Excitons in single-walled carbon nanotubes: environmental effect

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Abstract

The properties of excitons in semiconducting single-walled carbon nanotubes (SWCNTs), isolated in vacuum or a medium, and their contributions to the optical spectra of nanotubes are studied within the elementary potential model, in which an exciton is represented as a bound state of two oppositely charged quasi-particles confined to the nanotube surface. The emphasis is given on the influence of dielectric environment surrounding a nanotube on the exciton spectra. For nanotubes in environment with permittivity less than \( \sim 1.8 \) the ground-state exciton binding energies exceed the respective energy gaps, while the obtained binding energies of excitons in nanotubes in a medium with permittivity greater than \( \sim 4 \) are in good accordance with the corresponding experimental data and consistent with known scaling relation for the environmental effect. The stabilization process of single-electron spectrum in SWCNTs in media with rather low permittivities is discussed.

1 Introduction

The most of experimental works on optical properties of single-walled carbon nanotubes (SWCNTs) indicated that the exciton contributions were dominant in the nanotubes optical spectra [1]-[3] and the exciton binding energies were comparable to the corresponding energy gaps [4],[5]. These effects were explained (predicted) in the theoretical works [6]-[12] on the quasione-dimensional Wannier-like excitons in SWCNTs, which also yielded large, in comparison with the 3D case, exciton binding energies and revealed the determining influence of strong interparticle Coulomb interaction in one dimension on the optical properties of nanotubes. It was also shown (for example, in [13]), that the potential of interaction between electron and hole, which form an exciton, should be substantially weakened by the dielectric environment surrounding a nanotube. The dependence of exciton binding energy \( \mathcal{E} \) on the environmental permittivity \( \varepsilon_{\text{env}} \) obtained in [13]: \( \mathcal{E} \sim \varepsilon_{\text{env}}^{-\alpha} \) with \( \alpha = 1.4 \) is not similar to that in the 3D case (\( \alpha = 2 \)). As it was pointed out in [13], the relation \( \mathcal{E} \sim \varepsilon_{\text{env}}^{-\alpha} \) with \( \alpha = 1.4 \) is accurate only for nanotubes surrounded by media with high permittivity (\( \varepsilon_{\text{env}} \gtrsim 4 \)), because the results of calculations based on the Ohno potential chosen in [13] to model the unscreened Coulomb interaction between carbon \( \pi \)-orbitals is not sensitive to the value of the potential parameter only if the exciton radius is rather large. This takes place in the environmental permittivities range, which is of technological interest (silicon oxide environment, etc. [13]). However, in the most of experiments on optical response of SWCNTs individual nanotubes were isolated in media with low permittivities: the hydrocarbon environment of SDS micelles [1]-[3], [14] (by [15] the corresponding empirical \( \varepsilon_{\text{env}} = 2 - 2.5 \), while [4] used \( \varepsilon_{\text{env}} \sim 4 \)); the polymer matrix environment [5] (used \( \varepsilon_{\text{env}} = 2.5 \)); air [15],[16] (\( \varepsilon_{\text{env}} = 1 \)). This is why here, using an exciton model, which is not influenced by the exciton radius but depends on the tube radius and carriers effective masses (and thus on the nanotube chirality), we apply the scaling relation for exciton binding energies from [13] to excitons in SWCNTs in low-permittivity media (\( 1 \leq \varepsilon_{\text{env}} \lesssim 4 \)) to obtain the corresponding scaling parameter \( \alpha \).

