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## EXCITONS IN SINGLE-WALLED CARBON NANOTUBES: ENVIRONMENTAL EFFECT

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PACS 78.67.Ch  
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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 quasiparticles confined to the nanotube surface. The emphasis is given on the influence of the dielectric environment surrounding a nanotube on the exciton spectra. For nanotubes in the environment with a permittivity less than  $\sim 1.8$ , the ground-state exciton binding energies exceed the respective energy gaps, whereas 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 the known scaling relation for the environmental effect. The stabilization of a single-electron spectrum in SWCNTs in media with rather low permittivities is discussed.

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### 1. Introduction

The majority of experimental works on the optical properties of single-walled carbon nanotubes (SWCNTs) indicates that the exciton contributions are dominant in the optical spectra of nanotubes [1–3], and the exciton binding energies are comparable with the corresponding energy gaps [4, 5]. These effects were explained (predicted) in the theoretical works [6–12] on quasioone-dimensional Wannier-like excitons in SWCNTs which also yield large, in comparison with the 3D case, exciton binding energies and reveal the determining influence of the strong interparticle Coulomb interaction in one dimension on the optical properties of nanotubes. It was also shown (e.g., in [13]) that the interaction potential between an electron and a hole which form an exciton should be substantially weakened by the dielectric environment surrounding a nanotube. The dependence of the exciton

binding energy  $\mathcal{E}$  on the environment permittivity  $\varepsilon_{\text{env}}$  was obtained in [13]:  $\mathcal{E} \sim \varepsilon_{\text{env}}^{-\alpha}$  with  $\alpha = 1.4$  not similar to that in the 3D case ( $\alpha = 2$ ). As was pointed in [13], the relation  $\mathcal{E} \sim \varepsilon_{\text{env}}^{-\alpha}$  with  $\alpha = 1.4$  is accurate only for nanotubes surrounded by a medium 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 are not sensitive to the potential parameter only if the exciton radius is rather large. This occurs in the range of environment permittivities which is of technological interest (silicon oxide environment, etc. [13]). However, in the most of experiments on the optical response of SWCNTs, individual nanotubes were isolated in media with low permittivities: the hydrocarbon environment of SDS micelles [1–4, 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  $\varepsilon_{\text{env}} = 2.5$ ); and 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 the effective masses of carriers (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 modeled here as a bound state of two quasiparticles, whose 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 those in [19, 20] by the method of zero-range potentials [21, 22]. It turned out that, within the mentioned model, the binding energies of ex-

citons 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 obey the scaling relation from [13] with  $\alpha \simeq 1.4$  in the range  $\varepsilon_{\text{env}} \in [4, 16]$ . 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 [4] 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 the instability of the single-electron states of a nanotube with regard to the 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 an enhancement (blueshift) of the lowest optical transition energy like in experiments [15, 16]. The corresponding estimates are in satisfactory agreement with results of [15]. In addition, 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 the 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 the envelope function in the wave packet from products of the electron and hole Bloch functions, which represents the two-particle state of a large-radius rest exciton in a quasideimensional semiconducting nanotube with the longitudinal period  $a$ , is reduced to the 1D Schrödinger equation

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

$$-\infty < z < \infty, \quad (1)$$

with the exciton reduced effective mass  $\mu$ , the forbidden band width  $E_{\text{g}}$ , and the electron-hole (e-h) interaction potential

$$V(z) =$$

$$= - \int_{E_{\text{g}}^{\text{c}}} \int_{E_{\text{g}}^{\text{v}}} \frac{e^2 |u_{\text{c};0}(\mathbf{r}_1)|^2 |u_{\text{v};0}(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2}{((x_1 - x_2)^2 + (y_1 - y_2)^2 + (z + z_1 - z_2)^2)^{1/2}},$$

