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Soft polar molecular layers adsorbed on charged nanowire

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A selfconsistent theoretical approach is developed for describing an uncompensated charge carrier inside a perfect semiconductor quantum wire covered with a soft molecular layer. Deformation of the molecular layer under inhomogeneous carrier electric field is described in the model of liquid crystal with intrinsic electric dipole. The longitudinal quantization of a charge carrier is reduced to the spectral problem for nonlinear Schrodinger equation which is solved in terms of elliptic functions. The features of behavior of the system are as follows: the higher is the interaction, the higher is the nonlinearity; the lowest quantum levels experience the highest nonlinearity; the effect should be more pronounced for heavier holes. Under the increase of interaction the carrier is localized. The occurrence of localized states could be responsible for the experimentally observed decrease of conductivity in nanowires.

Key words: *liquid crystals, nonlinear Schrodinger equation, nanowire*

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1. Introduction

The creation of new mesoscopic objects and the prospects of their application to nanoelectronics generate interest in studying their fundamental properties [1]. Optical and conducting properties of such nanoobjects are conditioned with a set of energy quantum levels [2]. The effect of a structure of levels onto conductivity is found in quantum nanowires (an ordinary intrinsic semiconductor or carbon nanotube). The average free path of the carrier exceeds 10 microns in nanotube [3] which is important for quantization through the nanotube [4]. The conductivity of the nanowire is extremely sensitive to the appearance of adsorbed layers of NH_3

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molecules [5] and Langmuir-Blodgett thin film [6]. The contacting of nanotubes with a complicated organic medium causes new effects: small nanotube components to nematic liquid crystals lead to giant electromechanical effect [7], mixture of nanotubes and DNA results in the formation of a structurally ordered phase with each nanotube "wrapped" by DNA [8].

The present work shows that an interaction with a soft medium consisting of organic polar molecules changes the fundamental characteristic of nanowire: the energy spectrum of the carrier. The possibility of the carrier localization under the movement along the covered nanowire is shown .

2. Model of the system

The stationary Schrodinger equation for the additional carrier inside the intrinsic semiconducting quantum wire could be commonly written as [2,9]:

$$-\frac{\hbar^2}{2m_{\mathrm{ef}}}\Delta\psi + U(\boldsymbol{r})\psi = W\psi, \tag{1}$$

where $\psi(\boldsymbol{r})$ is the carrier wave function, m_{ef} is the carrier effective mass, $\hbar$ is Plank constant, Δ is Laplas operator, W is the total energy, $U(\boldsymbol{r})$ is potential energy, $\boldsymbol{r}(x, y, z)$ is a radius-vector of the particle. In semiconductors an approximation of the rectangular well being of the infinite depth is usually applied: $U(\boldsymbol{r}) \equiv U_0(\boldsymbol{r})$ where $U_0(\boldsymbol{r}) = 0$ inside and $U_0(\boldsymbol{r}) = \infty$ outside the well. An interaction with an adjacent medium leads to an additional potential $U_{\mathrm{int}}(\boldsymbol{r})$:

$$U(\boldsymbol{r}) = U_0(\boldsymbol{r}) + U_{\mathrm{int}}(\boldsymbol{r}). \tag{2}$$

An effect of the charge's field reaches its maximum if the molecules possess an intrinsic electric moment and the molecular system is soft. Electrical potential created by one dipole $\boldsymbol{d}$ could be written [10] as $\phi_i = \boldsymbol{d}_i\boldsymbol{R}/\varepsilon R^3$, where $\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}'$ is a radius-vector which connects the centre of the dipole $\boldsymbol{r}'$ and a point $\boldsymbol{r}$ of observation, ε is relative dielectric permeability of the medium. Summarizing the contributions of all dipoles of the adsorbed molecules in the layer we get potential of interaction:

$$U^e_{\mathrm{int}}(\boldsymbol{r}) = e\int n(\boldsymbol{r}')\phi(\boldsymbol{r} - \boldsymbol{r}')\mathrm{d}\boldsymbol{r}', \tag{3}$$

where $n(\boldsymbol{r}')$ is molecule concentration, e is the carrier charge. In its turn, the electric field intensity $\boldsymbol{E}(\boldsymbol{r}')$, created by the carrier, determines the potential of interaction between the carrier and an individual molecular dipole:

$$U^d_{\mathrm{int}}(\boldsymbol{r}') = -\boldsymbol{d}(\boldsymbol{r}')\boldsymbol{E}(\boldsymbol{r}'). \tag{4}$$