The exciton in a SWCNT is modelled here as a bound state of two quasi-particles, which opposite charges are smeared uniformly along infinitesimal narrow bands at the tube surface, with the interaction potential having the Coulomb attraction tail (see section 2, or [17],[18] for details). The single-electron spectrum and wave functions were obtained like in [19],[20] by the zero-range potentials method [21],[22]. It turned out, that within the mentioned model the binding energies of excitons in the ground state in nanotubes surrounded by a medium with \( \varepsilon_{\text{env}} \sim 4 \) were in good accordance with the corresponding experimental data from [4] and in

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the range $\varepsilon_{\text{env}} \in [4, 16]$ obey the scaling relation from [13] with $\alpha \simeq 1.4$. Moreover, for the same $\varepsilon_{\text{env}} \sim 4$ the differences between the ground-state exciton binding energies and those of the lowest excited states are also in good agreement with the respective experimental results of [1] and [5] (section 3). In the region $\varepsilon_{\text{env}} \lesssim 1.8$ the ground-state exciton binding energies exceed the corresponding energy gaps. This leads to instability of the nanotube single-electron states with regard to formation of excitons, which, however, become stabilized because of the additional screening effect stipulated by born excitons. Since some of the single-electron states have transformed into excitons the edges of the forbidden band move apart, and this results in the enhancement (blueshift) of the lowest optical transition energy like in experiments [15, 16]. The corresponding estimates are in satisfactory agreement with results of [15]. Besides, in the ranges of low environmental permittivities $\varepsilon_{\text{env}} \in [1, 1.75]$ and $\varepsilon_{\text{env}} \in [2, 4.5]$ the ground-state exciton binding energies satisfy the mentioned relation from [13] with slightly smaller values of parameter $\alpha$: 1.121 and 1.258, respectively (see section 3).

2 Model of exciton in a semiconducting SWCNT

By analogy with the 3D case it can be shown (like in [17]) that within the long-wave approximation the wave equation for the Fourier transform $\phi$ of envelope function in the wave packet from products of the electron and hole Bloch functions, which represents a two-particle state of large-radius rest exciton in a quasione-dimensional semiconducting nanotube with the longitudinal period $a$, is reduced to the following 1D Schrödinger equation:

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

$$-\infty < z < \infty,$$

(2.1)

with the exciton reduced effective mass $\mu$, the forbidden band width $E_g$ and the electron-hole (e-h) interaction potential

$$V(z) = -\int \int \int \frac{e^2 |u_{c,0}(r_1)|^2 |u_{v,0}(r_2)|^2 d^3r_1 d^3r_2}{[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z + z_1 - z_2)^2]^{1/2}},$$

$$E_3^a = E_2 \times (0 < z < a),$$

(2.2)

where $u_{c,v,k}(r)$ are the Bloch amplitudes of the Bloch wave functions $\psi_{c,v,k}(r) = \exp(ikz)u_{c,v,k}(r)$ of the conduction and valence band electrons of a SWCNT, respectively, and $k$ is the electron quasi-momentum. Assuming that the charges of electron and hole, which participate in the formation of exciton, are smeared uniformly along infinitesimal narrow bands at the nanotube surface we obtain from (2.2):

$$V_{R_0}(z) = -\frac{2e^2}{\pi |z|} K \left[ -\frac{4R_0^2}{z^2} \right],$$

(2.3)

where $K$ is the complete elliptic integral of the first kind and $R_0$ is the nanotube radius. This potential is the simplest approximation to the bare Coulomb potential, which accounts the finiteness of the nanotube diameter. At this point of the model SWCNTs differ only by their radii and the carriers effective masses. However, even the combination of these parameters allows to specify the nanotube chirality.

To take into account the screening of e-h interaction potential by the nanotube band electrons we have applied the Lindhard method (the so-called random phase approximation), according to which the analogue of quasione-dimensional electrostatic potential [23] screened by the nanotube $\pi$-electrons is given by the following expression [17]:

$$\varphi_{R_0}(z) = -\frac{2e^2}{\pi R_0} \int_0^\infty I_0(q)K_0(q)\cos(qz/R_0) \frac{dq}{1 + gaq^2I_0(q)K_0(q)},$$

(2.4)

where $I$ and $K$ are the modified Bessel functions of the first and second kind, respectively, and the dimensionless screening parameter

$$g_a = \frac{e^2 \hbar^4}{\pi m_0^2 R_0^2} \sum_s \int_{-\pi/\alpha}^{\pi/\alpha} \left| \frac{1}{E_3^{g,s,s}(k)} \left| \psi_{c,k,s} \right| \frac{\partial}{\partial z} \psi_{v,k,s} \right|^2 dk.$$

