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Influence of multi-level impurities on the dynamics of ultrashort electromagnetic pulses in carbon nanotubes

Alexander V. Zhukov[1], Roland Bouffanais[1], Natalia N. Konobeeva[2], Mikhail B. Belonenko[3] and Thomas F. George[4]

[1] *Singapore University of Technology and Design - 138682 Singapore*
[2] *Volgograd State University - 400062 Volgograd, Russia*
[3] *Lab of Nanotechnology, Volgograd Institute of Business - 400048 Volgograd, Russia*
[4] *Office of the Chancellor and Center for Nanoscience, Department of Chemistry & Biochemistry and Department of Physics & Astronomy, University of Missouri-St. Louis - St. Louis, MO 63121, USA*

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Abstract – Based on Maxwell's equations, we study the propagation of an ultrashort electromagnetic pulse through an array of carbon nanotubes with multi-level impurities. The effective equation for the vector potential of the electromagnetic field is first derived analytically and then solved numerically. We subsequently analyze the dependence of the pulse shape on the parameters of the energy spectrum of impurities, and more precisely on the impurity levels. Our analysis predicts a significant decrease in the pulse amplitude during the transient, which is associated with the competitive effects of dispersion and other nonlinear effects. We also uncover the effects of the hopping integrals and band gap of deep impurities on the pulse tail decay.

Introduction. – In this paper we consider the dynamics of electromagnetic pulses propagating in carbon nanotubes (CNTs) with multi-level impurities. Specifically, our focus is in cases for which transitions between the conduction band and impurity levels are allowed. The term "multi-level impurity" used here refers to the impurity whose energy levels are separated from both the conduction band and valence band of the carbon nanotube. The study of the influence of such impurities on the electronic structure —and thus the properties of semiconductors— has recently been the center of several scientific investigations [1–3]. Such an interest to this problem primarily finds its roots in the development of opto-, micro-, and especially microwave electronics. Stricter requirements on the quality of semiconductor materials entails the necessity to control the energy spectrum and the additional energy levels induced by the presence of the impurities. The presence of the latter can lead to both beneficial and undesirable results. Therefore, it is essential to study the influence of the presence of such impurities in order to minimize the negative consequences, while maximizing the positive impact on the functional characteristics of electronic devices.

Similar tasks were previously considered [4–7] for the "pure" case, where the presence of impurities was neglected. We note, however, that the inclusion of impurities changes notably the electron dispersion law, which determines the form of the coefficients in the governing equations derived in the approach by Belonenko *et al.* [4,5] and also the one by Leblond *et al.* [6,7]. Physically, this is due to transitions of electrons to impurity levels and back.

It is worth noting that, in recent years, CNTs have attracted much attention due to their unique properties that are widely used in modern micro- and nanoelectronics, as well as in nonlinear optical devices [8,9]. It is well known that carbon nanotubes of the zig-zag type possess semiconductor conductivity [10,11]. Therefore, it seems appropriate to study the influence of multi-level impurities on the propagation of electromagnetic pulses in this type of CNTs.

Statement of the problem and governing equations. – Consider the propagation of extremely short electromagnetic pulses in an array of carbon nanotubes with impurities, where we suppose the electric field to be directed along the nanotubes axes. The matrix form of

the Hamiltonian can be constructed as [12–14]

$$\mathcal{H} = \begin{pmatrix} 0 & f & \alpha_1 & \beta_1 & \gamma_1 & \Delta_1 \\ f^* & 0 & \alpha_2 & \beta_2 & \gamma_2 & \Delta_2 \\ \alpha_1^* & \alpha_2^* & t_1 & 0 & 0 & 0 \\ \beta_1^* & \beta_2^* & 0 & t_2 & 0 & 0 \\ \gamma_1^* & \gamma_2^* & 0 & 0 & t_3 & 0 \\ \Delta_1^* & \Delta_2^* & 0 & 0 & 0 & t_4 \end{pmatrix} \equiv \begin{pmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} \\ \mathcal{H}_{21} & \mathcal{H}_{22} \end{pmatrix}, \quad (1)$$

with

$$\mathcal{H}_{11} = \begin{pmatrix} 0 & f \\ f^* & 0 \end{pmatrix} \quad \text{and} \quad \mathcal{H}_{22} = \mathrm{diag}(t_1, t_2, t_3, t_4). \quad (2)$$

