STABILITY OF TRIONIC STATES IN ZIGZAG CARBON NANOTUBES

S. MARCHENKO[1, 2]

[1]Department of Theoretical Physics, I.I. Mechnikov Odesa National University
(2, Dvorianska Str., Odesa 65026, Ukraine; e-mail: Sergey.Marchenko@onu.edu.ua)

**[2]Department of Biophysics, Informatics, and Medical Equipment,
Odesa National Medical University**
(2, Valikhovskyi Lane, Odesa 65026, Ukraine)

The stability of trionic excitations in zigzag carbon nanotubes has been estimated. A trion is shown to be unstable with respect to the ground excitonic state and stable with respect to the excited one. So, trions in nanotubes of this type can be formed by capturing an electron or a hole by an excited exciton. In other words, the trion in a nanotube is an excimer complex, which results in the formation of a system with three energy levels (unexcited exciton–trion–excited exciton).

1. Introduction

Owing to their unique mechanical, optical, and electric properties, single-walled carbon nanotubes (SWNTs) have attracted much attention in various domains of researches within the last two decades [1]. One of the most interesting features of carbon nanotubes is a strong correlation between charge carriers, which manifests itself through the quantum confinement; this phenomenon is observed in one-dimensional (1D) structures about 1 nm in diameter.

The electron-electron repulsion and the electron-hole attraction, which play an important role in governing the electronic and optical properties of nanotubes [2], give rise to the formation of excitons with huge binding energies in semiconducting carbon nanotubes [3] and even in metallic carbon nanotubes [4].

2. Excitonic States

The simplest excitation in a semiconducting system consists in that an electron, after having absorbed energy, transits from the valence band into the conduction one. In this case, there emerges a hole in the valence band, which behaves as a positively charged particle. For instance, an electron and a hole, while interacting by means of only the Coulomb mechanism, can form bound states. Such states are called excitons. In general,

two types of excitons are distinguished: Frenkel and Wannier–Mott excitons.

Carbon nanotubes belong to the class of direct-band-gap semiconductors. Therefore, the annihilation of electron-hole pairs can take place in them, which is accompanied by a photon emission [5]. Excitons localized in carbon nanotubes have an additional restriction; namely, the nanotube diameter is fixed and, therefore, such excitons can be considered as inherently one-dimensional objects.

The Coulomb interaction is known to be considerably strengthened in quasi-1D systems. This circumstance enhances the stability of exciton-like excitations, which makes the existing Coulomb blockade much stronger. Together with strong polarization effects, all this results in that new excitons are hardly formed. In other words, a few excitons, being formed in a nanotube, could block the formation of new ones, so that the total exciton concentration may be scarce. The issue concerning the influence of the screening by excitons on the formation of new many-particle excitations was described in work [6].

The formation of excitons in carbon nanotubes is possible, if the energy that generates the electron-hole pair is equal or smaller than the energy gap width. In the case where the energy is sufficient for the electron to get into the conduction band and for the hole, respectively, into the valence one, both quasiparticles do not interact, remaining independent of each other.

In 1D nanotubes, the exciton radius is much larger than the lattice constant, so that those excitons are analogs of Wannier–Mott excitons taking place in three-dimensional crystals. The exciton mass equals the reduced mass of the electron and the hole,

$$\mu = \frac{m_e m_h}{m_e + m_h}, \tag{1}$$

where m_e and m_h are the effective masses of the electron and the hole, respectively. The specific value of effective mass depends on the nanotube crystal structure. It can

be calculated consistently using expressions from work [11]. Below, the interaction between the electron and the hole will be considered as purely Coulombic.

However, there arises a question: What should be taken as the dielectric permittivity? For a carbon nanotube, the effects of the screening by its charges manifest themselves only at distances of the order of the tube diameter. Therefore, as the first approximation, we may adopt that that $\varepsilon = 1$ for nanotubes. We note that if the nanotube is located in a certain medium, e.g., in micelles, the corresponding value of dielectric permittivity for this medium should be accepted, which would affect the energies of excitonic excitations.