(2.5)

Here $s$ numbers $\pi$-electron bands, which are mirror with respect to the Fermi level, because only for those bands the matrix element in (2.5) is nonzero [17, 19], and $m_0 = 0.415 m_e$ is the bare mass from [19, 20].
As it was mentioned above, most of existing experiments on the optical response of SWCNTs [11]-[5] dealt with nanotubes isolated not in vacuum but in media with the dielectric constants different from unity, therefore the corresponding screening of the e-h interaction potential should be also taken into account because a dielectric medium, surrounding a nanotube, should noticeably change the e-h interaction potential. For example, in experimental works [2]-[4],[14], which used the methods described in [1], investigated isolated SWCNTs were encased in the sodium dodecyl sulfate (SDS) cylindrical micelles disposed in heavy water. Because of these SDS micelles, which provided a pure hydrocarbon environment around individual nanotubes, the high permittivity solvent D2O did not reach nanotubes. However, the environment of hydrophobic hydrocarbon "tails" (−C12H25) of the SDS molecules has the permittivity greater than unity (by the experiment [15] it is about 2−2.5). In accordance with figure 1A from [1] and with [23] a simple model of a SWCNT in a dielectric environment was considered, namely: a narrow, infinite cylinder with radius \( R_0 \) in a medium with the dielectric constant \( \varepsilon_{\text{env}} \) and some internal screening parameter \( \varepsilon_{\text{int}} \). The corresponding analogue of potential (2.3) screened by environment within the framework of the mentioned model is given by [18]:

\[
\varphi_{R_0}(z) = -\frac{2e^2}{\pi R_0} \int_0^\infty \frac{I_0(q)K_0(q)\cos(qz/R_0)}{[\varepsilon_{\text{env}}I_0(q)K_1(q) + \varepsilon_{\text{int}}I_1(q)K_0(q)]} dq.
\]

(2.6)

The internal screening parameter \( \varepsilon_{\text{int}} \equiv \varepsilon_{\text{int}}(q) = 1 + g_0 q^2 I_0(q)K_0(q) \) according to (2.4). As it was shown further (section 3), potential (2.6) with this \( \varepsilon_{\text{int}} \) can be used to model the e-h interaction in SWCNTs isolated in medium with \( \varepsilon_{\text{env}} \geq 1.8 \) (e.g.: the SDS environment [4], the polymer matrix [5], etc.).

3 Calculation results. Environmental screening influence

The exciton binding energies and envelope functions were obtained within the above-stated exciton model using the wave equation (2.1) with the different e-h interaction potentials (2.4), (2.6) and the single-electron parameters (effective masses, single-particle wave functions, band gaps) calculated according [19],[20] within the zero-range potentials method [21],[22].

According to the wave equation (2.4) with the e-h interaction potential (2.4) screened only by the nanotube band electrons and that screened also by the external dielectric medium (2.6) we have calculated the binding energies of excitons in different SWCNTs in vacuum and in the SDS environment, respectively (see table 1).\(^1\) The experimental value of dielectric constant of the SDS environment \( \varepsilon_{\text{env}} = 2 \pm 2.5 \) was taken from [14]. Table 1 shows that for these values of \( \varepsilon_{\text{env}} \) there is only a qualitative similarity of the obtained results to the corresponding data from experimental work [4], though this \( \varepsilon_{\text{env}} \) is taken from experiment. However, if we, following [4], choose \( \varepsilon_{\text{env}} = 4.4 \) the ground-state exciton binding energies become almost identical to those obtained in [4] (see table 2). Moreover, for each considered SWCNT the obtained difference between the ground-state exciton binding energy and that of exciton in the lowest exited state also becomes almost equal to the respective experimental value from [4] \(^2\). The discrepancies between the data from table 2 and the corresponding results from [4] for the exciton binding energies and also for the differences \( E_{0;\text{even}}^* - E_{1;\text{odd}}^* \) and \( E_{11}^{2p} - E_{11}^{1u} \) appears to be inessential if the variation of \( \varepsilon_{\text{env}} \) in \( \pm 0.3 \) for different tubes in [4] is taken into account. It is also worth mentioning, that the obtained here differences \( \Delta E_{0;\text{even}}^* - \Delta E_{1;\text{odd}}^* \) are also very close to the respective results of experiment [5] on SWCNTs isolated in polymer matrices.

