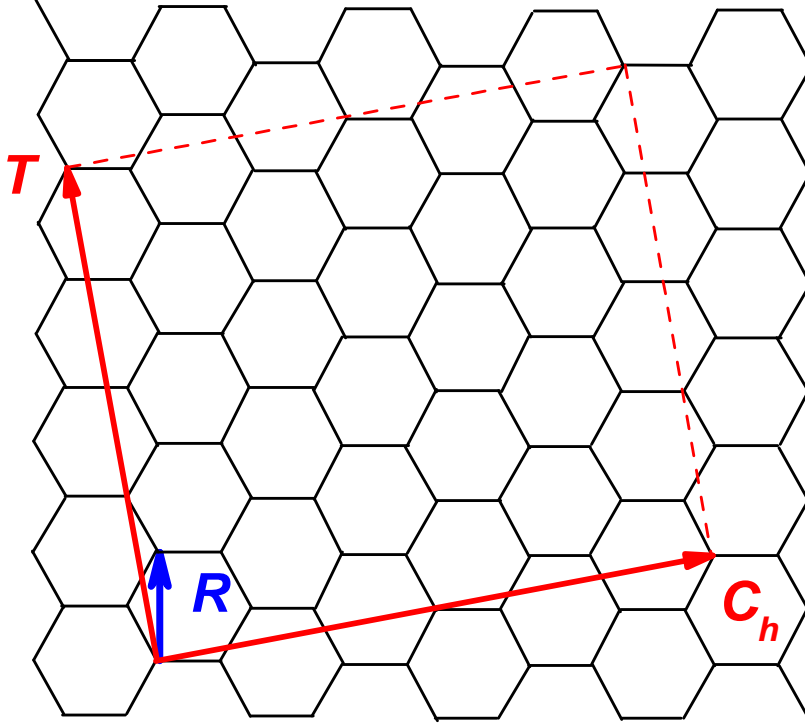


FIG. 1: (Color online) The chiral, \mathbf{C}_h , translational, \mathbf{T} , and symmetry, \mathbf{R} , vectors of a (4,2) CNT. The vectors are related by $\mathcal{N}\mathbf{R} = \mathbf{C}_h + \mathcal{M}\mathbf{T}$ with $\mathcal{N} = 28$, $\mathcal{M} = 6$. For a (10,5) CNT \mathbf{T} and \mathbf{R} are the same while \mathbf{C}_h , \mathcal{N} , and \mathcal{M} should be multiplied by a factor of 2.5.

concepts widely used in the theory of semiconductors¹².

We will first formulate our approach for a CNT of arbitrary chirality and then consider an example of the (10,5) CNT as one featured in most experimental studies⁷⁻⁹. Although our numerical calculation also overestimates the experimentally observed energy splitting between the exciton singlet dark and bright states, the calculated value is only 2 to 8 times larger than the experimental ones.

Taking into account the cylindrical geometry of the CNT the Coulomb matrix element between a conduction-band and a valence-band electrons can be written as^{1,13}

$$\langle c, \mu'_c, q'_c; v, \mu'_v, q'_v | V_C | c, \mu_c, q_c; v, \mu_v, q_v \rangle = \frac{e^2}{\kappa \pi} \sum_{m=-\infty}^{\infty} \int_{-\infty}^{\infty} dk K_m(|k|R) I_m(|k|R) \quad (1)$$

$$\times \langle c, \mu'_c, q'_c | e^{im\varphi} e^{ikz} | c, \mu_c, q_c \rangle \langle v, \mu'_v, q'_v | e^{-im\varphi} e^{-ikz} | v, \mu_v, q_v \rangle,$$

where the indices μ_s, μ'_s enumerate subbands within the band $s = c, v$ and the one-dimensional wave vectors q_s, q'_s from the interval $[-\frac{\pi}{|\mathbf{T}|}, \frac{\pi}{|\mathbf{T}|})$ enumerate the electron one-particle states within these subbands; κ is the static dielectric constant describing the screening effect of the core states, σ -bands and polarization of the surrounding material; $K_m(x)$ and $I_m(x)$ are the modified Bessel functions; R is the nanotube radius; and z and φ are the longitudinal and the azimuthal cylindrical coordinates. The matrix elements in the right-hand side of Eq. (1) are calculated on the wave