In this work, in order to estimate the energies of exciton-like excitations, we used the well-known Ritz method [7]. Recall that this method can be applied to evaluate the characteristic energy values from above. Note that we are interested in the stability of excitonic excitations with respect to one-electron states and the stability of trionic states with respect to the decay into an exciton and a hole (an electron). Therefore, if calculations are carried out in the framework of the same model, even this crude technique will produce qualitatively valid results.

To estimate the characteristic energy values, we use the Schrödinger equation written down in the form

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{e^2}{\sqrt{x^2 + d^2}} \right] \Psi = E\Psi. \tag{2}$$

Here, μ is the reduced exciton mass, e the elementary charge, x the distance between the electron and the hole measured along the nanotube, and d is a parameter, which depends on the nanotube diameter and, in the first approximation, is equal to it. One should pay attention that the potential in this equation is an even function. Therefore, the excitonic states in nanotubes are divided into two series, each composed of either even or odd characteristic wave functions. The exciton spectrum for the odd-function series is similar to those, which are typical of other hydrogenic systems. Optical transitions are allowed between the states in the even- and odd-function series. Taking into account that, in the odd-state series, the wave functions vanish at $x = 0$, the characteristic energy values for those states can be found as characteristic values of Eq. (2) determined at the semiaxis $(0, +\infty)$ with the boundary condition

$$\Psi(0) = 0. \tag{3}$$

Analogously, the spectrum for the even-function series is determined by the boundary condition

$$\Psi'(0) = 0. \tag{4}$$

The Hamiltonian in Eq. (2) can be used, when the dielectric permittivity of the medium, in which the nanotube is located, is close to 1. The application of a cut-off Coulomb potential in the model is associated with the necessity to remove the unphysical singularity at the zero point, which stems from the one-dimensionality of the problem. However, if one changes to a consequent consideration of a nanotube as a cylinder, this potential can be used as the basis for a more exact potential expressed via an elliptic integral, which was done, e.g., in work [8].

The main criterion for the choice of trial functions in the method used is their correspondence to boundary conditions. We also demand that they have to be integrable and smooth. However, it is not a rigorous requirement, but would only simplify the calculations. The behavior of the selected exciton wave functions completely coincides with that of exact functions presented graphically and described in [9].

We used the trial functions of the following forms:

$$\Psi_{\text{even}}(x) = C_1 \exp\left[-\alpha x^2\right] \tag{5}$$

for the even-function series and

$$\Psi_{\text{odd}}(x) = C_2 x \exp\left[-\alpha x^2\right] \tag{6}$$

for the odd-function one. It is necessary to get rid of dimensional coefficients. Therefore, let us change to the system of atomic units, in which $\mu = 1$, $\hbar = 1$, and $e = 1$. The Bohr radius of an exciton serves as a unit length. Evidently, it depends on the effective mass of an exciton and the nanotube diameter. Therefore, the nanotube diameter in the final equation must be expressed in terms of introduced atomic units.

In this case, the ground state in the even-function series approximately coincides with the minimum of the function

$$I_1(\alpha) = \frac{\hbar^2\sqrt{2\pi\alpha}}{8\mu} - \frac{1}{2}e^2 e^{\alpha d^2} K_0[\alpha d^2], \tag{7}$$

and, in the odd-function series, with the minimum of the function

$$I_2(\alpha) = \frac{\hbar^2\sqrt{2\pi\alpha}}{14\alpha\mu} + \frac{1}{8}\frac{e^2\sqrt{\pi}}{\alpha} U\left[\frac{1}{2}, 0, 2\alpha d^2\right]. \tag{8}$$

Here, $K_n(x)$ is the modified second-kind Bessel function, and $U(a, b, z)$ is the confluent hypergeometric function.

