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Acoustoelectronic effect in semiconductor quantum dots with a multilayer shell

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Abstract. Ultrasound is an effective method of targeted delivery of drugs using quantum dots and removal of quantum dots from the human body. Ultrasound improves drug delivery using quantum dots, but affects their energy structure. In this work, a model of the spherical quantum dot of the core/shell type and the bionanocomplex based on it, exposed to the influence of an acoustic wave, is developed on the basis of the electron-deformation coupling method. Within the framework of this model, the influence of acousto-electron effects on the modulation of the radiation energy of the CdSe quantum dot with different shell structure was investigated. The influence of ultrasound on the energy spectrum of the charge carriers of the CdSe / ZnS/CdS/ZnS quantum dot – human serum albumin bionanocomplex was investigated. It is shown that the ultrasonic wave leads to a decrease in the ground state energy of electron and hole and a decrease in the band gap width of quantum dot. The regularities of change in the radiation energy of the CdSe QDs with different shell structures under the influence of ultrasound depending on the surface concentration of human serum albumin have been established.

Keywords: CdSe / ZnS/CdS/ZnS quantum dot, core/shell structure, acoustic wave, human serum albumin, bionanocomplex, modulation of the energy.

1 Introduction

Semiconductor nanoheterostructures containing quantum dots (QDs) exhibit a notable quantum yield in photoluminescence, making them a promising material for developing heterolasers [1], solar cells [2], and applications in medicine [3, 4]. Nevertheless, the elevated surface area-to-volume ratio of QDs results in a heightened density of surface defects, commonly known as traps. These traps act as centers for non-radiative recombination of carriers within QDs, detrimentally impacting the overall performance of solar cells [5]. Additionally, the transfer of electric charge from QDs to organic molecules leads to a reduction in the intensity of photoluminescence [6].

A viable solution to mitigate these challenges involves the creation of quantum dots with a protective shell, often referred to as core/shell QDs, which incorporates one or more layers. Surface passivation of QDs using shells composed of diverse materials

has proven to be an effective strategy for reducing surface defects. This approach holds the potential to broaden the absorption spectrum, expedite the transfer of current carriers, and minimize recombination losses. Particularly noteworthy is the positive impact achieved through the utilization of a multilayer shell.

In a specific study [6], it was demonstrated that CdSe-core QDs with multicomponent ZnS/CdS/ZnS structures as shells, when maintained at a thin thickness, significantly outperform both thin and thick ZnS shells in suppressing the reduction of the quantum yield of QD photoluminescence. Furthermore, research [7] underscores that a judicious choice of the shell substantially enhances the efficiency of solar cells based on core/shell QDs.

An important factor that affects the spectral characteristics of radiation of the quantum dots (QDs) is elastic deformation [8, 9]. The source of elastic deformations can be both internal factors (the mismatch of lattice parameters, the point defects) and external factors. In particular, the cause of periodic deformation can be an acoustic wave. Such deformation can occur during electromagnetic irradiation of QDs. In this case, the thermo-deformation mechanism of sound generation is used [10]. Also, the QDs are widely used in medicine and can be exposed to ultrasound.

Recently, ultrasonic treatment has been used for the synthesis of semiconductor quantum dots [11-13]. The influence of ultrasound makes the quantum dots more monodisperse (uniform in sizes) and allows increasing the intensity of photoluminescence. The use of ultrasound makes it possible to better control the morphology and reduce the surface defects of QDs [13].

Also, ultrasound is an effective method of targeted delivery of drugs using QDs and removal of QDs from the human body [14]. In work [15] it was shown that ultrasound improves the drug delivery using QDs.

The QDs with a multi-layer shell also undergo significant deformations due to the mismatch of lattice parameters of the contacting layers. Therefore, there is a need to develop a model of the core-multilayer shell QD, that is exposed to an acoustic wave.

The review [16] reports on the results of researches on the self-consistent coupling between the optical properties of QDs with dynamic deformation and electric fields of surface acoustic waves.