Generally it is necessary to supplement a set (3), (4) by material equations

$$n(\boldsymbol{r}') = n(\boldsymbol{E}(\boldsymbol{r}')), \qquad \boldsymbol{d}(\boldsymbol{r}') = \boldsymbol{d}(\boldsymbol{E}(\boldsymbol{r}')). \tag{5}$$

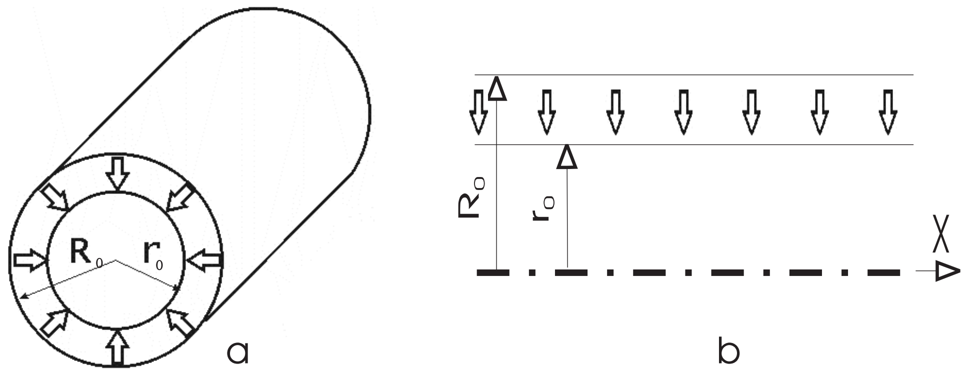

Figure 1. Cylindrical quantum wire with adsorbed polar molecules. Empty arrows indicate the direction of electric dipole vectors. (a) General view. (b) Crossection along the nanowire axes Ox.

The system has to be convenient for calculations, so the part of degrees of freedoms have to be soft only. The liquid crystals of the layered smectic A [11] satisfy these requirements. The system of long linear molecules is rigid in the direction along the layer (i. e., surface of a nanowire) and is soft in the direction perpendicular to layer. Let us assume a dipole directed along the axes of the molecules and perpendicular to the layer [11]. See geometry of the system in figure 1.

The Schrodinger equation (1) with potentials (2)–(4) transforms into a nonlinear integral-differential one. Such equations are solved using approximation methods [9] only. Let us show that the approximation of a long nanowire reduces the nonlocal contribution to the local one. Rewrite an integral (3) in cylindrical coordinates (figure 1) to divide coordinates: $\psi(\boldsymbol{r}) = \psi(x)\psi_\perp(y,z)$, $\quad W = W_x + W_\perp$. We also assume, that all modifications $\psi(x)$ occur on the scales $\sim L \gg r, R$ (see photo in [6]).

In order to analytically evaluate the potential of interaction between the carrier and a molecular dipole (4), the space integration is substituted by finding a flux:

$$U^d_{\text{int}}(x,r') = -\boldsymbol{E}\boldsymbol{d} = -\frac{2\tau(x)d}{\varepsilon r'}, \tag{6}$$

$$\tau(x) = e|\psi(x)|^2 F_\perp\,, \qquad F_\perp = \int |\psi(y,z)|^2 \mathrm{d}y\mathrm{d}z. \tag{7}$$

Here $\tau(x)$ is the local linear density of charge and it is taken into account that the dipole moment is directed to the centre of the nanowire (3). Relative error of the approximation is $\sim (R/L)^2 \ll 1$.