functions

$$\langle \mathbf{r} | s, \mu_s, q_s \rangle = \frac{1}{\sqrt{N}} \sum_{b=A,B} C_b(s, \mu_s, q_s) \sum_{\mathbf{R}_b} e^{i\mu_s \varphi_b} e^{iq_s z_b} \Phi_b(\mathbf{r} - \mathbf{R}_b) \equiv e^{iq_s z} u_{s, \mu_s, q_s}(\mathbf{r}), \quad (2)$$

where $\mathbf{r} \equiv (\varphi, z)$, N is the number of unit cells of graphene in the structure, the index $b = A, B$ accounts for the two atoms within the unit cell of graphene, $\mathbf{R}_b = (\varphi_b, z_b)$ is a position of an atomic site, $\Phi_b(\mathbf{r} - \mathbf{R}_b)$ is the p_z -atomic orbital forming the π -bond. The coefficients $C_A(c, \mu, q) = e^{i\varphi_c(\mu, q)}/\sqrt{2}$, $C_A(v, \mu, q) = -e^{i\varphi_v(\mu, q)}/\sqrt{2}$, $C_B(c, \mu, q) = C_B(v, \mu, q) = 1/\sqrt{2}$ with the phases $\varphi_s(\mu, q)$ given in¹⁴ are obtained by diagonalization of the nearest-neighbor tight-binding Hamiltonian for graphene¹¹. $u_{s, \mu_s, q_s}(\mathbf{r})$ is the periodic in z (with the period $|\mathbf{T}|$) Bloch amplitude. Due to this periodicity the product $u_{s', \mu', q'}^*(\mathbf{r}) u_{s, \mu, q}(\mathbf{r})$ can be expanded into a Fourier series over the one-dimensional reciprocal lattice vectors $g_n = 2\pi n/|\mathbf{T}|$, and we obtain

$$\langle s', \mu', q' | e^{im\varphi} e^{ikz} | s, \mu, q \rangle = L \sum_n \langle s', \mu', q' | B_n(m) | s, \mu, q \rangle \delta_{k, q' - q - g_n},$$

where L is the length of the CNT. The coefficients of this expansion are given by

$$\begin{aligned} \langle s', \mu', q' | B_n(m) | s, \mu, q \rangle &= \frac{1}{NL} \sum_{b'} C_{b'}^*(s', \mu', q') \sum_{\mathbf{R}_{b'}} e^{-i\mu' \varphi_{b'}} e^{-iq' z_{b'}} \\ &\times \sum_b C_b(s, \mu, q) \sum_{\mathbf{R}_b} e^{i\mu \varphi_b} e^{iq z_b} J(\mathbf{R}_b, \mathbf{R}_{b'}), \end{aligned}$$

where

$$J(\mathbf{R}_b, \mathbf{R}_{b'}) = \int_0^{2\pi} d\varphi \int_{-L/2}^{L/2} dz e^{im\varphi} e^{-ig_n z} e^{i(q' - q)z} \Phi_{b'}^*(\mathbf{r} - \mathbf{R}_{b'}) \Phi_b(\mathbf{r} - \mathbf{R}_b). \quad (3)$$

Overlapping of the atomic orbitals makes the integral different from zero only for $\mathbf{R}_b = \mathbf{R}_{b'}$. Next, because $e^{i(q' - q)z}$ is a slow function of z , one can replace $e^{i(q' - q)z} \rightarrow e^{i(q' - q)z_b}$.

Now consider the symmetry vector, \mathbf{R} , of a CNT with the coordinates¹¹ $R_z \equiv \tau = \frac{\mathcal{M}|\mathbf{T}|}{N}$, $R_\varphi \equiv \psi = \frac{2\pi}{N}$. The condition that $e^{im\varphi}$ varies slowly [and, therefore, one can replace $e^{im\varphi} \rightarrow e^{im\varphi_b}$ under the integral in Eq. (3)] reads $|m\psi| < 2\pi$ or

$$|m| < \mathcal{N}. \quad (4)$$

Similarly, the condition that $e^{-ig_n z}$ varies slowly and one can replace $e^{-ig_n z} \rightarrow e^{-ig_n z_b}$ under the integral in Eq. (3) reads $|g_n \tau| < 2\pi$ or

$$|n| < \frac{\mathcal{N}}{\mathcal{M}}. \quad (5)$$

Otherwise, fast oscillations cause the integral $J(\mathbf{R}_b, \mathbf{R}_{b'})$ to vanish.