Here, $|f|$ gives the energy spectrum of the CNTs; t_i is the energy of the electron localized on the i-th level of the impurity (for definiteness we consider the impurity with 4 distinct levels —this particular choice being justified and explained below); and α, β, γ, and Δ are the hopping integrals for transitions between an impurity level and one of the CNT sublattices. The Hamiltonian is written in the electron states basis $|\psi\rangle = (\phi_1, \phi_2, \psi_1, \psi_2, \psi_3, \psi_4)^T$, where ϕ_1 and ϕ_2 correspond to states of an electron with a given momentum for CNT sublattices, and ψ_i is the state of an electron localized in the i-th energy level of the impurity. Note that by writing the Hamiltonian in the form given by eq. (1), we implicitly use the assumption that impurities are uniformly distributed throughout the CNT. The latter implies that the hopping integral is actually simply given by the quantity $n_0\Delta$, where Δ is the hopping integral for transition between the impurity and the nanotube lattice site near which the impurity is localized, and n_0 is the impurity concentration.

We can write the effective Hamiltonian in the form [2]

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_{11} - \mathcal{H}_{12}\mathcal{H}_{22}^{-1}\mathcal{H}_{21}. \quad (3)$$

Next, we solve the eigenvalue problem based on the above effective Hamiltonian and find the quantities $E_{1,2} = E_{1,2}(p, s)$ which determine the electron spectrum:

$$E_{1,2} = \frac{1}{2}\left\{R + Q \pm \sqrt{\Theta}\right\}, \quad (4)$$

where

$$\Theta = (R-Q)^2 - 4\left(\epsilon D^* + \epsilon^* D - |\epsilon|^2 - |D|^2\right),$$
$$R = -\left(\frac{|\alpha_1|^2}{t_1} + \frac{|\beta_1|^2}{t_2} + \frac{|\gamma_1|^2}{t_3} + \frac{|\Delta_1|^2}{t_4}\right),$$
$$Q = -\left(\frac{|\alpha_2|^2}{t_1} + \frac{|\beta_2|^2}{t_2} + \frac{|\gamma_2|^2}{t_3} + \frac{|\Delta_2|^2}{t_4}\right),$$
$$D = \frac{\alpha_1\alpha_2^*}{t_1} + \frac{\beta_1\beta_2^*}{t_2} + \frac{\gamma_1\gamma_2^*}{t_3} + \frac{\Delta_1\Delta_2^*}{t_4}.$$

Here, we have taken into account that the dispersion law —which describes the properties of the CNTs— has the form [11]

$$\epsilon(p,s) \equiv f = \eta\left\{1 + 4\cos(ap_x)\cos\left(\frac{\pi s}{m}\right) + 4\cos^2\left(\frac{\pi s}{m}\right)\right\}^{1/2}, \quad (5)$$

where $s = 1, 2 \ldots m$, $\eta \approx 2.7\,\text{eV}$, $a = 3b/2\hbar$, and $b = 0.142\,\text{nm}$ is the nearest-neighbor distance between carbon atoms. In further calculations we use the solution $E_1(p, s)$, corresponding to the CNT conduction band, and the plus sign in eq. (4). Here we must emphasize that the Hamiltonian formalism we use supposes the ballistic regime. This means that the electrons are not quick enough to respond to the applied EM field.

The quantities R and Q describe the change of electron dispersion due to the transition of an electron from one sublattice of graphene to the impurity level and back to the same sublattice, for the first and second sublattices, respectively. The quantity D describes the change of the electron dispersion due to the transition of an electron from one sublattice of graphene to the impurity level and back to the other sublattice. These quantities are exactly equal to zero in the absence of impurities. In general, they are proportional to both the overlap of the wave functions of electrons situated on the sublattices of graphene and the ones on the impurities, and the concentration of impurities.