Let us find the material equation (5) for the thin molecular layer. The condition $F_i = -k\delta = -\nabla U^d_{\text{int}}$ of an equilibrium elastic displacement $\delta = 2\tau d/k\varepsilon r'^2$ of a dipole for attraction (retraction) in the region of more intensive fields and the condition of conservation of a number of the molecules lead to the potential of the carrier in a self-consistent field under elastic displacement of dipoles:

$$U^e_{\text{int}} = U^{e0}_{\text{int}} - G|\psi(x)|^2\,, \tag{8}$$

$$U_{\rm int}^{\rm e0} = -\frac{4\pi}{\varepsilon} dne(R_0 - r_0), \qquad G = \frac{8\pi n_0 d^2 e^2 F_\perp}{k\varepsilon R^3}(R_0 - r_0). \tag{9}$$

Then the equation (1) can be written for 1D movement of the carrier inside nanowire:

$$-\frac{\hbar^2}{2m_{\rm ef}}\frac{\partial^2\psi(x)}{\partial x^2} + \left[U_{\rm int}^{e0} - G|\psi(x)|^2\right]\psi(x) = W_x\psi(x). \tag{10}$$

Here $-L < x < +L$, and $U_{\rm int}^{\rm e0}$, G are parameters of linear and nonlinear interaction of the carrier with an elastic molecular subsystem, correspondingly. Signum of the linear parameter of interaction depends on a charge signum and the direction of the dipoles. The nonlinear interaction always decreases the system energy (the even powers of a charge and dipole in parameter G).

3. Analysis of the system's spectrum

Using the method standard in quantum mechanics [9] we introduce new variables:

$$k_{\rm p}^2 = \left(W_x - U_{\rm int}^{\rm e0}\right)\frac{2m_{\rm ef}}{\hbar^2}, \qquad 2g = G\frac{2m_{\rm ef}}{\hbar^2}, \tag{11}$$

where $k_{\rm p}$ is a component of the wave vector of the particle along the quantum wire, g is the renormalized parameter of the interaction. Then equation (10) transforms into

$$\psi''(x) + k_{\rm p}^2\psi(x) + 2g|\psi(x)|^2\psi(x) = 0. \tag{12}$$

Multiplying this equation by $\mathrm{d}\psi(x)$ and integrating we obtain the integral of the equation. Devision of variables and the further integration results in elliptic integrals of the first type. The choice of constants yields even and odd solutions of Schrodinger equations:

$$\psi_{\rm even} = b\ cn\ \kappa x, \qquad \psi_{\rm odd} = k'_{\rm m} b\ sd\ \kappa x, \tag{13}$$

where $k_{\rm m}$, $k'_{\rm m} = \sqrt{1-k_{\rm m}^2}$ are elliptic moduli, $cn\ y$, $sn\ y$, $sd\ y = sn\ y/dn\ y$ are elliptic functions, κ is a constant which is related with $k_{\rm m}$ and b by equations:

$$b^2 = \frac{1}{2g}(-k_{\rm p}^2 + \kappa^2), \qquad k_{\rm m} = \frac{b\sqrt{g}}{\kappa}. \tag{14}$$

Other two equations which set the relation between $k_{\rm m}, \kappa, b$ are given by boundary conditions $\psi(\pm L) = 0$ and normalization condition $\int|\psi(x)|^2\mathrm{d}x = 1$. These four equations form a selfconsistent system for parameters $b, \kappa, k_{\rm m}, k_{\rm p}$. Excluding b, κ it is possible to find the following solution for $k_{\rm p}$:

$$k_{\rm p}^2 = \left(1 - 2k_{\rm m}^2\right)\frac{K^2(k_{\rm m})}{L^2}n^2. \tag{15}$$

where n is the number of the level, $k_{\rm m}$ is the solution of the equation

$$\frac{2}{gL}K(k_{\rm m})\left[E(k_{\rm m}) - k'^2_{\rm m}K(k_{\rm m})\right] = \frac{1}{n^2}, \tag{16}$$