Notice that the application of the Ritz variational method brings about a numerical series (in our case, we obtained it in the form of functions (7) and (8)), every
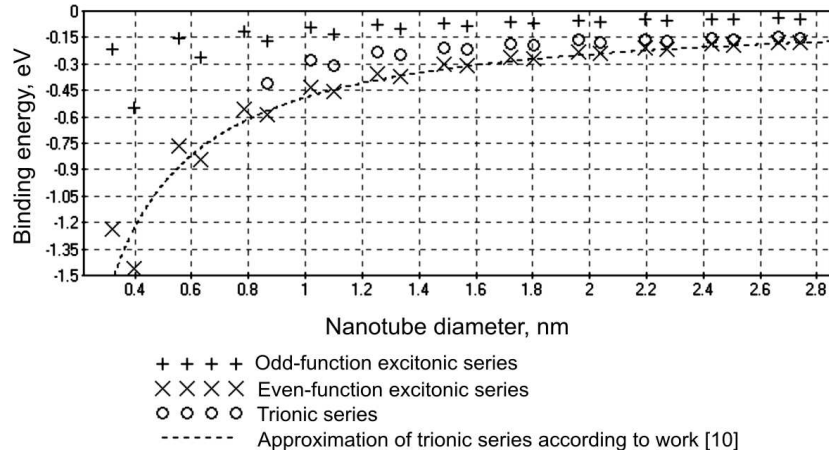
Fig. 1. Dependences of the binding energies for trions and excitons of both series on the nanotube diameter, in which a quasiparticle is localized, and the plot of approximation expression

term of which is either greater than or equal to the exact solution. Therefore, the smallest term in the series – in our case, it is the extremum of the corresponding function – is the closest to the exact solution, approaching it from above.

The choice of functions is rather crude. However, this crudeness in the choice of trial functions can only elevate the energies of ground states. Therefore, if the binding energy of an exciton obtained in the framework of the variational method turns out higher than the energy gap width in the nanotube, the same relation between those quantities remains valid for the accurate solution as well.

The function minima lie in the negative region, with the first minimum being located at a lower energy than the second one. The fact that the energy of ground states lies in the negative region means that the state is bound, i.e. it does exist in the case concerned.

In Fig. 1, the dependences of the exciton energy on the diameter of a nanotube, in which the exciton is localized, are depicted for both series. Note that a substantial spread in the exciton binding energies for small nanotube diameters becomes narrower for larger diameters, so that the differences between excitonic spectra for wide nanotubes are less pronounced than for narrow ones.

3. Trionic States

The trion is a bound state consisting of either two electrons and a hole or two holes and an electron. In fact, it is an ionized state of the excitonic molecule (biexciton). The term "charged exciton" can also be found quite often. For the first time, the experimental observation of

the trionic state in carbon nanotubes was described in work [10], the results of which we will refer to below.

In order to find the characteristic values of trion binding energy, we should solve the corresponding Schrödinger equation, analogously to what was done in the exciton case. To simplify the model, we neglect the difference between the effective masses of electrons and holes; actually, their masses differ from each other by less than 3% [11]. Hence, let the trion mass be simply equal to the effective mass of a hole. Then, assuming the interaction between each pair of particles composing the trion to be purely Coulombic, it is possible to write down the Hamiltonian for a one-dimensional trion in a nanotube in the form

$$\hat{H} = -\frac{\hbar^2}{2m_h}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial \xi_1^2} + \frac{\partial^2}{\partial \xi_2^2}\right] - \frac{e^2}{\sqrt{(x-\xi_1)^2 + d^2}} -$$

$$-\frac{e^2}{\sqrt{(x-\xi_2)^2 + d^2}} + \frac{e^2}{\sqrt{(\xi_1-\xi_2)^2 + d^2}}, \qquad (9)$$

where x, ξ_1, and ξ_2 are the coordinates of the electron and two holes, respectively; e is the electron charge; d is a parameter depending on the nanotube diameter (as was done in the case of excitons, it can be taken equal to the value of diameter itself); and m_h is the trion mass, which coincides in our case with the hole one.