Note, that as can be seen from eq. (4), the contribution of the higher energy levels of the impurity to the quantities R, Q, and D —which determine the influence of impurities on the spectrum of carbon nanotubes— decreases with increasing level number. Moreover, the rate of decrease is inversely proportional to the energy level, and is directly proportional to the square of the hopping integral. This leads to the fact, that the contribution of multi-level impurities to the electron dispersion of the CNTs is essentially determined by the structure of the few lower energy levels.

Accounting for the dielectric and magnetic properties of the CNTs, Maxwell's equations, for the vector potential $\mathbf{A}$ can be written as [15]

$$\frac{\partial^2\mathbf{A}}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} + \frac{4\pi}{c}\mathbf{j} = 0, \quad (6)$$

where $\mathbf{A}$ is assumed to have the form $\mathbf{A} = (0, 0, A(x,t))$, and $c\mathbf{E} = -\partial\mathbf{A}/\partial t$. Let us write the standard expression for the current density:

$$j_0 = e\sum_{qs} v_s\left(q - \frac{e}{c}A(t)\right)n_{qs}, \quad (7)$$

where $v_s(p) = \partial E_1(p,s)/\partial p$, and n_{qs} stands for the average number of electrons with a momentum $\mathbf{q}$. The latter is represented through a standard Fermi distribution, namely $n_{qs} = \{1 + \exp(\epsilon(q,s)/k_BT)\}^{-1}$, where $\epsilon(q,s)$ is given by eq. (5) and all the numerical calculations were

performed for $T = 300\,\mathrm{K}$. Let us further expand $v_s(p)$ in a Fourier series:

$$v_s(p) = \sum_k A_{ks} \sin(kp), \tag{8}$$

with

$$A_{ks} = \int_{-\pi/a}^{\pi/a} v_s(p) \sin(kp)\, \mathrm{d}p. \tag{9}$$

Note that we consider ultrashort pulses of characteristic duration τ_p, which satisfies the relation

$$\tau_p \ll \tau_{\mathrm{rel}}, \tag{10}$$

where τ_{rel} is the characteristic relaxation time of the electromagnetic field in the ensemble of carbon nanotubes. Following ref. [16], $\tau_{\mathrm{rel}} \approx 10^{-12}\,\mathrm{s}$, so we conclude that the condition (10) is fulfilled if we consider τ_p in the range between $10^{-14}\,\mathrm{s}$ to $10^{-13}\,\mathrm{s}$. The dimensionless form of eq. (6) reads

$$\frac{\partial^2 \mathcal{A}}{\partial x'^2} - \frac{1}{c^2}\frac{\partial^2 \mathcal{A}}{\partial t'^2} + \mathrm{sign}(\mathcal{A}_1)\sin(\mathcal{A}) + \sum_{k=2}^{\infty} \frac{\mathcal{A}_k}{|\mathcal{A}_1|}\sin(k\mathcal{A}) = 0, \tag{11}$$

where

$$\mathcal{A} = \frac{ea}{c}A, \qquad x' = x\frac{ea}{c}\sqrt{8\pi\gamma}, \qquad t' = t\frac{ea}{c}\sqrt{8\pi n_0 \gamma |\mathcal{A}_1|},$$

$$\mathcal{A}_1 = \sum_{s=1}^{m} \int_{-\pi/a}^{\pi/a} \frac{\cos(ap)\cos(\pi s/m)}{\sqrt{1+4\cos^2(\pi s/m)}} \times \frac{\exp\left(-\beta\epsilon_s(p)\right)}{1+\exp\left(-\beta\epsilon_s(p)\right)}\,\mathrm{d}p,$$

$$\mathcal{A}_k = \sum_{ps} A_{ks}\cos(akp)\frac{\exp\left(-\beta\epsilon_s(p)\right)}{1+\exp\left(-\beta\epsilon_s(p)\right)}. \tag{12}$$