$$E_{\text{g}}^a = E_2 \times (0 < z < a). \quad (2)$$

Here,  $u_{\text{c},\text{v};k}(\mathbf{r})$  are the Bloch amplitudes of the Bloch wave functions  $\psi_{\text{c},\text{v};k}(\mathbf{r}) = \exp(ikz)u_{\text{c},\text{v};k}(\mathbf{r})$  of the conduction and valence band electrons of a SWCNT, respectively, and  $k$  is the electron quasimomentum. Assuming that the charges of an electron and a hole which participate in the formation of an exciton are smeared uniformly along infinitesimal narrow bands at the nanotube surface, relation (2) yields

$$V_{R_0}(z) = -\frac{2e^2}{\pi|z|} \text{K} \left[ -\frac{4R_0^2}{z^2} \right], \quad (3)$$

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 a nanotube diameter. At this point of the model, SWCNTs differ only by their radii and the effective masses of carriers. However, even the combination of these parameters allows one to specify the nanotube chirality.

To take the screening of the e-h interaction potential by band electrons of a nanotube into account, we have applied the Lindhard method (the so-called random phase approximation), according to which the analog of the quasideimensional electrostatic potential (3) screened by the nanotube  $\pi$ -electrons is given by the expression [17]

$$\varphi_{R_0}(z) = -\frac{2e^2}{\pi R_0} \int_0^\infty \frac{I_0(q)K_0(q) \cos(qz/R_0)}{1 + g_a q^2 I_0(q)K_0(q)} dq, \quad (4)$$

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

$$g_a = \frac{e^2 \hbar^4}{\pi m_{\text{b}}^2 R_0^2} \times$$

$$\times \sum_s \int_{-\pi/a}^{\pi/a} \frac{1}{E_{\text{g};s,s}^3(k)} \left| \left\langle \psi_{\text{c};k,s} \left| \frac{\partial}{\partial z} \right| \psi_{\text{v};k,s} \right\rangle \right|^2 dk. \quad (5)$$

Here,  $s$  numbers  $\pi$ -electron bands which are mirror with respect to the Fermi level (only for those bands, the matrix element in (5) is nonzero [17, 19]), and  $m_{\text{b}} = 0.415m_{\text{e}}$  is the bare mass from [19, 20].

As was mentioned above, most of existing experiments on the optical response of SWCNTs [1–5] dealt with nanotubes isolated not in vacuum but in media

with the dielectric constants different from 1. 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], the investigated isolated SWCNTs were encased in 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 solvent D<sub>2</sub>O with high permittivity did not reach nanotubes. However, the environment of hydrophobic hydrocarbon “tails” (–C<sub>12</sub>H<sub>25</sub>) of SDS molecules has the permittivity greater than 1 (by the experiment [15] it is about 2–2.5). In accordance with Fig. 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 the medium with a dielectric constant  $\varepsilon_{\text{env}}$  and some internal screening parameter  $\varepsilon_{\text{int}}$ . The corre-

sponding analog of potential (3) screened by the environment within the framework of the mentioned model is given by [18]

$$\varphi_{R_0}(z) = -\frac{2e^2}{\pi R_0} \times \int_0^\infty \frac{I_0(q)K_0(q) \cos(qz/R_0)}{[\varepsilon_{\text{env}}I_0(q)K_1(q) + \varepsilon_{\text{int}}I_1(q)K_0(q)]q} dq. \quad (6)$$

The internal screening parameter  $\varepsilon_{\text{int}} \equiv \varepsilon_{\text{int}}(q) = 1 + g_a q^2 I_0(q)K_0(q)$  according to (4). As it will be shown further (Section 3), potential (6) with this  $\varepsilon_{\text{int}}$  can be used to model the e-h interaction in SWCNTs isolated in a medium with  $\varepsilon_{\text{env}} \gtrsim 1.8$  (e.g.: the SDS environment [4], the polymer matrix [5], *etc.*).