Provided that Eqs. (4), (5) are satisfied, we get

$$\langle s', \mu', q' | B_n(m) | s, \mu, q \rangle = \frac{1}{NL} \sum_b C_b^*(s', \mu', q') C_b(s, \mu, q) \sum_{\mathbf{R}_b} e^{-ig_n z_b} e^{i\varphi_b(m - \mu' + \mu)}. \quad (6)$$

It is a standard procedure to make a transformation from the electron-electron to the e-h representation¹². Introducing the electron (σ_c) and hole (σ_h) spin indices and changing the variables of the electron, q_c , and hole, q_h , wave vectors to those of the exciton center of mass, $Q = q_c + q_h$, and relative motion, $q = (q_c - q_h)/2$, we obtain the direct and exchange matrix elements for the e-h Coulomb interaction in a CNT:

$$\langle c, \mu'_c, \sigma'_c; v, \mu'_v, \sigma'_h; Q', q' | V_{dir} | c, \mu_c, \sigma_c; v, \mu_v, \sigma_h; Q, q \rangle = -2 \frac{e^2}{\kappa} \delta_{\sigma'_c, \sigma_c} \delta_{\sigma'_h, \sigma_h} L \delta_{Q', Q} \quad (7)$$

$$\begin{aligned} & \times \sum_n \sum_m K_m(|q' - q - g_n| R) I_m(|q' - q - g_n| R) \\ & \times \langle c, \mu'_c, Q/2 + q' | B_n(m) | c, \mu_c, Q/2 + q \rangle \langle v, \mu_v, q - Q/2 | B_{-n}(-m) | v, \mu'_v, q' - Q/2 \rangle, \\ & \langle c, \mu'_c, \sigma'_c; v, \mu'_v, \sigma'_h; Q', q' | V_{exch} | c, \mu_c, \sigma_c; v, \mu_v, \sigma_h; Q, q \rangle \\ & = 2 \frac{e^2}{\kappa} (-1)^{1+\sigma'_c+\sigma_c} \delta_{\sigma'_c+\sigma'_h, 0} \delta_{\sigma_c+\sigma_h, 0} L \delta_{Q', Q} \sum_n \sum_m K_m(|Q - g_n| R) I_m(|Q - g_n| R) \\ & \times \langle c, \mu'_c, Q/2 + q' | B_n(m) | v, \mu'_v, -Q/2 + q' \rangle \langle v, \mu_v, q - Q/2 | B_{-n}(-m) | c, \mu_c, q + Q/2 \rangle. \end{aligned} \quad (8)$$

The spin structure of the exchange matrix element can be expressed as $(1 - \sigma_e \sigma_h)/2$ in terms of the electron, σ_e , and the hole, σ_h , Pauli matrices. This term is different from zero only for the singlet state (with the zero total spin).

Note that $K_m(x) I_m(x) \approx 1/2x$ for $x \gg |m|$. Therefore, some restriction on n is absolutely necessary, as otherwise one would obtain a logarithmically divergent series for either of the Coulomb matrix elements. On the other hand, the exact form of this restriction might vary with chirality and be different from Eq. (5). The same refers to Eq. (4), as $K_m(|x|) I_m(|x|) \approx 1/2|m|$ for $|m| \gg |x|$.

The screening of the direct Coulomb interaction by the π -electrons can be calculated in the static limit within the random phase approximation (r.p.a.)^{1,6}. At zero temperature one obtains

$$\varepsilon(m, k, \omega) = 1 - \frac{2e^2}{\kappa L} K_m(|k| R) I_m(|k| R) \mathcal{P}_0(m, k, \omega), \quad (9)$$

where

$$\mathcal{P}_0(m, k, 0) = -4 L^2 \sum_{\mu, \mu', q, n} \frac{\langle v, \mu', q - k + g_n | B_n(-m) | c, \mu, q \rangle \langle c, \mu, q | B_{-n}(m) | v, \mu', q - k + g_n \rangle}{E_c(\mu, q) + E_c(\mu', q - k + g_n)} \quad (10)$$

is obtained by evaluating the irreducible polarization bubble in r.p.a.¹⁵, and $E_c(\mu, q)$ describes electron energy dispersion in the μ -th subband of the conduction band.

