Effects of environmental and exciton screening in single-walled carbon nanotubes

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Abstract. The ground-state exciton binding energy for single-walled carbon nanotubes (SWCNTs) in vacuum calculated ignoring the screening of Coulomb interaction appears to be much greater than the corresponding band gap. The most essential contributions to the screening of electron-hole (e-h) interaction potential in semiconducting SWCNTs, which return the ground-state exciton binding energy into the energy gap, are considered. Our estimates on the screening effects and exciton binding energies are in satisfactory agreement with the corresponding experimental data for concrete nanotubes.

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1. Introduction
As it was shown in the recent works on optical spectra of SWCNTs, both theoretical [1]-[5] and experimental [6]-[11], the study of excitonic contributions in those spectra is of prime importance. Evidently, the quasione-dimensional large-radius exciton problem can be reduced to the 1D system of two quasi-particles with the potential having Coulomb attraction tail. Indeed, within the framework of the so-called long-wave approximation the wave equation for the envelope function Fourier transform \( \phi \) of a large-radius rest exciton in a semiconducting SWCNT with the longitudinal period \( a \) is reduced to the following 1D Schrödinger equation:

\[
-\frac{\hbar^2}{2\mu} \phi''(z) + V(z)\phi(z) = \mathcal{E} \phi(z), \quad \mathcal{E} = E_{\text{exc}} - E_g, \quad -\infty < z < \infty,
\]

(1)

with the exciton reduced effective mass \( \mu \) and the e-h interaction potential

\[
V(z) = -\int \int_{E^3_0}^{E^3_0} \frac{e^2 |u_{c,0}(r_1)|^2 |u_{v,0}(r_2)|^2 dr_1 dr_2}{((x_1 - x_2)^2 + (y_1 - y_2)^2 + (z + z_1 - z_2)^2)^{1/2}}, \quad E^3_0 = E_2 \times (0 < z < a).
\]

(2)

Here \( u_{c,v,q}(r) \) are the Bloch amplitudes of the Bloch wave functions \( \psi_{c,v,q}(r) = \exp(iqz)u_{c,v,q}(r) \) of the conduction and valence band electrons of a SWCNT, respectively, \( q \) is the electron quasi-momentum. Under the assumption that the charges of electron and hole participating in the formation of exciton are smeared uniformly along infinitesimal narrow bands at the nanotube wall we obtain from (2):

\[
V_{R_0}(z) = -\frac{e^2}{4\pi^2 |z|} \int_0^{2\pi} \int_0^{2\pi} \frac{d\alpha_1 d\alpha_2}{(1 + (4R_0^2/z^2)\sin^2 \frac{\alpha_1 - \alpha_2}{2})^{1/2}} = -\frac{2e^2}{\pi |z|} K \left[ -\frac{4R_0^2}{z^2} \right],
\]

(3)
where K is the complete elliptic integral of the first kind and $R_0$ is the tube radius. This potential is the simplest approximation to the bare Coulomb potential, which accounts the finiteness of the nanotube diameter.

Due to the parity of the interaction potential the exciton states should split into the odd and even series. In [12] we show that for the bare e-h interaction potentials $V(z) = -e^2/|z|$ and (3), and for the e-h interaction potentials screened by the nanotube bound electrons or by free charges, which may appear in a SWCNT at rather high temperature, the binding energy of even excitons for SWCNTs in vacuum in the ground state well exceeds the energy gap. This may lead to instability of the single-electron states at least in the vicinity of the energy gap with respect to formation of excitons. In [12] we also briefly discussed the factors, which could prevent the collapse of single-electron states in isolated semiconducting SWCNTs. Here we present more detailed analysis of those factors (with the corresponding calculations), namely we consider: the environmental screening of e-h interaction for nanotubes in a medium (section 2) and the screening by excitons, which appear in a nanotube in vacuum due to the mentioned instability of single-electron states (section 3). These screening effects substantially weaken the e-h interaction and return the exciton ground-state binding energy into the corresponding band gap. Particularly, the appearance of a rather small concentration of excitons stabilizes the single-electron states in SWCNT preventing their further conversion into excitons. The obtained data and estimates were compared with the corresponding experimental results (section 4).