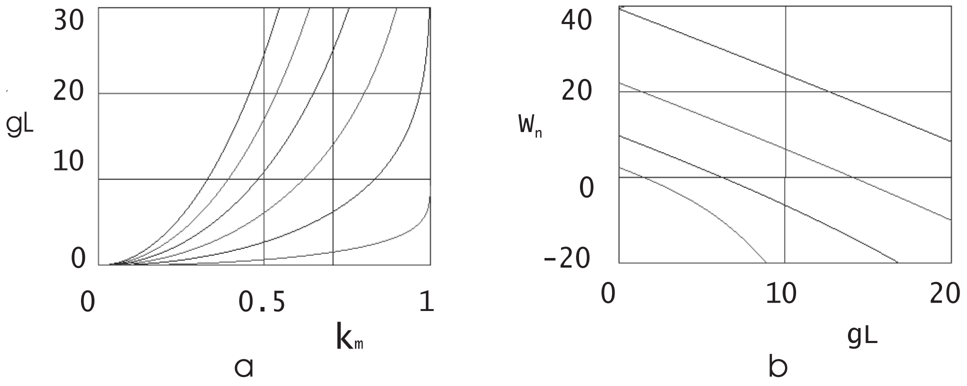

Figure 2. Dependence between dimensionless parameter of interaction gL and elliptic modulus $k_{\mathrm{m}}^{(n)}$ for $n = 1$ (bottom curve), $2, \ldots, 6$. (b) Renormalized energy of levels $W_n = k_{\mathrm{p}}^2 L^2$ depending on gL according to equation (15).

Parameter k_{p}^2 (square of quasimomentum) determines a spectrum of the carrier (11), which can be investigated experimentally.

Let us graphically analyse the dependence k_{p}^2 of the system on parameters. Equation (16) determines the relation between a parameter k_{m} which describes the nonlinearity and the dimensionless parameter of interaction gL. This dependence is presented in figure 2a which permits to make some conclusions. Namely, the greatest nonlinearity ($k_{\mathrm{m}}^{(n)}$) is observed under the greatest parameter gL and for the lowest levels. Parameter k_{p}^2 (11) which describes the energy spectrum pass to a zero value under $k_{\mathrm{m}} = 1/\sqrt{2}$. Figure 2 (b) gives the dependence of energy levels on a parameter of interaction. The nonlinearity is observed for the first level.

Under extremely weak interaction ($gL, k_{\mathrm{m}} \to 0$) the nonlinearity disappears and (15) transforms into the well-known solution [9] for a rectangular potential well of infinite depth. The extremely strong interactions could be realized not for such a high value of the parameter g but for a sufficiently long nanowire ($Lg \to \infty, k_{\mathrm{m}} \to 1$). Here we use an asymptotical behavior of elliptic functions [12]. Then equations (16), (15) transform into

$$\frac{K(k_{\mathrm{m}})n}{L} = \frac{g}{2n}, \qquad k_{\mathrm{p}}^2 = -\left(\frac{g}{2n}\right)^2, \qquad (Lg \to +\infty) \tag{17}$$

and the carrier is localized ($k_{\mathrm{p}}^2 < 0$) into soliton-like states, the energy does not depend on L. Such localized states could be responsible for the decrease of conductivity in chemisorption sensors based on nanowires [5] and in nanowires covered with Langmuir-Blodgett thin film [6]. The carrier wave function and the molecular layer deformation are shown in figure 3.

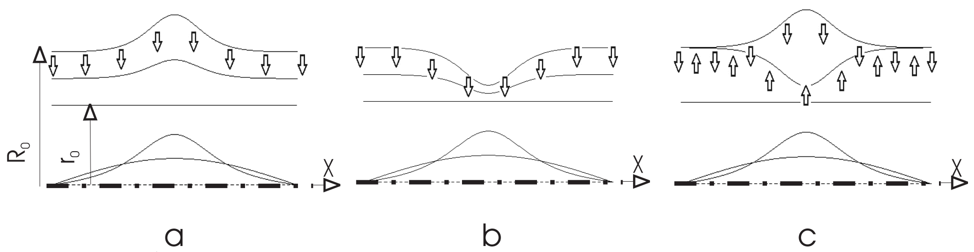

Figure 3. Form of the wave function of the carrier in dependence on elliptic modulus $k_{\rm m}$ for the first level (along Ox) according to equations (13). Elliptic modulus is $k_{\rm m} = 0$ for $g = 0$ (for comparison) and $k_{\rm m} = 0.8$. Deformation of the molecular layer in the case of (a) molecules polarization directed to the nanowire axes and hole carrier; (b) molecules polarization directed to the nanowire axes and electron carrier; (c) antiferroelectric dipoles ordering and hole carrier.