The single-particle self-energy correction to the electron energy within the r.p.a. is described by an exchange graph¹⁵. It takes the form

$$\Sigma_s(\nu, p, \omega) = -2 \frac{e^2}{\kappa} L \sum_{\mu, q, n, m} K_m(|q - p - g_n| R) I_m(|q - p - g_n| R) \quad (11)$$

$$\times \langle v, \mu, q | B_n(m) | s, \nu, p \rangle \langle s, \nu, p | B_{-n}(-m) | v, \mu, q \rangle \frac{1}{\varepsilon(m, p - q + g_n, \omega)},$$

where $s = c, v$.

The above results should be plugged into the two-particle Schrödinger equation in the momentum space¹² (which it is more convenient to write down in the variables q_c, q_h):

$$\begin{aligned} \sum_{\mu_c, \mu_v, q_c, q_h, \sigma_c, \sigma_h} \langle c, \mu'_c, q'_c, \sigma'_c; v, \mu'_v, q'_h, \sigma'_h | H_0 + V_{dir} + V_{exch} | c, \mu_c, q_c, \sigma_c; v, \mu_v, q_h, \sigma_h \rangle \mathcal{A}_{\mu_c, \sigma_c; \mu_v, \sigma_h}^{eh}(q_c, q_h) \\ = E \mathcal{A}_{\mu'_c, \sigma'_c; \mu'_v, \sigma'_h}^{eh}(q'_c, q'_h), \end{aligned} \quad (12)$$

where the direct Coulomb interaction (7) should be further screened with the static dielectric constant (9) and

$$\begin{aligned} \langle c, \mu'_c, q'_c, \sigma'_c; v, \mu'_v, q'_h, \sigma'_h | H_0 | c, \mu_c, q_c, \sigma_c; v, \mu_v, q_h, \sigma_h \rangle \\ = [E_c(\mu'_c, q'_c) + \Sigma_c(\mu'_c, q'_c, 0) + E_c(\mu'_v, -q'_h) - \Sigma_v(\mu'_v, -q'_h, 0)] \delta_{\mu_c \mu'_c} \delta_{\mu_v \mu'_v} \delta_{q_c q'_c} \delta_{q_h q'_h} \delta_{\sigma_c \sigma'_c} \delta_{\sigma_h \sigma'_h}. \end{aligned}$$

Solution of Eq. (12) yields the exciton energy levels.

We choose the origin ($\mu = 0, q = 0$) at the Γ -point in the \mathbf{k} -space of graphene¹¹. Then, for semiconductor CNTs, the lowest conduction subband and the uppermost valence subband have extrema at $\mu_1 = [\mathcal{N}/3]$, $q_1 \approx 0$ and $\mu_2 = [2\mathcal{N}/3] = \mathcal{N} - \mu_1$, $q_2 \approx 0$, where the square brackets denote rounding to the nearest integer. The e-h pairs at these extrema are degenerate because of the valley degeneracy in graphene (which is due to the time-reversal symmetry). Thus far, from our formulation it is not evident how this degeneracy is lifted. Indeed, our expansion of the Coulomb matrix elements is over longitudinal reciprocal lattice vectors and it is not clear how it affects the azimuthal motion. All the information about it is hidden inside the chirality-dependent coefficients (6). Fortunately, for every particular chirality one can obtain analytical expressions for these coefficients. Below we will consider an example of the (10, 5) CNT.

We will limit our consideration by the A -excitons⁶ which are formed by e-h pairs with both the electron and the hole from the same valley [or vicinity of one of the points (μ_i, q_i) , $i = 1, 2$]. Due to (i) the time-reversal symmetry between the states originating from the two different valleys of graphene and (ii) the mirror-like symmetry between the conduction and valence bands in our model of CNTs (the particle-hole symmetry), the eigenstates of the exciton Hamiltonian corresponding to a given exciton wave vector Q are either bonding (A_2) or anti-bonding (A_1) combinations of the states originating from the different valleys^{1,6}. Then a simple consideration⁶ leads to the conclusion that, for A_1 -excitons, the spin singlet and triplet states are degenerate. We will be interested in excitons optically excited by light polarized parallel to the CNT axis. For such excitons $\mathcal{A}_{\mu_c, \sigma_c; \mu_v, \sigma_h}^{eh}(q_c, q_h) \propto \delta_{\mu_c, \mu_v}$ ¹⁴.