### 3. Calculation Results. Environmental Screening Influence

The exciton binding energies and the envelope functions were obtained within the above-stated exciton model using the wave equation (1) with the different e-h interaction potentials (4), (6) and the single-electron parameters (effective masses, single-particle wave functions, band gaps) calculated according to [19, 20] within the method of zero-range potentials [21, 22].

According to the wave equation (1) with the e-h interaction potential (4) screened only by band electrons of a nanotube and that screened also by the external dielectric medium (6), we have calculated the binding energies of excitons in different SWCNTs in vacuum and in the SDS environment, respectively (see Table 1).<sup>1</sup> The experimental dielectric constant of the SDS environment  $\varepsilon_{\text{env}} = 2 \div 2.5$  was taken from [15]. 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 the experimental work [4], though this  $\varepsilon_{\text{env}}$  is taken from experiment. However, if we choose  $\varepsilon_{\text{env}} = 4.4$ , following [4], then 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 an exciton in the lowest

**Table 1.** The ground-state exciton binding energies  $\mathcal{E}_{0;\text{even}}$  for different SWCNTs in vacuum (according to the wave equation (1) with screened potential (4)) and in the medium with  $\varepsilon_{\text{env}} = 2 \div 2.5$  from [15] (according to (1) with screened potential (6)), and 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 $\varepsilon_{\text{env}} = 2 \div 2.5$	$E_{11}^b$ (eV) [4]
(6, 4)	0.6825	0.0651	1.210	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	1.010	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 (1) with screened potential (6), the difference between the exciton binding energies in the ground state and the first excited one  $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$ , and the corresponding experimental data from [4] and [5]

Chirality	$\mathcal{E}_{0;\text{even}}$ (eV) in medium $\varepsilon_{\text{env}} = 4.4$	$E_{11}^b$ (eV) [4]	$\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$ (eV)	$E_{11}^{2g} - E_{11}^{1u}$ (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	0.30
(7, 5)	0.32	0.28	0.287	0.240	0.28
(9, 4)	0.30	0.33	0.267	0.280	–

<sup>1</sup> The ground state of an exciton corresponds to the even envelope function  $\phi(z)$  ( $z$  is the distance along the tube axis between an electron and a hole), and the lowest excited state corresponds to the odd one, further the excited states of different parities actually alternate.

excited state also becomes almost equal to the respective experimental value from [4].<sup>2</sup> The discrepancies between the data from Table 2 and the corresponding results from [4] for the exciton binding energies and for the differences  $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$  and  $E_{11}^{2g} - E_{11}^{1u}$  appear 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  $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$  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  $\varepsilon_{\text{env}} \gtrsim 2$  occur already inside of the respective band gaps. The applicability of the effective-mass approximation may seem questionable for such large exciton binding energies  $\mathcal{E}_{0;\text{even}}$  in vacuum. However, it is not the effective-mass approximation that causes a 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 the exciton envelope function as  $\epsilon_c(k) - \epsilon_v(-k)$ , by their expansion up to the quadratic terms  $\epsilon_c(k) - \epsilon_v(-k) \simeq E_g + \hbar^2 k^2 / 2\mu$ . But such a replacement only increases the kinetic part of the exciton energy operator and thus can only reduce the absolute values of (negative) exciton binding energies. Therefore, without the effective-mass approximation, the exciton binding energies come even larger. In addition, 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 the nanotube diameter  $2R_0$  which is much larger than the nanotube longitudinal period  $a$  which, in its turn, is of the order of the tube lattice parameter ( $\sim 0.142$  nm for CNTs).<sup>3</sup> Thus, the long-wave approximation formalism is also applicable.

<sup>2</sup> Recall that the difference between the binding energies of an exciton in two different states and the difference between the corresponding excitation energies are equal, so one can compare  $\mathcal{E}_{0;\text{even}} - \mathcal{E}_{1;\text{odd}}$  and  $E_{11}^{2g} - E_{11}^{1u}$  from [4] and  $E_{2p} - E_{1s}$  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.