Numerical analysis. – Equation (11) is solved numerically using the direct difference cross-type scheme [17,18]. Note that the series in eq. (11) is rapidly convergent [19], which leads us to initially consider the first 20 terms of that series. We subsequently decreased that number of leading order terms considered until no variation of the solution could be observed in the eighth decimal place. Eventually, all the calculations were performed with the obtained lowest number of leading order terms, which for different nanotubes varied between 12 and 14. Note that the approach developed in [7] is asymptotic, and works perfectly well on a large time scale when a steady-state solution is reached. However, when short time scales are considered, the processes leading to the transition from the initial shape of the pulse to the steady one are of great importance, and hence the imperative need to resort to our numerical approach.

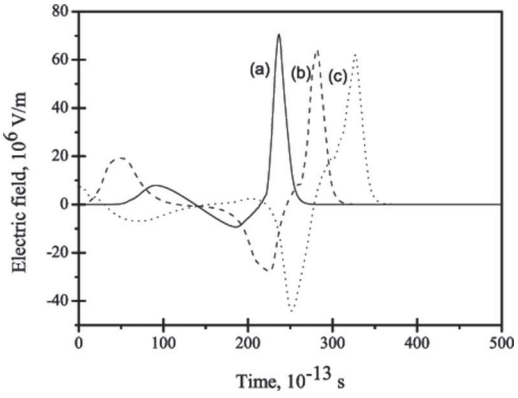

Fig. 1: Time dependence of the electric field for different values of the distance x traveled perpendicular to the CNT axis ($R = 0.2$, $Q = 0.3$, $D = 0.5$): (a) $x = 1.0 \cdot 10^{-5}\,\mathrm{m}$; (b) $x = 1.5 \cdot 10^{-5}\,\mathrm{m}$; (c) $x = 2.0 \cdot 10^{-5}\,\mathrm{m}$.

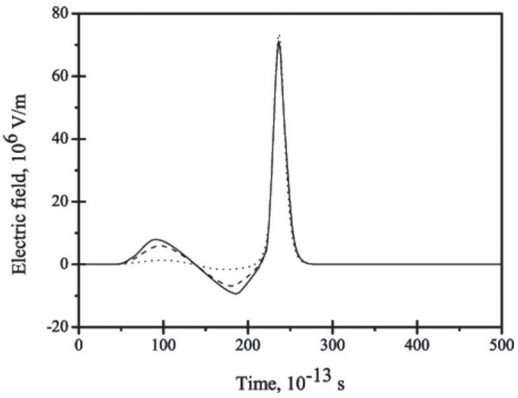

Fig. 2: Time dependence of the electric field for different values of the parameter R ($Q = 0.3$, $D = 0.5$, $x = 1.0 \cdot 10^{-5}\,\mathrm{m}$): $R = 0.2$ (solid); $R = 0.4$ (dashed); $R = 1.0$ (dotted).

The problem was originally considered on the infinite line with the condition that the electric field tends to zero at infinity. In practice, we have implemented absorbing boundary conditions in the numerical scheme. More specifically, the computational domain was gradually supplemented by layers in which the pulse is absorbed. In this study, our focus is on results for which pulse shape changes are observable.

The initial condition is chosen as

$$\mathcal{A}(x,t) = \mathcal{A}_0 \arctan\left\{\exp\left(x - vt\right)/\gamma\right\}, \tag{13}$$

where $\mathcal{A}_0$ is the pulse amplitude, $\gamma = \left(1 - v^2/c^2\right)^{1/2}$, and c is the speed of light.