For (10, 5) CNT $\mathcal{N} = 70$, $\mathcal{M} = 15$ (see Fig. 1). Therefore, $\mu_1 = 23$, $\mu_2 = 47$ while Eq. (5) takes the form $|n| \leq 4$. Eq. (6) yields (after a summation over the CNT unit cell)

$$\langle s', \mu', q' | B_n(m) | s, \mu, q \rangle = \sum_l \left[C_A^*(s', \mu', q') C_A(s, \mu, q) + C_B^*(s', \mu', q') C_B(s, \mu, q) e^{-\frac{4\pi i n}{21}} e^{\frac{2\pi i l}{7}} \right]$$

$$\times \frac{I_{l,n}}{14L} \delta_{m-\mu'+\mu,5l}, \quad (13)$$

where

$$I_{l,n} = \frac{(-1)^{n+l} \sin \frac{5\pi(3n-l)}{14} \sin \frac{3\pi(n-5l)}{14}}{\sin \frac{\pi(3n-l)}{14} \sin \frac{\pi(n-5l)}{14}} - 1. \quad (14)$$

If $n - 5l \bmod 14 = 0$ then $I_{l,n} = 14$. Otherwise, if $3n - l \bmod 14 = 0$ then $I_{l,n} = -1$. In other words, $I_{l,n}$ peaks when $n - 5l \bmod 14 = 0$.

Let us consider the matrix element (13) between the subbands $\mu' = \mu_1 = 23$ and $\mu = \mu_2 = 47$. The condition that it does not vanish is $m - \mu' + \mu = m + 24 = 5l$. The smallest $|m|$ satisfying this condition is obtained for $m = 1$ which gives $l = 5$. $I_{l,n}$ peaks for $n - 5l = n - 25 \bmod 14 = 0$ which yields $n = -3$. Thus, we have not only demonstrated that there is an intervalley coupling due to the short-range part of the e-h Coulomb interaction in a (10,5) CNT but determined that the coupling is dominated by the Fourier component with $m = \pm 1$, $n = \mp 3$. Similarly, one can determine higher values of $|m|$ which give substantial contributions to the intervalley coupling (*e.g.* $m = \pm 6$, $n = \pm 2$; $m = \mp 9$, $n = \pm 1$; *etc.*).

The above discussion affects only the direct Coulomb interaction. To emphasize the difference between the direct and exchange matrix elements we give the expressions for the coefficients entering Eqs. (7), (8) for $Q = 0$. As we are only interested in excitons optically excited in parallel polarization, we set $\mu'_c = \mu'_v = \mu'$, $\mu_c = \mu_v = \mu$. As our model implies a mirror-like symmetry between the conduction and valence-band states of CNTs, one can also set $\varphi_c(\mu, q) = \varphi_v(\mu, q) = \varphi(\mu, q)$. Then for the coefficients entering Eq. (7) we have

$$\begin{aligned} & \langle c, \mu', q' | B_n(m) | c, \mu, q \rangle \langle v, \mu, q | B_{-n}(-m) | v, \mu', q' \rangle \\ &= \frac{1}{196 L^2} \sum_l \cos^2 \left[\frac{\varphi(\mu, q) - \varphi(\mu', q')}{2} - \frac{\pi(3l - 2n)}{21} \right] I_{l,n}^2 \delta_{m-\mu'+\mu,5l}, \end{aligned} \quad (15)$$

while for the coefficients entering Eq. (8) one obtains

$$\begin{aligned} & \langle c, \mu', q' | B_n(m) | v, \mu', q' \rangle \langle v, \mu, q | B_{-n}(-m) | c, \mu, q \rangle \\ &= \frac{1}{196 L^2} \sum_l \sin^2 \frac{\pi(3l - 2n)}{21} I_{l,n}^2 \delta_{m,5l}. \end{aligned} \quad (16)$$