Let us qualitatively account for the effect of the actual factors, since the elementary model was considered. The following factors lead to the increase of localization.

1. Strong interaction of the carrier with a thick molecular layer. The nonlinearity causes the growth of localization, but the analytical description is inconvenient.

2. Displacement of molecules along the nanowire in the direction of stronger fields.

3. Rotation of the dipole groups increases both nonlinear and linear (which becomes nonlinear) interactions and makes them nonlocal ones.

The effect of localization decreases in the cases:

1. the molecules do not have an intrinsic dipole moment (as a rule an induced moment is smaller than the intrinsic one);

2. the increase of temperature.

Each of the listed factors requires a separate research for the account.

In order to make the comparison with the experimental research of a nanowire spectrum or conductivity it is necessary to take into account an inertia of molecular cover. As it is seen in figure 2b energy levels are displaced downwards almost in parallel manner under the increase of the interaction gL. Really the situation strongly depends on the relation between the lifetime of an excited state $\tau_{\rm e}$ and the relaxation time of a molecular system $\tau_{\rm M}$. If $\tau_{\rm M} \ll \tau_{\rm e}$ then the molecular layer has the time to be set up under the modification of an electrical field of the carrier, and the spectrum looks like the one in figure 2b. If $\tau_{\rm M} \gg \tau_{\rm e}$ the molecular layer has no time to be set up, the carrier comes on an energy level which is defined by deformation of the molecular layer in the ground state of the carrier. This also concerns the behaviour of the carrier which tunnels in the nanowire. If $\tau_{\rm M} \sim \tau_{\rm e}, \tau_{\rm tunn}$ the excitation and tunneling of the carrier have to be considered together with the excitation of the molecular system.

4. Conclusion

It is shown, that the nonlinear interaction exists for the carrier inside the quantum nanowire being in contact with a soft polar medium. In the approximation of a long wire and thin molecular layer, the longitudinal quantization for the additional carrier can be described using nonlinear Schrodinger equations, and the spectral problem is solved analytically. The effect of nonlinear interaction and possible localization have to be more pronounced for heavier holes. Linear interaction changes a signum depending on a signum of the carrier charge and polarization of molecules.

The energy spectrum of the carrier hardly depends on the rigidity of the molecular system and on the intrinsic dipole moment of molecules. Crystalization or solidification of a molecular film under a phase transition result in a discontinuous growth of a rigidity and an appropriate decline of the parameter of nonlinear interaction, while the localization of longitudinal movement of the carrier disappears. I. e., under such a phase transition in a molecular system the temperature dependence of conductivity of nanowire should possess discontinuity. Therefore, nanowire can be used as a sensor of state of the molecular system being in contact. The obtained results could be used in order to explain the decrease of conductivity in chemisorption sensors.

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М'які полярні молекулярні шари на зарядженому нанодроті

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Самоузгоджений теоретичний підхід розроблено для опису незкомпенсованого носія заряда всередені напівпровідникового квантового дроту, що вкритий м'яким молекулярним шаром. Деформація молекулярного шару в неоднорідному електричному полі носія описана в моделі рідкого кристала з власним електричним дипольним моментом. Продольне квантування носія заряда зведено до спектральної проблеми для нелінійного рівняння Шредингера. Самоузгоджене рішення спектральної проблеми отримано в термінах еліптичних функцій. Система має таку поведінку: чим вища взаємодія, тим більша нелінійність; найнижчі квантові рівні відчувають найбільшу нелинійність; ефект має бути більш відчутним для більш важких дірок; при зростанні взаємодії енергетичні рівні знижуються і носій локалізується. Поява локалізованих станів може бути відповідальною за зменшення провідності в нанодротах, що наблодають в експерименті.

Ключові слова: *рідкі кристали, нелінійне рівняння Шредингера, нанодріт*

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