Table 1 also shows that the ground-state binding energies of excitons in nanotubes in vacuum are substantially larger than the corresponding band gaps, while those in nanotubes in the medium with \( \varepsilon_{\text{env}} \geq 2 \) occur already inside of the respective band gaps. The applicability of effective-mass approximation may seem questionable for such large exciton binding energies \( \varepsilon_{0;\text{even}}^* \) in vacuum. However, it is not the effective-mass approximation that causes so great absolute value of the exciton ground-state energy. The matter is that the effective-mass approximation consists in the replacement of the original dispersion relations for the valence and conduction bands, which come in the equation for exciton envelope function as \( \epsilon_+(k) - \epsilon_-(−k) \), by their expansion to the quadratic terms \( \epsilon_+(k) - \epsilon_-(−k) \sim E_g + h^2k^2/2\mu \). But such a replacement only increases the kinetic part of exciton energy operator and thus can only reduce the absolute values of (negative) exciton binding energies.

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\(^1\) The ground state of exciton corresponds to the even envelope function \( \phi(z) \) (\( z \) is the distance along the tube axis between electron and hole) and the lowest excited state corresponds to the odd one, further the excited states of different parity actually alternate.

\(^2\) Recall, that the difference between the binding energies of exciton in two different states and the difference between the corresponding excitation energies are equal, so one can compare \( E_{0;\text{even}}^* - E_{1;\text{odd}}^* \) and \( E_{11}^{2p} - E_{11}^{1u} \) from [4] and \( E_{2p} - E_{1u} \) from [5]. Recall also, that the exciton states in [4] with the even z-inversion symmetry were indexed by 1 and those with the odd one by 2.
Table 1: The ground-state exciton binding energies $\mathcal{E}_{0;\text{even}}$ for different SWCNTs in vacuum (according to the wave equation (2.1) with screened potential (2.4)) and in the medium with $\varepsilon_{\text{env}} = 2 \div 2.5$ from [15] (according to (2.1) with screened potential (2.6)), and also the corresponding results from experimental work [4].

| Chirality | $2R_0$ (nm) | $\mu$ ($m_e$) | $E_g$ (eV) | $\mathcal{E}_{0;\text{even}}$ (eV) in vacuum | $\mathcal{E}_{0;\text{even}}$ (eV) in medium $\varepsilon_{\text{env}} = 2 \div 2.5$ | $E_{1;\text{even}}$ (eV) [4] |
|-----------|-------------|---------------|------------|---------------------------------|---------------------------------|-----------------|
| (6, 4)    | 0.6825      | 0.0651        | 1.21       | 2.53                            | 1.09 $\div$ 0.82                | 0.38            |
| (6, 5)    | 0.7468      | 0.0510        | 1.10       | 2.25                            | 0.95 $\div$ 0.71                | 0.33            |
| (9, 1)    | 0.7468      | 0.0748        | 1.117      | 2.46                            | 1.07 $\div$ 0.81                | 0.38            |
| (8, 3)    | 0.7711      | 0.0644        | 1.076      | 2.32                            | 1.00 $\div$ 0.75                | 0.35            |
| (7, 5)    | 0.8174      | 0.0530        | 1.01       | 2.10                            | 0.90 $\div$ 0.68                | 0.28            |
| (9, 4)    | 0.9029      | 0.0522        | 0.9176     | 1.95                            | 0.84 $\div$ 0.63                | 0.33            |