One can see that the latter matrix element is independent of μ, μ' . Therefore, for the spin singlet states, all the matrix elements of the exciton Hamiltonian have an exchange contribution of the form

$$\Delta_{exch} = \frac{e^2}{49 \kappa L} \sum_{n=-4}^4 \sum_{l=-13}^{13} K_{5l}(|g_n|R) I_{5l}(|g_n|R) \sin^2 \frac{\pi(3l - 2n)}{21} I_{l,n}^2. \quad (17)$$

The strength of optical transitions is determined by the matrix element of the spacially homogeneous part of the probability current density

$$\langle 0 | \hat{\mathbf{j}}_0 | exc \rangle = \sum_{\mu, q, \sigma} \mathcal{A}_{\mu, \sigma; \mu, -\sigma}^{eh}(q, -q) \langle v, \mu, q | \mathbf{v} | c, \mu, q \rangle, \quad (18)$$

TABLE I: Calculated energies and optical transition strengths for A -excitons in a (10,5) CNT for the spectral region of the E_{11} optical transition.

Triplet energy (meV)	Singlet energy (meV)	Transition strength (arb. units)	Assignment	Comment	Experimental value
809		[9.4]	A2		
972		[0.00009]	A1		
	972	0.019	A1		
				$\Delta=13$ meV	1.7 ± 6 meV [9]
	985	7.9	A2	E11	992 meV [16]
1055		[0.00005]	A1		
	1055	0.0003	A1		
1056		[0.0002]	A1		
	1056	0.0002	A1		
1062		[0.05]	A2		
	1073	0.13	A1		
1073		[0.0002]	A1		
	1075	0.86	A2		
1114		[0.02]	A2		
1139		[0.000004]	A1		
	1139	0.013	A1		
	1142	1.52	A2		
1146		[0.00008]	A1		
	1146	0.18	A1		
1148		[0.00006]	A1		
	1149	0.6	A1		
1226		[0.2]	A2		
	1269	0.12	A1		
1270		[0.0006]	A1		
	1273	0.76	A2		
1274		[0.0002]	A1		
	1274	0.48	A1		
1276		[0.003]	A2		
	1279	1.28	A2		

where the interband velocity matrix elements, $\langle v, \mu, q | \mathbf{v} | c, \mu, q \rangle$ are given in¹⁴. Eq. (18) shows that only the spin singlet exciton states with $Q = 0$ are optically active.

We have solved numerically the eigenvalue problem associated with Eq. (12) for the A -excitons with $Q = 0$ in a (10,5) CNT. Although our formalism leaves some freedom in choosing a particular form of Eqs. (4), (5), once this choice has been made, there is only one adjustable parameter, the dielectric constant κ . We followed Ando¹ and varied κ in the range from 2 to 7. For the (10, 5) CNT the best result was achieved for $\kappa = 6$. For our numerical calculations we used the values of the nearest-neighbor transfer integral $\gamma_0 = 3$ eV and graphene lattice constant $a = 2.46 \text{ \AA}$ ¹ and took the CNT length $L = 30 |\mathbf{T}|$. In Table I are shown the calculated energies of exciton states in the spectral region of the E_{11} optical transition. The calculated splitting between the exciton singlet dark and bright states is

TABLE II: Calculated energies and optical transition strengths for A -excitons in a (10,5) CNT for the spectral region of the E_{22} optical transition.

Triplet energy (meV)	Singlet energy (meV)	Transition strength (arb. units)	Assignment	Comment	Experimental value
1350		[4.6]	A2		
1437		[0.006]	A1		
	1437	0.03	A1		
	1439	0.88	A2		
1440		[0.13]	A2		
1443		[0.00002]	A1		
	1443	0.015	A1		
	1445	2.2	A2		
1459		[8.6]	A2		
1512		[0.0002]	A1		
	1512	0.001	A1		
	1528	5.7	A2	E22	1577 meV [16]
1584		[0.0003]	A1		
	1586	0.1	A1		
1586		[0.001]	A1		
	1587	0.19	A1		
1593		[0.5]	A2		
1615		[0.005]	A1		
	1615	0.04	A1		
	1617	1.2	A2		
1619		[1.7]	A2		
	1625	0.09	A1		
1627		[0.05]	A1		
1631.7		[0.7]	A1		
	1631.7	0.89	A1		
	1631.9	0.06	A1		
1632.1		[0.24]	A1		
	1633.1	0.26	A1		
1633.8		[0.29]	A1		
	1636.7	0.03	A1		
1639.9		[0.2]	A1		
	1644	0.5	A2		
1670.5		[0.8]	A2		
	1678.8	0.004	A1		
1678.9		[0.01]	A1		
	1680.0	0.01	A1		
1680.1		[0.001]	A1		
	1680.5	0.01	A1		
1680.6		[0.001]	A1		
	1684	0.9	A2		