<sup>3</sup> This is actually exact in the case of zigzag  $(n, 0)$  semiconducting tubes. For chiral  $(n, m)$  nanotubes, we considered a different longitudinal parameter concerned with the extended zone scheme used for the calculations of the band structure of chiral tubes (for details see [19]).

In what follows, we will return to the discussion of the seeming instability of nanotube single-electron states with respect to the formation of excitons in SWCNTs in media with  $\varepsilon_{\text{env}} < 2$ . Now, we consider the interval of environmental dielectric constants  $\varepsilon_{\text{env}} \gtrsim 2$  in more details.

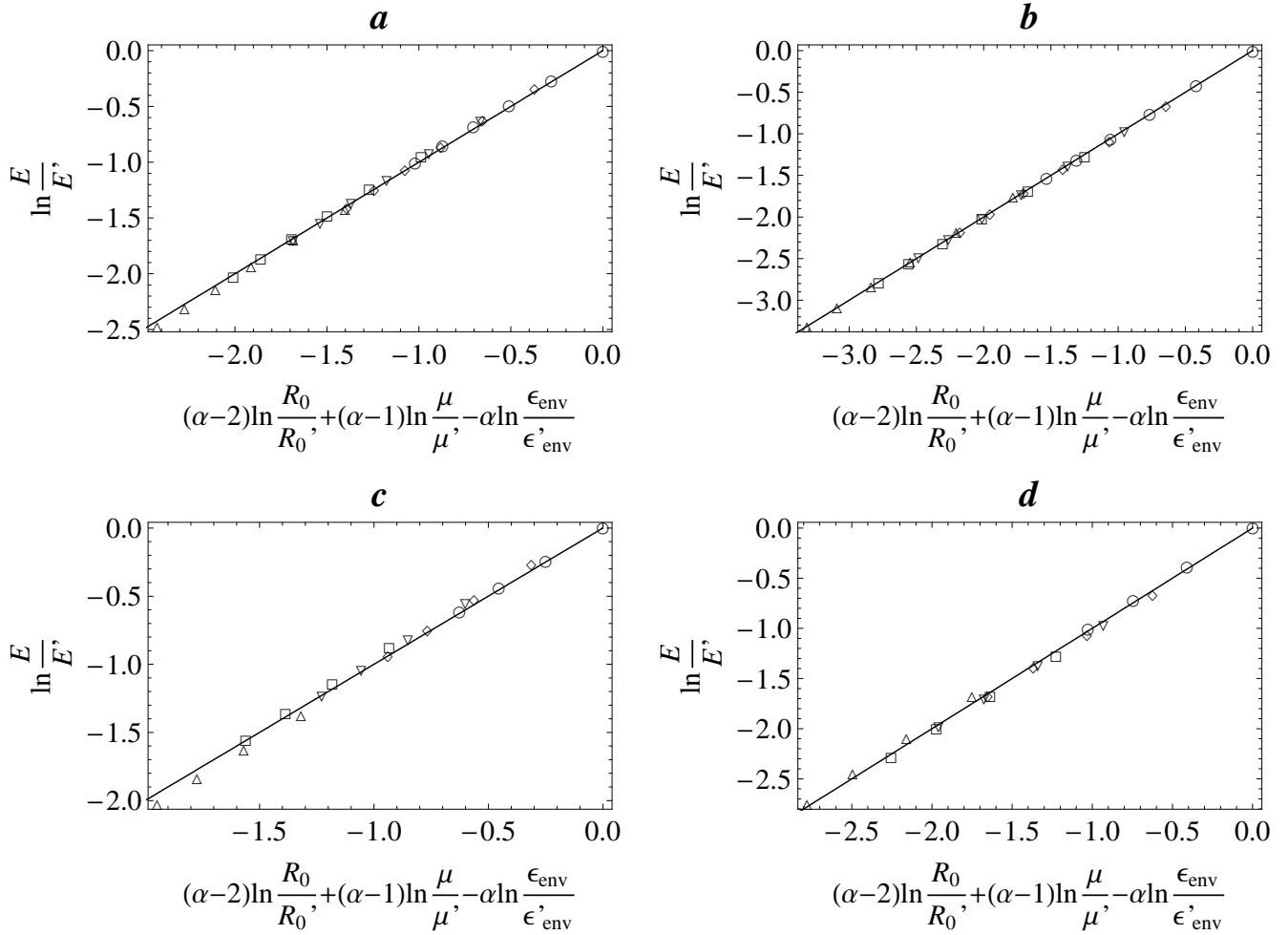
To reveal the general dependence of the binding energies of excitons in SWCNTs on the environmental dielectric constant, the corresponding scaling relation from [13] is applied. After taking the logarithm, this relation yields

