Excitons in semiconductor carbon nanotubes: A momentum-space perspective

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ABSTRACT

We give an exposition of an approach toward excitons in semiconductor carbon nanotubes allowing for separation of the short-range and long-range parts of the electron–hole Coulomb interaction. The approach is applied to account for the exciton fine structure and excitonic effects in optical absorption. It is shown that the energy positions of the E_{ii} optical transitions with $i > 2$ are strongly affected by the short-range part of the electron–hole Coulomb interaction.

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1. Introduction

Excitonic effects in semiconductor single-wall carbon nanotubes (CNTs) are revealed in chirality and diameter dependences of optical transition energies observed in Raman and photoluminescence excitation (PLE) experiments [1–3] and in exciton fine-structure splittings measured using magneto-PL spectroscopy [4–7]. They are governed by both the long-range and the short-range parts of the electron–hole Coulomb interaction. The long-range part is responsible for the exciton formation out of an electron and a hole from given subbands (and valleys) while the short-range part accounts for the exciton fine structure stemming from inter-subband (inter-valley) coupling. A difficulty arises from the fact that at short distances the Coulomb interaction is singular. The standard way to avoid this singularity while accounting for the short-range part of the electron–hole interaction 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

$$V(r) = \frac{U}{\sqrt{(rU/e^2)^2 + 1}}, \tag{1}$$

where U is the energy cost to place two electrons on a single site. This method results in a reasonable approximation [1,8–12] but does not allow one to *separate* the short-range and the long-range parts of the interaction potential and obscures the underlying physics.

Recently we have proposed an alternative treatment [13] where the Coulomb interaction is approached from the momentum-space perspective. The matrix elements of the Coulomb potential are expanded into a series over CNTs one-dimensional (1D) reciprocal lattice vectors, $g_n = 2\pi n/|\mathbf{T}|$, where $\mathbf{T}$ is the CNT translational vector [14]. 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.

In this paper we will first formulate two problems in exciton physics of CNTs for which this treatment appears to be particularly advantageous. Then we will proceed with formulation of the approach and give all necessary technical details. Next we will demonstrate applications of our treatment to the problems formulated earlier.

2. Fine structure of exciton levels

We define the two perpendicular axes K_1 and K_2 in the reciprocal space of graphene as being parallel, respectively, to the circumferential and translational directions of a given CNT with chiral indices $(\tilde{n}, \tilde{m})$ [14]. Then the single-particle states of the CNT can be characterized by a pair of coordinates $(\mu/R, q)$, as shown in Fig. 1. Here μ is the integer subband index assuming values from 0 to $\mathcal{N} - 1$, $\mathcal{N} = 2(\tilde{n}^2 + \tilde{m}^2 + \tilde{n}\tilde{m})/d_R$ is the number of hexagons within the CNT unit cell, d_R is the greatest common divisor of $2\tilde{n} + \tilde{m}$ and $2\tilde{m} + \tilde{n}$, R is the CNT radius, and q is the 1D wave vector from the CNT Brillouin zone $[-\pi/|\mathbf{T}|, \pi/|\mathbf{T}|)$. For *semiconductor* CNTs the positions of the relevant K and K' points have the (K_1, K_2) coordinates of $(\mathcal{N}/3R, 0)$ and $(2\mathcal{N}/3R, 0)$, respectively.

The subbands in the conduction and valence bands closest to the Fermi level have the μ-indices determined by integers nearest to $\mathcal{N}/3$ and $2\mathcal{N}/3$. Due to valley degeneracy in graphene, the single-particle states in these subbands are degenerate, as shown in Fig. 2.

Light polarized parallel to the CNT axis causes optical transitions between a subband in the valence band and a subband in the con-
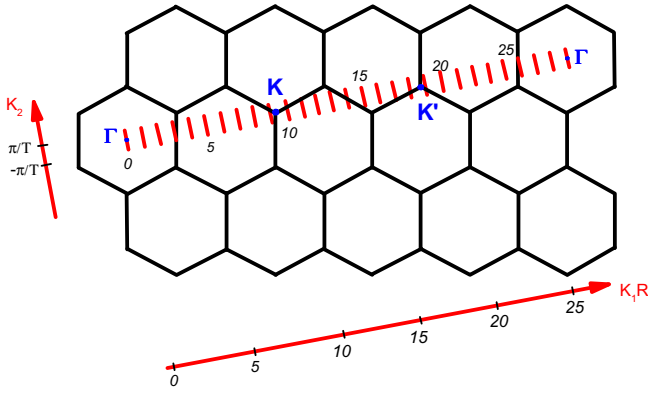
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Fig. 1. Coordinate axes in the reciprocal space of graphene and 1D Brillouin zones corresponding to various subbands of (4,2) CNT.

duction band having the same indices μ [15,16]. Exciton states with both the electron and the hole from the same valley are known as A-excitons [12]. The valley degeneracy leads to existence of the two degenerate A-exciton states, originating, respectively from the K and K' valleys of graphene. We will denote them as $|KK\rangle$ and $|K'K'\rangle$. As one can see from Fig. 1, the distance separating the K and K' points (or corresponding subbands) in the momentum space is larger than both the inter-subband separation and the size of the 1D Brillouin zone. Therefore, the coupling between the $|KK\rangle$ and $K'K'\rangle$ excitons is due to the *short-range* interaction.