Figure 1 shows that there is a significant change in the pulse shape over time depending on the passed distance. It is worth noting that there is a decrease in amplitude of the pulse, which can be associated with the formation

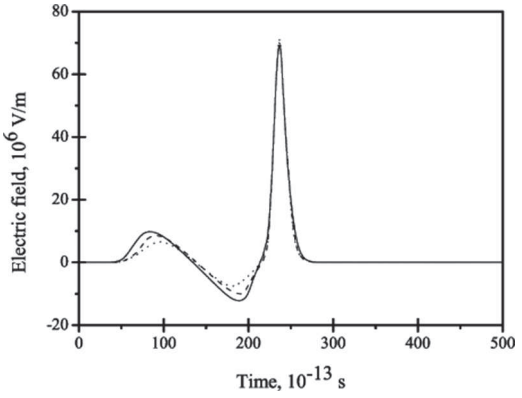

Fig. 3: Time dependence of the electric field for different values of the parameter D ($R = 0.2$, $Q = 0.3$, $x = 1.0 \cdot 10^{-5}$ m): $D = 0.1$ (solid); $D = 0.4$ (dashed); $D = 0.6$ (dotted).

of a stable pulse shape, for which the "decay" of a pulse, defined by dispersion, is compensated by the nonlinearity. Such a formation of the stable pulse leads also to the appearance of the "tail" of zero area following the main pulse.

Now, we look into the effects of the parameters R, Q, and D on the propagation of pulses in the CNT. A typical dependence on the parameter R is shown in fig. 2, revealing the significant influence of the energy spectrum parameters on the behavior of a pulse propagating in the CNT. Note that the parameters R and Q carry the same weight, that is, their influence on the dynamics of the pulse is equal; this fact is consistent with the symmetry of the two sublattices. It is important to note that this behavior has important practical applications. In particular, by doping CNTs with various types of impurities, we can reduce losses during the passage of extremely short pulses in an array of carbon nanotubes. Also, it follows from the calculations and from the dependence on R shown in fig. 2, that doping should be done with the multi-level impurities having significant overlap (hopping) integrals with the carbon atoms forming the carbon nanotubes.

Figure 3 displays the time dependence of the electric field, determined by the potential in eq. (11), for different values of D. The influence of the parameter D is more important quantitatively —as compared to the influence of R and Q— and can be traced to its physical origin. Indeed, the value of D determines the interaction of two impurity sublattices and their influence on the electrons of the CNT. Note also that the closer the energy levels of impurities to the CNT Fermi level, the greater are the values of R, Q, and D; therefore, the smaller is the magnitude of the "tail" formed by the propagation of extremely short pulses in the system of CNTs. Physically this can be attributed to the change of the effective mass of the electron in the conduction band of CNTs due to a greater interaction with the impurity, changing nonlinearities in the system, which in turn leads to a change in the pulse shape.

Thus, the introduction of impurities can significantly affect the behavior of the pulse propagating in a system of carbon nanotubes. This is due, primarily, to the change of the electron dispersion. Physically, the dispersion change is due to the fact that in the presence of impurities, not only the direct transition of an electron from one carbon atom to another is possible, but also processes mediated by the impurity can take place (governed by the parameter D), as well as processes associated with the transition to an impurity atom and back to the same carbon atom (described by the parameters R and Q). Our calculations show that the first process is more important, which physically is quite clear: an additional current flowing through a carbon nanotube appears. Therefore, one can relate the changes in the shape of ultrashort pulses to variations in certain parameters of the impurity system.

Conclusions. – i) The effective equation for the dynamics of ultrashort optical transitions between the levels of deep impurities and conduction bands of CNT has been derived.

ii) It is shown that the resulting change in a pulse shape is due to the influence of the impurity levels on the electron dispersion of CNTs.

iii) We predict a decrease in the amplitude of the pulse due to transition processes in a nonlinear system, namely to the competition between dispersion and nonlinearity during the formation of a stable pulse shape.

iv) We reveal the influence of hopping integrals and band gaps of deep impurities on the form of an pulse, which is manifested in the decay of the "tail" following the main pulse.

v) The predicted effects can apparently be tested experimentally in a relatively straightforward manner using successfully proved techniques (see ref. [20] and references therein).

* * *

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