$$\ln \frac{\mathcal{E}}{\mathcal{E}'} \approx (\alpha - 2) \ln \frac{R_0}{R'_0} + (\alpha - 1) \ln \frac{\mu}{\mu'} - \alpha \ln \frac{\varepsilon_{\text{env}}}{\varepsilon'_{\text{env}}}, \quad (7)$$

where  $\alpha$  equals 1.40 [13], and  $\mathcal{E}'$ ,  $R'_0$ ,  $\mu'$ ,  $\varepsilon'_{\text{env}}$  are some quantities which do not influence the relation and are introduced just to make the corresponding variables dimensionless. The ground-state exciton binding energies obtained using the wave equation (1) with potential (6) were substituted into (7) 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 (7) was valid when  $\alpha \simeq 1.258$  (see Figure, *a*). It should be noted that, for the same set of nanotubes, but for the environmental dielectric constants  $\varepsilon_{\text{env}} \in [4, 16]$ , 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  $\varepsilon_{\text{env}} \gtrsim 4$ , which 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 (7), but with  $\alpha \simeq 1.89$  for the range  $\varepsilon_{\text{env}} \in [2, 4.5]$  (see Figure, *b*) and with  $\alpha \simeq 1.93$  for the range  $\varepsilon_{\text{env}} \in [4, 16]$ . This is clear because the radii of excitons in SWCNTs even in the first excited state (especially in media with large  $\varepsilon_{\text{env}}$ ) are close to those of 3D excitons, for which, as is well known,  $\alpha = 2$ .

As was mentioned above, the obtained binding energies of excitons in the ground state in semiconducting SWCNTs in vacuum appeared to be larger than the corresponding band gaps (Table 1). More precisely, for the considered set of nanotubes surrounded by a medium with  $\varepsilon_{\text{env}} = 1.75 - 1.85$ , the ground-state exciton binding energy becomes equal to the corresponding energy gap. For smaller values of  $\varepsilon_{\text{env}}$ , the ground-state exciton binding energy exceeds the respective energy gap, and this may lead to the instability of the single-electron



General dependence of the binding energy of an exciton in SWCNTs of different chirality types ((8, 0)  $\circ$ , (7, 5)  $\diamond$ , (9, 7)  $\nabla$ , (15, 7)  $\square$ , and (28, 0)  $\triangle$  with diameters  $\sim$  0.63, 0.82, 1.09, 1.52, and 2.19 nm and with band gaps  $\sim$  1.42, 1.01, 0.76, 0.54, and 0.37 eV, respectively) on the environmental dielectric constant  $\epsilon_{\text{env}}$ , the nanotube radius  $R_0$ , and the effective masses of carriers  $\mu$ . The abscissa and the ordinate represent the right- and left-hand sides of (7), respectively. Black solid lines are plotted using the least-squares method. (a) the dependence of the binding energies of excitons in the ground state in SWCNTs surrounded by media with  $\epsilon_{\text{env}} \in [2, 4.5]$  ( $\epsilon_{\text{env}}$  changes with a step of 0.5), the points correspond to (7) with  $\alpha = 1.258$ , the primed quantities from (7) are the respective parameters of the (8, 0) nanotube in a medium with  $\epsilon_{\text{env}} = 2$ ; (b) the points similar to (a), but for the first excited exciton state and  $\alpha = 1.89$ ; (c) the dependence of the unstabilized binding energies of excitons in the ground state in SWCNTs surrounded by media with  $\epsilon_{\text{env}} \in [1, 1.75]$  ( $\epsilon_{\text{env}}$  changes with a step of 0.25), the points correspond to (7) with  $\alpha = 1.121$ , the primed quantities from (7) are the respective parameters of the (8, 0) nanotube in vacuum; (d) the points similar to (c), but for the first excited exciton state and  $\alpha = 1.838$