2. Environmental screening

Evidently, a dielectric medium, surrounding a nanotube, should substantially change the e-h interaction potential. In experimental works [6]-[8] (which used the methods described in [9]) investigated individual nanotubes were not in vacuum but encased in sodium dodecyl sulfate (SDS) cylindrical micelles disposed in D_2O. Because of these SDS micelles, which provided a pure hydrocarbon environment around individual nanotubes, the high permittivity solvent D_2O did not reach nanotubes. However, the environment of hydrophobic hydrocarbon "tails" (-C_12H_25) of the SDS molecules has the permittivity greater than unity (according to [11] it’s about 2.2.5). Following the figure 1A from [9] we considered a simple model of a SWCNT in a dielectric environment: a narrow, infinite cylinder with radius $R_0$ in a medium with the dielectric constant $\varepsilon_{\text{env}}$ and the internal dielectric constant $\varepsilon_{\text{int}}$.

Let us find a screened analogue of potential (3) for this model under the assumption about axially symmetrical charge localization at nanotube’s (cylinder’s) wall. To obtain the sought screened potential $\varphi$ we consider as in [13] the following boundary problem for the one-dimensional Fourier transform of the Laplace equation:

$$-\Delta_{2D}\varphi(k, r_{2D}) + k^2 \varphi(k, r_{2D}) = 0, \quad r_{2D} \leq R_0, \quad \varphi(k, 0) < \infty, \quad \varphi(k, \infty) = 0$$

and two standard boundary conditions for the potential at the tube surface:

$$\varphi(z, R_0 - 0) = \varphi(z, R_0 + 0),$$

$$\varepsilon_{\text{env}} \frac{\partial \varphi(z, r_{2D})}{\partial r_{2D}} \Big|_{r_{2D} = R_0 - 0} - \varepsilon_{\text{int}} \frac{\partial \varphi(z, r_{2D})}{\partial r_{2D}} \Big|_{r_{2D} = R_0 + 0} = 4\pi\sigma(z),$$

where $r_{2D}$ is the transverse component of the radius-vector and $\sigma = (e/2\pi R_0)\delta(z)$ is the surface density of the screened charge distribution. Due to the axial symmetry of charges distribution the differential equation in (4) can be reduced to the modified Bessel equation (with different solutions for $r_{2D} < R_0$ and $r_{2D} > R_0$), from which one can simply obtain the 1D screened potential:

$$\varphi(z, R_0) = -\frac{2e}{\pi R_0} \int_0^\infty \frac{I_0(k)K_0(k)\cos(kz/R_0)}{[\varepsilon_{\text{env}}I_0(k)K_1(k) + \varepsilon_{\text{int}}I_1(k)K_0(k)]k}dk,$$
where $I_i$ and $K_i$ are the modified Bessel functions of the order $i$ of the first and second kind, respectively. For a nanotube in medium internal screening is mainly induced by the nanotube $\pi$-electrons and in this case we take $\varepsilon_{\text{int}}(k)$ obtained in [12] in section 3.

3. Screening induced by excitons

As it was mentioned above, since the large exciton ground-state binding energy exceeds the corresponding energy gap, then the single-electron states in any nanotube in vacuum ($\varepsilon_{\text{env}} = 1$) should be unstable with respect to the formation of excitons. But with the advent of some number of excitons in the tube the additional screening effect, stipulated by a rather great polarizability of excitons in the longitudinal electric field, appears. Under certain critical concentration of excitons the ground-state exciton binding energy becomes smaller than the energy gap and the conversion of single-electron states into excitons ends. Hence, here we’ll obtain the upper and lower limits for the critical concentration of excitons.

As is well known, the permittivity of any dielectric, and so the permittivity of the exciton gas, can be given as follows:

$$\varepsilon_{\text{exc}} = 1 + 4\pi\alpha, \quad \alpha = 2e^2n \sum_k \frac{|\langle \Psi_0| r |\Psi_k \rangle|^2}{E_0 - E_k},$$

(7)

where $\alpha$ is the polarizability of the exciton gas in the static electric field, $n$ is the bulk concentration of excitons, $\Psi_0$ and $E_0$ are the exciton eigenfunction and binding energy, which correspond to the ground state, and $\Psi_k$ and $E_k$ are those, which correspond to all excited states of exciton. According to (7) the upper and lower limits for $\alpha$ are:

$$\frac{2e^2n}{E_0 - E_1} |\langle \Psi_0| r |\Psi_1 \rangle|^2 \leq \alpha \leq \frac{2e^2n}{E_0 - E_1} \sum_k |\langle \Psi_0| r |\Psi_k \rangle|^2 = \frac{2e^2n}{E_0 - E_1} |\langle \Psi_0| r^2 |\Psi_0 \rangle|,$$