Table 2: The ground-state exciton binding energies $\mathcal{E}_{0;\text{even}}$ for different SWCNTs in the medium with $\varepsilon_{\text{env}} = 4.4$ from [4] according to (2.1) with screened potential (2.4), the difference between the exciton binding energy in the ground state and first excited one $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$, and also the corresponding experimental data from [4] and [5].

| Chirality | $\mathcal{E}_{0;\text{even}}$ (eV) in medium $\varepsilon_{\text{env}} = 4.4$ | $E_{1;\text{even}}$ (eV) [4] | $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$ (eV) | $E_{11}^{\text{exp}} - E_{11}^{\text{ex}}$ (eV) [4] | $E_{2p} - E_{1s}$ (eV) [5] |
|-----------|---------------------------------|-----------------|---------------------------------|-----------------|-----------------|
| (6, 4)    | 0.39                            | 0.38            | 0.346                            | 0.325            | -               |
| (6, 5)    | 0.33                            | 0.33            | 0.302                            | 0.285            | 0.31            |
| (9, 1)    | 0.38                            | 0.38            | 0.340                            | 0.315            | -               |
| (8, 3)    | 0.36                            | 0.35            | 0.317                            | 0.295            | 0.3             |
| (7, 5)    | 0.32                            | 0.28            | 0.287                            | 0.24             | 0.28            |
| (9, 4)    | 0.30                            | 0.33            | 0.267                            | 0.28             | -               |

Therefore, without the effective-mass approximation, the exciton binding energies come even larger. Besides, the calculations of the exciton radii (for example, as the root-mean-square deviation of the envelope function Fourier transform $\phi(z)$ from the origin on the tube axis) show that for the ground state in vacuum they are of the order of nanotube diameter $2R_0$, which is much larger than the nanotube longitudinal period $\alpha$, which in its turn is of the order of tube lattice parameter ($\sim 0.142$ nm for CNTs). Thus, the long-wave approximation formalism is also applicable. Later on we will return to the discussion of seeming instability of the nanotube single-electron states with respect to formation of excitons in SWCNTs in media with $\varepsilon_{\text{env}} < 2$, and for now let us consider in greater detail the interval of environmental dielectric constants $\varepsilon_{\text{env}} \gtrsim 2$.

To reveal the general dependence of binding energies of excitons in SWCNTs on the environmental dielectric constant the corresponding scaling relation from [13] is applied. According to [13] after taking the logarithm one can obtain from the mentioned relation:

$$
\ln \frac{\mathcal{E}}{\mathcal{E}'} \approx (\alpha - 2) \ln \frac{R_0}{R_0'} + (\alpha - 1) \ln \frac{\mu}{\mu'} - \alpha \ln \frac{\varepsilon_{\text{env}}}{\varepsilon_{\text{env}}'}, \tag{3.1}
$$

where $\alpha$ according to [13] equals 1.40, and $\mathcal{E}'$, $R_0'$, $\mu'$, $\varepsilon_{\text{env}}'$ are some magnitudes, which do not influence on the relation, and introduced here just to make the corresponding variables dimensionless. The ground-state exciton binding energies obtained using the wave equation (2.1) with potential (2.4) for the set of SWCNTs with different diameters ($2R_0 \in [0.63, 2.19]$ nm) surrounded by media with permittivities in the range of interest indicated by [4] and [15] ($\varepsilon_{\text{env}} \in [2, 4.5]$). Using the least-squares method we found that for these ranges of the nanotubes diameters and environmental permittivities relation (3.1) was valid when $\alpha \simeq 1.258$ (see figure 1(a)). It should be noted, that for the same set of nanotubes, but for the environmental dielectric constants range $\varepsilon_{\text{env}} \in [4, 16]$ the calculated value of $\alpha$ directly approaches that obtained in [13]. According to [13] the scaling relation with $\alpha = 1.40$ is accurate only in the region $\varepsilon_{\text{env}} \gtrsim 4$, this explains the discrepancy between $\alpha$ obtained here and that from [13] in the region $\varepsilon_{\text{env}} \lesssim 4$.