$\Delta = 13$ meV, which is only 2 to 8 times larger than the experimental values between 1.7 and 6 meV⁹. Although the spin triplet exciton states are optically inactive, the magnitude analogous to the square of the absolute value of Eq. (18) is useful in determining the bonding versus anti-bonding character of the triplet states. For this reason the corresponding values are listed in Table I in square brackets. In Table II we give the energies of excitonic levels in the spectral region of the E_{22} optical transition. Our numerical results are in a surprisingly good agreement with the available experimental data. This suggests that the accurate treatment of the e-h Coulomb interaction in CNTs is more important for exciton physics than the details of the CNT band structure.

To summarize, we have proposed a new approach toward excitons in CNTs whereby the matrix elements of the e-h Coulomb interaction are expanded into a series over CNT's one-dimensional reciprocal lattice vectors. We have shown that only a few terms of this expansion give a non-vanishing contribution to the Coulomb matrix elements. Our treatment allows one to single out Fourier components of the Coulomb potential responsible for the intervalley coupling and formation of the exciton fine structure for each particular CNT chirality.

The author would like to thank the Kavli Institute for Theoretical Physics (UC, Santa Barbara) for a fellowship and hospitality. This research was supported by the National Science Foundation in part under Grant No. NSF PHY05-51164 and in part under Grant No. HRD-0833178.

-
- ¹ T. Ando, J. Phys. Soc. Jpn. **66**, 1066 (1997); *ibid.* **73**, 3351 (2004); *ibid.* **75**, 024707 (2006).
 - ² C.D. Spataru, S. Ismail-Beigi, L.X. Benedict, and S.G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
 - ³ C.L. Kane and E.J. Mele, Phys. Rev. Lett. **93**, 197402 (2004).
 - ⁴ H. Zhao and S. Mazumdar, Phys. Rev. Lett. **93**, 157402 (2004).
 - ⁵ V. Perebeinos, J. Tersoff, and P. Avouris, Phys. Rev. Lett. **92**, 257402 (2004); Nano Lett. **5**, 2495 (2005).
 - ⁶ J. Jiang, R. Saito, Ge.G. Samsonidze, A. Jorio, S.G. Chou, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. B **75**, 035407 (2007).
 - ⁷ J. Shaver, J. Kono, O. Portugall, V. Krstić, G.L.J.A. Rikken, Y. Miyauchi, S. Maruyama, and V. Perebeinos, Nano Lett. **7**, 1851 (2007).
 - ⁸ I.B. Mortimer and R.J. Nicholas, Phys. Rev. Lett. **98**, 027404 (2007).
 - ⁹ A. Srivastava, H. Htoon, V.I. Klimov, and J. Kono, Phys. Rev. Lett. **101**, 087402 (2008).
 - ¹⁰ R. Matsunaga, K. Matsuda, and Y. Kanemitsu, Phys. Rev. Lett. **101**, 147404 (2008).
 - ¹¹ R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College, London, 1998).
 - ¹² G.L. Bir and G.E. Pikus, *Symmetry and Strain-induced Effects in Semiconductors* (Wiley, New York, 1974), § 27.
 - ¹³ J. Schwinger, L.L. De Raad, Jr., K.A. Milton, and W.-y. Tsai, *Classical Electrodynamics* (Westview Press, Boulder CO, 1998), Ch. 18.
 - ¹⁴ S.V. Goupalov, A. Zarifi, and T.G. Pedersen, Phys. Rev. B **81**, 153402 (2010).
 - ¹⁵ S. Doniach and E.H. Sondheimer, *Green's Functions for Solid State Physicists* (Imperial College, London, 1998) Ch. 6.
 - ¹⁶ R.B. Weisman and S.M. Bachilo, Nano Lett. **3**, 1235 (2003).