The following acousto-electron effects can be observed during the ultrasonic treatment of the core/shell QDs:

the periodic deformation due to self-consistent electron-deformation coupling leads to the local periodic shift of the bottom of conduction band (the top of valence band) and, accordingly, to the modulation of the energy of electron and hole [17];

the ultrasonic wave leads to a change in the mismatch of lattice parameters of the contacting materials of QD core and shell layers and, accordingly, both to a change in the energy of electron and hole and to a change in the conditions for the formation of nanoclusters [18];

the emergence of gradient of the refractive index under the action of ultrasound leads to a periodic change in the direction of radiation of the QD-based laser heterostructure [18];

the propagation of ultrasound in a certain direction leads to an increase in the size of QDs in this direction, and, accordingly, to a distortion of their shape and a change in the energy of electron and hole;

a change in the QD volume under the influence of ultrasound leads to a shift of the bottom of conduction band (the top of valence band), which causes a change in the band gap and, accordingly, a change in the spectral characteristics of QDs.

In this work, a theoretical model of the modulation of radiation energy of QD with a multilayer shell under the influence of a spherical acoustic wave was constructed and the influence of an ultrasonic wave on the radiation energy of the QD – human serum albumin (HSA) bionanocomplex was investigated.

2 The deformation of QD under the influence of a spherical acoustic wave

Consider the spherical semiconductor QD of the core/shell type (the shell is a material with a larger band gap compared to the core material, Fig. 1), which is exposed to an electromagnetic wave. In this case, the shell is a transparent medium for the radiation that is absorbed by the QD core. As a result, there is a heat flux from the core to the shell, which generates sound oscillations [10, 19].

An ultrasonic wave has spherical symmetry [10, 20]. Due to the heat flux, the additional pressure occurs on the surface of the QD core, which leads to oscillations of its surface and the generation of sound in the nanosystem.

The process of generation and propagation of acoustic oscillations in QF with a multilayer shell is described by the equation:

$$\rho^{(i)} \frac{\partial^2 u_l^{(i)}}{\partial t^2} = \sum_j \frac{\partial \sigma_{lj}^{(i)}}{\partial x_j}, \tag{1}$$

where $\rho^{(i)}$, $\sigma_{lj}^{(i)}$ are the density and the components of the strain tensor of the materials of core and layers of the QD, respectively ($i = 0$ corresponds to the core; $i = 1, 2, \ldots$ corresponds to the shell layers);

$$\sigma_{lj}^{(i)} = K^{(i)} \sum_k \varepsilon_{kk}^{(i)} \delta_{lj} + 2\mu^{(i)} \left(\varepsilon_{lj}^{(i)} - \delta_{lj} \frac{1}{3} \sum_k \varepsilon_{kk}^{(i)} \right). \tag{2}$$

Here $K^{(i)}$, $\mu^{(i)}$ are the modules of comprehensive compression and shift of the core and shell layers, respectively; $\varepsilon_{lj}^{(i)}$ are the components of the deformation tensor:

$$\varepsilon_{lj}^{(i)} = \frac{1}{2} \left(\frac{\partial u_l}{\partial x_j} + \frac{\partial u_j}{\partial x_l} \right). \tag{3}$$

Let's write the displacement vectors $\vec{u}^{(i)}(t, \vec{r})$ as the sum of longitudinal and transverse displacements $\vec{u}^{(i)}(t, \vec{r}) = \vec{u}_L^{(i)}(t, \vec{r}) + \vec{u}_T^{(i)}(t, \vec{r})$, for which

$$\operatorname{rot} \vec{u}_L^{(i)}(t, \vec{r}) = 0, \qquad \operatorname{div} \vec{u}_T^{(i)}(t, \vec{r}) = 0.$$

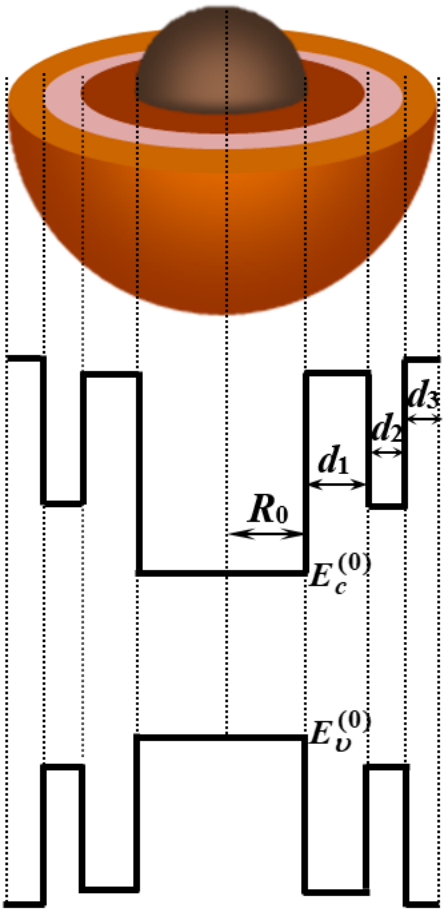

Fig. 1. The geometric model and band scheme
of the CdSe-core / ZnS/CdS/ZnS-shell quantum dot