The binding energies of excitons in the first excited state in SWCNTs also obey relation (3.1), but with $\alpha \simeq 1.89$ for the range $\varepsilon_{\text{env}} \in [2, 4.5]$ (see figure 1(b)) and with $\alpha \simeq 1.93$ for the range $\varepsilon_{\text{env}} \in [4, 16]$. This
The upper and lower limits of the exciton concentration $n$ can be given as follows [13]:

$$
\frac{\varepsilon_{\text{exc}} - 1}{4\pi} \frac{\varepsilon_0 - \varepsilon_1}{2\varepsilon_2} \left| \int_{-\infty}^{\infty} z^2 |\phi_0(z)|^2 \, dz \right|^{-1} 
\leq n \leq \frac{\varepsilon_{\text{exc}} - 1}{4\pi} \frac{\varepsilon_0 - \varepsilon_1}{2\varepsilon_2} \left| \int_{-\infty}^{\infty} z \phi_0(z) \phi_1(z) \, dz \right|^{-2},
$$

(3.2)
where $\phi$ is the component of Fourier transform of the corresponding exciton envelope function, it depends only on the distance $z$ between the electron and hole along the tube axis. Each $\phi$ is the solution of wave equation (2.1) with potential (2.6), where $\varepsilon_{\text{env}} \lesssim 1.8$ and $\varepsilon_{\text{int}} \equiv \varepsilon_{\text{int}}(q) = \varepsilon_{\text{exc}} + 1 + \mu q^2 I_0(q) K_0(q)$ (according to (2.4) and (2.5)).

The ground-state envelope function $\phi_0$ is the even solution of the 1D Schrödinger equation (2.1), which satisfies the boundary condition $\phi'(0) = 0$, $\phi_1$ is the odd solution of (2.1), which corresponds to the lowest excited exciton state and satisfies the boundary condition $\phi(0) = 0$, $\varepsilon_0$ and $\varepsilon_1$ are the corresponding exciton binding energies (eigenvalues of (2.1)), and $\varepsilon_{\text{exc}}$ is the incipient excitons contribution to the dielectric function of a nanotube.

Varying $\varepsilon_{\text{exc}}$ in (2.6) substituted into wave equation (2.1) one can match $\varepsilon_0$ to the energy gap. Further, $\varepsilon_1$ 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 (3.2) the upper and lower limits for the critical concentration of excitons $n_c$. Using the obtained $n_c$ one 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 within the effective mass approximation the lowest optical transition energy $E_{11}$ should be blueshifted by

$$\delta E_{11} = \frac{(\hbar \bar{n}_c)^2}{2\mu},$$

(3.3)

like in experiments [15] and [16]. Here $\bar{n}_c = n_c \pi R_0^2$ is the linear critical concentration of excitons.

According to experiment [15] this blueshift is about $40 - 55$ meV for SWCNTs in air (vacuum, $\varepsilon_{\text{env}} = 1$) with respect to those encased in SDS micelles [3] (in this case according to [15] $\varepsilon_{\text{env}}$, at least, larger than 2). By [33] this blueshift gives the linear critical concentration of excitons $\bar{n}_c$, which should be born in a SWCNT to stabilize the nanotube single-electron spectrum, about 80 $\mu$m$^{-1}$ for nanotubes with diameters $\sim 1$ nm and about 50 $\mu$m$^{-1}$ for nanotubes with diameters $\sim 1.5 - 2$ nm. The corresponding estimates in accordance with (3.2) are about 100 – 150 $\mu$m$^{-1}$ for SWCNTs with diameters $\sim 1$ nm (e.g., for the (9, 7) tube $\bar{n} \in [110, 115] \mu$m$^{-1}$) and about 50 – 100 $\mu$m$^{-1}$ for SWCNTs with diameters $\sim 1.5 - 2$ nm (e.g., for the (28, 0) tube $\bar{n} \in [50, 55] \mu$m$^{-1}$).