(8)

where $\Psi_1$ and $E_1$ correspond to the lowest excited exciton state. Further, assuming that the external electric field is longitudinal (directed along the $z$-axis, nanotube axis) and simplifying matrix elements in (8), in the long-wave limit we can write the upper and lower limits for the concentration of excitons in the following form:

$$\frac{\varepsilon_{\text{exc}} - 1}{4\pi} \frac{E_0 - E_1}{2e^2} \int_{-\infty}^{\infty} z^2 |\phi_0(z)|^2 \mathrm{d}z \lesssim n \lesssim \frac{\varepsilon_{\text{exc}} - 1}{4\pi} \frac{E_0 - E_1}{2e^2} \int_{-\infty}^{\infty} z \phi_0(z) \phi_1(z) \mathrm{d}z,$$

(9)

where each $\phi$ is the component of Fourier transform of the corresponding exciton envelope function, it depends only on the distance $z$ between the electron and hole. Each $\phi$ is the solution of wave equation (1) with potential (6), where $\varepsilon_{\text{env}} = 1$ and $\varepsilon_{\text{int}} = \varepsilon_{\text{exc}} = \text{const}$ as the screening induced by the nanotube bound electrons is negligible in comparison with $\varepsilon_{\text{exc}}$. $\phi_0$ is the even function, which corresponds to the exciton ground state and satisfies the 1D Schrödinger equation (1) and the boundary condition at the origin $\phi'(0) = 0$, and $\phi_1$ is the odd function, which corresponds to the lowest excited exciton state and satisfies the same equation, but the boundary condition $\phi(0) = 0$ at the origin.

Varying $\varepsilon_{\text{exc}}$ in (6) substituted into wave equation (1) one can match $E_0$ to the energy gap. Further, $E_1$ can be obtained from the same equation with the fixed $\varepsilon_{\text{exc}}$ and with the corresponding boundary condition. These magnitudes allow to calculate from (9) the rough upper and lower limits for the critical concentration of excitons $n_c$. Further, knowing $n_c$ we can calculate the shift of the forbidden band edges, which move apart due to the transformation of
some single-electron states into excitons. This results in the enhancement of energy gap and hence the lowest optical transition energy $E_{11}$ should be blueshifted by

$$\delta E_{11} = \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{(\pi \hbar \tilde{n}_e)^2}{2}$$  \hspace{1cm} (10)$$

as in [10] and [11]. Here $\tilde{n}_e = n_e \pi R_0^2$ is the linear critical concentration of excitons and $m_{e,h}^*$ are the electrons and holes effective masses ($m_e^* \approx m_h^*$ for all SWCNTs).

4. Calculation results. Discussion

Parameters of electronic structure of nanotubes used in this work, were calculated as in [14], [15] within the framework of the zero-range potentials method [16], [17].

Using potential (6) we’ve calculated the exciton binding energy for nanotube (7, 5) ($R_0 = 0.4087$ nm, band gap $E_g = 1.01$ eV) in the SDS hydrocarbon medium (by [11] its dielectric constant $\varepsilon_{\text{env}} = 2 \pm 2.5$). The experimental value of the exciton binding energy for (7, 5) tube encased in the SDS micelle is about $0.62 \pm 0.05$ eV [8]. Our result in this case is $0.90 \div 0.68$ eV. Recall, that in [3] this binding energy was obtained using $\varepsilon = 2.559$.

The experimental value of blueshift for the (7, 5) SWCNT is $\delta E_{11} = 40 \div 55$ meV [11]. By (10) for the (7, 5) tube this gives $\tilde{n}_e \sim 100$ $\mu$m$^{-1}$, while from estimates (9) it follows that $\tilde{n}_e \in [150, 160]$ $\mu$m$^{-1}$. The discrepancy may be stipulated by ignoring of the collective effects in exciton gas and by using of the Schrödinger equation near the band edge instead of the Bethe-Salpeter equation with the energy-dependent potential [18].

The exciton binding energy was also calculated for the (8, 0) nanotube ($R_0 = 0.315$ nm, band gap $E_g = 1.415$ eV). According to (1) with (6) we have $1.26 \div 0.97$ eV, which is close to that in [2] (about $0.86 - 1$ eV). Recall that the results on the (8, 0) nanotube in [2] are in good agreement with those obtained in [7] by interpolation of experimental data for another nanotubes in SDS micelles.

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