Actually, any trion includes three two-particle bound states: two excitonic and one hole–hole. Therefore, it is quite natural to construct the wave functions of a trion as products of the wave functions that correspond to those states. This means that the wave function should be tried as a combination of three Gaussian exponents corresponding to three components describing two-particle
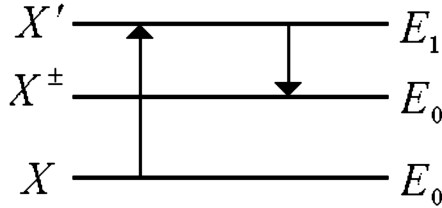
Fig. 2. To generate a trion, an exciton must be transferred into the excited state, which gives rise to the appearance of absorption and emission lines similar to those observed at luminescence. Here, $E_0(X)$ is the energy of the ground excitonic state, $E_0(X^\pm)$ the energy of the ground trionic state, and $E_1(X^\pm)$ the energy of the first excited excitonic state

states and a plane wave, the latter describing the motion of the center of masses of the system as a whole. Specifically,

$$\Psi_{X\pm} = C_3(\xi_1 - \xi_2)\exp\left[-\alpha\{(x - \xi_1)^2 + (x - \xi_2)^2\}\right] \times$$

$$\times \exp\left[-\beta(\xi_1 - \xi_2)^2\right]\exp\left[-ip(x + \xi_1 + \xi_2)\right], \qquad (10)$$

where α and β are small parameters. The presence of a difference between the hole coordinates, which enters as a multiplier into the wave function, testifies that the probability of a state, in which the holes—the components of the trion—come closer to each other, diminishes and tends to zero, if the holes approach at an infinitesimally short distance between them.

The function to be minimized is not presented here because of its cumbersome expression, which does not bear any physical information. The minima of the functions were determined numerically.

Zigzag nanotubes, whose diameters are narrower than 1 nm, were not considered because of the following reason: such narrow nanotubes were not observed as independent objects, but only as one of the layers in a multiwalled tube.

As was written above, the experiment, in which the lines that could be identified as trionic were observed for the first time, was made not earlier than at the beginning of 2011 (see its description in work [10]). In a series of experiments dealing with the observation of trionic lines, an approximate dependence of the trionic excitation energy on the nanotube diameter was established. For a medium with the dielectric permittivity $\varepsilon_{\rm env} = 3.5$, this dependence looks like $E_{X\pm} \approx 40/d$. For the sake of comparison with our results, the following expression bringing about "vacuum" energies should be used:

$$E_{X\pm} \approx \frac{40}{d}\varepsilon_{\rm env}^2. \qquad (11)$$

This dependence is plotted in Fig. 1. In agreement with theoretical predictions, the values estimated with the use of the variational technique approach from above those following from the experiment.

An interesting fact consists in that the binding energy of a trion turned out to have a higher value with respect to the corresponding exciton energy in the even-function series for all examined specimens, being at the same time lower than the binding energy of exciton excitations in the off-function series (Table). Recall that the excitons in the even-function series correspond to the first excited state, whereas those in the even-function series to the ground one. Hence, a trion can emerge as a result of the capture of a free electron in the conduction band or a hole in the valence band by excitons, which gives rise to a lowering of the total energy of the system. The emerging trion is a so-called excimer complex, because an excited exciton takes part in its generation.

Excimer complexes with the binding energies exceeding the energy of the ground state cannot exist infinitely

T a b l e. Energies of excitonic-family particles for various zigzag nanotubes and their comparison with the energy gap width: (n, m) are indices of the nanotube chirality, d the nanotube diameter, $E(X_{\rm even})$ and $E(X_{\rm odd})$ the exciton energies for the even- and odd-function, respectively, $E(X^\pm)$ is the trion energy, and $E_{\rm gap}$ the energy gap width [11]