In the limit where electron–hole coupling is neglected, exciton states are also spin degenerate. This degeneracy is lifted by the electron–hole exchange interaction which splits a spin degenerate exciton state into a spin singlet and a spin triplet. As the spin–orbit interaction in graphene and CNTs is negligible, the spin degree of freedom of electrons is decoupled from the incident light. As a result, only the spin singlet exciton state is optically active [11].

Coupling between the exciton states $|KK\rangle$, $|K'K'\rangle$ can be written in the form

$$\widehat{V} = \begin{pmatrix} \Delta & \Delta + D \\ \Delta + D & \Delta \end{pmatrix}, \qquad (2)$$

where all the matrix elements are assumed to be real and Δ is the exchange matrix element vanishing for the spin triplet state and different from zero for the spin singlet. The eigenvalues and eigenstates of this matrix are

$$E_+ = 2\Delta + D, \quad |KK\rangle + |K'K'\rangle,$$
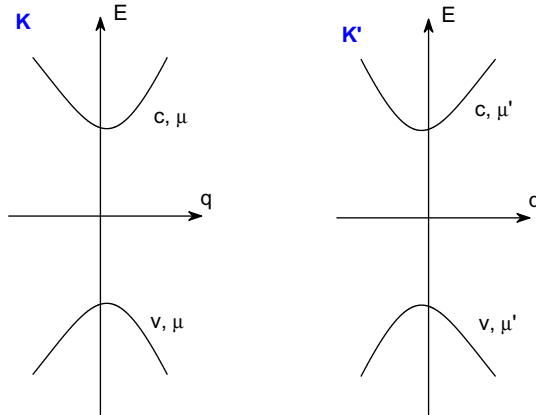$$E_- = -D, \quad |KK\rangle - |K'K'\rangle.$$

Fig. 2. Subbands closest to the Fermi level of (4, 2) CNT originating from the K and K' valleys of graphene. For this CNT $\mu = 9$, $\mu' = 19$.

The eigenstates are bonding and anti-bonding combinations of the states $|KK\rangle$ and $|K'K'\rangle$ and we will call the corresponding excitons A_+ and A_-, respectively. Clearly, out of these two states, only the bonding state, A_+ is optically active. One can also see from this analysis that spin-singlet and spin-triplet states of the anti-bonding exciton, A_-, are degenerate.

As the bonding state, A_+, is optically active for light polarized parallel to the CNT axis, z, its wave function transforms as the z-component of a vector under symmetry operations of the CNT. In group-theoretical notations the corresponding irreducible representation is called A_2 [12]. This representation is odd with respect to the C_2 rotation around the axis perpendicular to z. The antibonding state, A_-, transforms according to the scalar representation, A_1.

The splitting between the dark A_- and the bright A_+ spin-singlet exciton states can be measured experimentally with the help of the magneto-PL spectroscopy [4,6,7]. It is therefore important to be able to calculate the energies $E_\pm$ and to understand their dependence on CNT chiralities.

3. Energy positions of E_{33} and E_{44} optical transitions

Considerable efforts have been made to document chirality and diameter dependences for energies of up to four optical transitions in semiconductor single-wall CNTs [1–3,17,18]. The transition energies for parallel polarization with respect to the CNT axis are denoted by E_{ii} ($i = 1, 2, 3, 4, \ldots$) for a transition between ith subband in the valence band and ith subband in the conduction band, counted from the Fermi energy. Originally E_{ii} referred to the energies of van Hove singularities in the joint density of states [17,18]. This notation continues to be in use after the importance of excitonic and many body effects for optical properties of CNTs has been realized [8–12,19–21].

It has been shown [21] that partial cancellation of the electron self-energy and the exciton binding energy results in relatively small many body modifications of the transition energies E_{ii} for the first two optical transitions ($i = 1, 2$) [1,18]. However, the situation changes drastically for higher optical transitions ($i = 3, 4, \ldots$) [1–3]. Even though calculations within an extended tight binding method accounting for many body effects [1] are in good agreement with experimental data for E_{33} and E_{44} transition energies [2,3], there is no clear physical understanding what makes the higher lying exciton energies so different as compared to their lower lying counterparts.

In this section we will analyze optical absorption of semiconductor CNTs neglecting electron–hole coupling and try to understand why inclusion of this coupling might affect the lower and higher lying optical transitions in a different manner.

The number of states in a given energy subband of a CNT is equal to the number of CNT unit cells in a sample. This provides a convenient way to use not too long CNTs containing, say, 20 unit cells to illustrate partial contributions of various subbands to optical absorption in the case when no many body effects are taken into account. In this case absorption cross section can be found using Fermi's golden rule

$$\sigma_{abs}(\omega) \propto \sum_{\mu,q} \frac{|\langle c, \mu, q | v_z | v, \mu, q \rangle|^2}{E_c(\mu, q) - E_v(\mu, q)} \delta(\hbar\omega - E_c(\mu, q) + E_v(\mu, q)), \quad (3)$$

where $\langle c, \mu, q | v_z | v, \mu, q \rangle$ is the velocity interband matrix element for the parallel polarization of light [15,16] and $E_s(\mu, q)$ describes energy dispersion in the μth subband of the s-band ($s = c, v$). The quasi-descrete character of the energy spectrum due to the finite length of the CNT allows one to distinguish different δ-functional contributions to absorption spectrum neglecting spectral line broadening. The partial contributions to the optical absorption spectrum due