The discrepancies in values of $\bar{n}_c$ obtained from experimental data and those estimated using relation (3.2) may be stipulated by ignoring the collective effects in exciton gas and effects of dynamical screening of the e-h interaction potential.

It is also worth mentioning, that in the considered range $\varepsilon_{\text{env}} \in [1, 1.75]$ of seeming instability of the single-electron spectrum the unstabilized (calculated without the described stabilization) binding energies of excitons in the ground state in different SWCNTs obey relation (4.1) with $\alpha = 1.21$ (see figure 1(c)), the respective binding energies of excitons in the lowest excited states satisfy (3.1) with $\alpha = 1.838$ (see figure 1(d)).

4 Summary

In summary, the spectra of excitons in SWCNTs have been studied within the effective-mass and long-wave approximations and elementary potential model on the basis of zero-range potentials method [19, 20]. These spectra are highly influenced by the dielectric environment surrounding a nanotube. The obtained binding energies $E$ of excitons in the ground state and the differences between the ground and first excited exciton energy levels in nanotubes surrounded by medium with permittivity $\varepsilon_{\text{env}} \sim 4$ are in good accordance with the corresponding experimental data from [4] and [5]. Also, in the range of $\varepsilon_{\text{env}} \in [4, 16]$ the ground-state exciton binding energies $E$ obey the relation from [13]: $E \sim \varepsilon^{-\alpha}$, where $\alpha = 1.4$. However, in the ranges of permittivities $\varepsilon_{\text{env}} \in [1, 1.75]$ and $\varepsilon_{\text{env}} \in [2, 4.5]$ these binding energies satisfy the mentioned relation with slightly smaller values of $\alpha$: 1.121 and 1.258, respectively. These results are very close to those from [10], in which $\alpha = 1.2$ was obtained for the whole interval $\varepsilon_{\text{env}} \in [1, 4]$ using a model, in which SWCNT was represented as a dielectric cylinder with some internal permittivity surrounded by a medium with another dielectric constant. In contrast to our model the nature of high internal nanotube permittivity in the region of low environmental permittivities is not explained in [10] (there is only an estimate). However, the conclusion about the important role of $\varepsilon_{\text{int}}$ in the exciton parameters calculation for this region of $\varepsilon_{\text{env}}$ is made in [10] and this also explains the discrepancy in the result on $\alpha$ with that obtained in [13] using only $\varepsilon_{\text{env}}$.

In the range $\varepsilon_{\text{env}} \in [1, 1.75]$ the ground-state exciton binding energies $E$ exceed the corresponding energy gaps. This leads to instability of the nanotube single-electron states with respect to formation of excitons, but due to their high polarizability in the external electric field the incipient excitons induce the additional screening effect, which returns the ground-state exciton binding energy into the respective energy gap and thus stabilize the nanotube single-electron spectrum. Because of the transformation of some single-electron states into excitons the edges of the forbidden band move apart, and this results in the enhancement (blueshift) of the
lowest optical transition energy $E_{11}$ like in experiments [15], [16]. The corresponding estimates for $\varepsilon_{env} = 1$ are in satisfactory agreement with results of [15].

Finally, the present work is initially based on the special version of independent particle theory, namely, the zero-range potentials method modelling the self-consistent periodic potential in a nanotube by the system of universal Fermi pseudo-potentials located at the carbon atoms positions. This method has exhibited for determination of band structure and optical spectra of carbon nanotubes very good accordance with the corresponding extended LCAO calculations and experimental data. However, for explanation of the stability of SWCNTs band spectra in vacuum and low-permittivity media with respect to the exciton formation we had to explicitly refer to many-particle effects, which in parallel with stabilization resulted in a slight broadening of the band gap. Note, that this treatment though formally being alternative to the quasiparticle approach (as in [7]) and band gap renormalization formalism (as in [11]) does not principally contradict to them and apparently well agrees with the experimentally defined relative energy parameters of excitons.

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