(n, m)	d, nm	$E(X_{\rm odd})$, eV	$E(X^\pm)$, eV	$E(X_{\rm even})$, eV	$E_{\rm gap}$, eV
(4,0)	0.3214	−1.2434	−	−0.2154	2.0749
(5,0)	0.3980	−1.4602	−	−0.5511	2.3423
(7,0)	0.5526	−0.7691	−	−0.1530	1.3416
(8,0)	0.6304	−0.8392	−	−0.2612	1.4153
(10,0)	0.7861	−0.5561	−	−0.1172	0.9774
(11,0)	0.8641	−0.5911	−0.3293	−0.1720	1.0115
(13,0)	1.0202	−0.4363	−0.2288	−0.0948	0.7667
(14,0)	1.0983	−0.4563	−0.2188	−0.1280	0.7865
(16,0)	1.2546	−0.3583	−0.1652	−0.0796	0.6302
(17,0)	1.3328	−0.3721	−0.1581	−0.1020	0.6431
(19,0)	1.4892	−0.3042	−0.1328	−0.0679	0.5348
(20,0)	1.5674	−0.3132	−0.1268	−0.0842	0.5439
(22,0)	1.7238	−0.2644	−0.1019	−0.0601	0.4643
(23,0)	1.8020	−0.2712	−0.0968	−0.0720	0.4711
(25,0)	1.9585	−0.2333	−0.0769	−0.0535	0.4103
(26,0)	2.0367	−0.2391	−0.0739	−0.0628	0.4156
(28,0)	2.1932	−0.2090	−0.0700	−0.0484	0.3675
(29,0)	2.2715	−0.2130	−0.0676	−0.0557	0.3717
(31,0)	2.4280	−0.1890	−0.0633	−0.0441	0.3328
(32,0)	2.5062	−0.1930	−0.0624	−0.0501	0.3362
(34,0)	2.6628	−0.1740	−0.0576	−0.0404	0.3040
(35,0)	2.7410	−0.1760	−0.0567	−0.0454	0.3069

long. They should decay within rather a short time interval by means of an optical or radiationless transition.

We should emphasize that a trion can emerge only if an excited exciton captures a hole or an electron and lowers its energy. In turn, the excited exciton can emerge, if an unexcited exciton absorbs energy. Therefore, we have a three-level luminescence system (Fig. 2). This fact can be used for the identification of nanotubes and in technological facilities (systems with pumping).

4. Conclusions

Trionic excitation in zigzag SWNTs are shown to be excimers formed, when an excited exciton captures a free electron or a hole. The excited excitonic state in SWNTs is unstable with respect to the trionic one. Together with the instability of a trion with respect to the ground excitonic state, this fact gives rise to the emergence of a three-level energy system. Taking into account low concentrations, this circumstance points to a principle capability of developing an excimer infra-red radiation source, which would operate in the one-photon mode.

1. *Carbon Nanotubes: Advanced Topics in the Synthesis*, edited by A. Jorio *et al.* (Springer, Berlin, 2008).
2. T. Ando, J. Phys. Soc. Jpn. **66**, 1066 (1997).
3. F. Wang *et al.*, Science **308**, 838 (2005).
4. F. Wang *et al.*, Phys. Rev. Lett. **99**, 227401 (2007).
5. J. Chen, V. Perebeinos, M. Freitag, J. Tsang, Q. Fu, J. Liu, and Ph. Avouris, Science **310**, 1171 (2005).
6. V.M. Adamyan, O.A. Smyrnov, and S.V. Tishchenko, J. Phys.: Conf. Ser. **129**, 012012 (2008).
7. R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. 1.
8. O.A. Smyrnov, Ukr. J. Phys. **55**, 1217 (2010).
9. M.S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, Annu. Rev. Phys. Chem. **58**, 719 (2007).
10. R. Matsunaga, K. Matsuda, and Y. Kanemitsu, Phys. Rev. Lett. **106**, 037404 (2011).
11. S.V. Tishchenko, Low Temp. Phys. **32**, 953 (2006).

ОЦІНКА СТАБІЛЬНОСТІ ТРІОННИХ СТАНІВ
У ВУГЛЕЦЕВИХ НАНОТРУБКАХ ТИПУ ЗИГЗАГ

С. Марченко

Р е з ю м е

Оцінено стабільності тріонних збуджень у вуглецевих нанотрубках типу зигзаг. Показано, що тріон є нестабільним відносно основного екситонного стану та стабільним відносно збудженого. Отже, тріони в нанотрубках цього типу можуть бути утворені за рахунок захоплення дірки або електрона екситоном, що знаходиться у збудженому стані. Тобто, тріон у нанотрубці є ексимерною сполукою, що приводить до появи трирівневої енергетичної системи (незбуджений екситон–тріон–збуджений екситон).