states of nanotubes with regard to the formation of excitons. However, the incipient excitons induce an additional screening stipulated by their great polarizability in the longitudinal electric field. This effect essentially weakens the e-h interaction. At a 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. The upper and lower limits of the exciton concentration

$n$  can be given as [18]

$$\frac{\epsilon_{\text{exc}} - 1}{4\pi} \frac{\mathcal{E}_0 - \mathcal{E}_1}{2e^2} \left| \int_{-\infty}^{\infty} z^2 |\phi_0(z)|^2 dz \right|^{-1} \leq n \leq \frac{\epsilon_{\text{exc}} - 1}{4\pi} \frac{\mathcal{E}_0 - \mathcal{E}_1}{2e^2} \left| \int_{-\infty}^{\infty} z \phi_0(z) \phi_1(z) dz \right|^{-2}, \quad (8)$$

where  $\phi$  is a component of the Fourier transform of the corresponding exciton envelope function and depends only on the distance  $z$  between the electron and the hole along the tube axis. Each  $\phi$  is the solution of the wave equation (1) with potential (6), where  $\varepsilon_{\text{env}} \lesssim 1.8$  and  $\varepsilon_{\text{int}} \equiv \varepsilon_{\text{int}}(q) = \varepsilon_{\text{exc}} + 1 + g_a q^2 I_0(q) K_0(q)$  (according to (4) and (5)). The ground-state envelope function  $\phi_0$  is the even solution of the 1D Schrödinger equation (1) which satisfies the boundary condition  $\phi'(0) = 0$ ,  $\phi_1$  is the odd solution of (1) which corresponds to the lowest excited exciton state and satisfies the boundary condition  $\phi(0) = 0$ ,  $\mathcal{E}_0$  and  $\mathcal{E}_1$  are the corresponding exciton binding energies (eigenvalues of (1)), and  $\varepsilon_{\text{exc}}$  is the contribution of incipient excitons to the dielectric function of a nanotube. Varying  $\varepsilon_{\text{exc}}$  in (6) substituted into the wave equation (1), one can match  $\mathcal{E}_0$  to the energy gap. Further,  $\mathcal{E}_1$  can be obtained from the same equation with the fixed  $\varepsilon_{\text{exc}}$  and with the corresponding boundary condition. These quantities allow us to calculate the upper and lower limits for the critical concentration of excitons  $n_c$  from (8). Using the obtained  $n_c$ , we can calculate a shift of the forbidden band edges which move apart due to the transformation of some single-electron states into excitons. This results in an enhancement of the energy gap. Hence, within the effective mass approximation, the lowest optical transition energy  $E_{11}$  should be blueshifted by

$$\delta E_{11} = \frac{(\pi \hbar \tilde{n}_c)^2}{2\mu}, \quad (9)$$

like in experiments [15] and [16]. Here,  $\tilde{n}_c = n_c \pi R_0^2$  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],  $\varepsilon_{\text{env}}$  is at least larger than 2). By (9), this blueshift gives the linear critical concentration of excitons  $\tilde{n}_c$  which should be born in a SWCNT to stabilize its single-electron spectrum. Its value is about  $80 \mu\text{m}^{-1}$  for nanotubes with diameters  $\sim 1$  nm and about  $50 \mu\text{m}^{-1}$  for nanotubes with diameters  $\sim 1.5 - 2$  nm. The corresponding estimates in accordance with (8) are about  $100 - 150 \mu\text{m}^{-1}$  for SWCNTs with diameters  $\sim 1$  nm (e.g., for the (9, 7) tube  $\tilde{n} \in [110, 115] \mu\text{m}^{-1}$ ) and about  $50 - 100 \mu\text{m}^{-1}$  for SWCNTs with diameters  $\sim 1.5 - 2$  nm (e.g., for the (28, 0) tube,  $\tilde{n} \in [50, 55] \mu\text{m}^{-1}$ ). The discrepancies in values of  $\tilde{n}_c$  obtained from experimental data and those estimated using relation (8) may be caused by ignoring the collective effects in the exciton gas and the 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 the 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 (7) with  $\alpha = 1.121$  (see Figure, c), the respective binding energies of excitons in the lowest excited states satisfy (7) with  $\alpha = 1.838$  (see Figure, d).

#### 4. Summary

The spectra of excitons in SWCNTs have been studied within the effective-mass and long-wave approximations and an elementary potential model within the method of zero-range potentials [19],[20]. These spectra are highly influenced by the dielectric environment surrounding a nanotube. The obtained binding energies  $\mathcal{E}$  of excitons in the ground state and the differences between the ground and first excited exciton energy levels in nanotubes surrounded by a medium with permittivity  $\varepsilon_{\text{env}} \sim 4$  are in good accordance with the corresponding experimental data from [4] and [5]. In the range of  $\varepsilon_{\text{env}} \in [4, 16]$ , the ground-state exciton binding energies  $\mathcal{E}$  obey the relation [13]  $\mathcal{E} \sim \varepsilon_{\text{env}}^{-\alpha}$ , 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 which is surrounded by a medium with another dielectric constant. In contrast to our model, the nature of a 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 calculation of exciton parameters 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  $\mathcal{E}$  exceed the corresponding energy gaps. This leads to the instability of the single-electron states of a nanotube with respect to the 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 stabilizes the single-electron spectrum of a nanotube. Due to the transformation of some single-electron states into excitons, the edges of the forbidden

band move apart, and this results in an enhancement (blueshift) of the lowest optical transition energy  $E_{11}$  like that in experiments [15, 16]. The corresponding estimates for  $\varepsilon_{\text{env}} = 1$  are in satisfactory agreement with results of [15].

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

The author is grateful to Prof. V.M. Adamyan for useful and interesting discussions.

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Received 13.08.09

#### ЕКСИТОНИ В ОДНОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБКАХ: ЕКРАНУВАННЯ ЗОВНІШНІМ СЕРЕДОВИЩЕМ

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#### Резюме

Досліджено властивості екситонів у напівпровідникових одношарових вуглецевих нанотрубках (ВНТ), ізольованих у вакуумі або середовищі, а також їх внесок в оптичні властивості нанотрубок. Використано елементарну потенціальну модель, у якій екситон представлено як зв'язаний стан двох протилежно заряджених квазічастинок на поверхні нанотрубки. Наголос зроблено на аналізі впливу на екситонні спектри діелектричного середовища, яке оточує нанотрубку. Для нанотрубок у середовищі з діелектричною проникністю, меншою за  $\sim 1,8$ , енергії зв'язку екситонів у основних станах перевищують величини відповідних заборонених зон, у той час

як отримані енергії зв'язку екситонів у нанотрубках у середовищах з діелектричною проникністю, більшою ніж  $\sim 4$ , добре узгоджуються з відповідними експериментальними даними та відомою залежністю енергій зв'язку екситонів у

ВНТ від властивостей зовнішнього середовища. Розглянуто процес стабілізації одноелектронного спектра в одношарових ВНТ у середовищах з малими діелектричними проникностями.