As a result, we get:

$$\Delta\vec{u}_l^{(i)} = \frac{1}{c_l^{(i)2}}\frac{\partial^2\vec{u}_l^{(i)}}{\partial t^2}, \tag{4}$$

$$\Delta\vec{u}_T^{(i)} = \frac{1}{c_T^{(i)2}}\frac{\partial^2\vec{u}_T^{(i)}}{\partial t^2}, \tag{5}$$

where $c_l^{(i)} = \sqrt{\frac{3K^{(i)} + 4\mu^{(i)}}{3\rho^{(i)}}}$, $c_T^{(i)} = \sqrt{\frac{\mu^{(i)}}{\rho^{(i)}}}$ are the longitudinal and transverse velocities of acoustic oscillations in the QD core and shell materials, respectively.

The transverse acoustic wave $\left(\vec{u}_T^{(i)}\right)$ in (5) does not lead to a change in the QD volume, since $\mathrm{div}\vec{u}_T^{(i)}(t,\vec{r}) = 0$. And the propagation of longitudinal wave is accompanied by volume expansion and compression.

Let's move on to the scalar potential:

$$\vec{u}_{1l}^{(i)} = \vec{\nabla}\varphi^{(i)}, \tag{6}$$

Then equation (4), taking into account (6), can be written in the form:

$$\Delta\varphi^{(i)} = \frac{1}{c_l^{(i)2}} \frac{\partial^2 \varphi^{(i)}}{\partial t^2}. \tag{7}$$

The solution of equation (7) for quantum dot and matrix materials will have the following form:

$$\varphi^{(0)} = \frac{A^{(0)} \sin\left(\omega t - \frac{\omega r}{c_l^{(0)}} + \alpha^{(0)} \right)}{r}, \quad 0 \le r \le R_0, \tag{8}$$

$$\varphi^{(i)} = \frac{A^{(i)} \sin\left(\omega t - \frac{\omega r}{c_l^{(i)}} + \alpha^{(i)} \right)}{r}, \quad R_{i-1} \le r \le R_i, \; i = 1, 2, \ldots, n; \tag{9}$$

where the constants $A^{(i)}$, $\alpha^{(i)}$ are chosen in such a way that the following conditions are fulfilled:

$$\begin{cases} \sigma_{rr}^{(i)}(t)\big|_{r=R_i} = \sigma_{rr}^{(i+1)}(t)\big|_{r=R_i}; \\ u_r^{(i)}(t)\big|_{r=R_i} = u_r^{(i+1)}(t)\big|_{r=R_i}; \\ \sigma_{rr}^{(n)}(t)\big|_{r=R_n} = -\sigma_0 \sin \omega t. \end{cases} \tag{10}$$

The last boundary condition of the system (10) determines the influence of the acoustic wave on the strained state of nanosystem as the action of a periodic forcing force with frequency ω, where σ_{us} is the amplitude of the mechanical strain created by the acoustic wave on the QD surface. Here $\sigma_{rr}^{(i)}(\vec{r})$ are the radial components of dynamic strains of the quantum dot or matrix materials caused by the action of the acoustic wave. Since we are considering a spherically symmetric system, i.e., the displacement vector has only a radial component u_r, then the radial strain will have the form:

$$\sigma_{rr}^{(i)} = \left(K^{(i)} + \frac{4}{3}\mu^{(i)} \right) \frac{\partial u_r^{(i)}}{\partial r} + \left(K^{(i)} - \frac{2}{3}\mu^{(i)} \right) \frac{2u_r^{(i)}}{r}. \tag{11}$$

The components of deformation tensor and the comprehensive deformation of QD materials can be determined as follows:

$$\varepsilon_{rr}^{(i)} = \frac{\partial u_r^{(i)}}{\partial r^{(i)}}, \quad \varepsilon_{\theta\theta}^{(i)} = \varepsilon_{\varphi\varphi}^{(i)} = \frac{u_r^{(i)}}{r^{(i)}}, \quad \mathrm{Sp}\varepsilon^{(i)} = \varepsilon_{rr}^{(i)} + \varepsilon_{\theta\theta}^{(i)} + \varepsilon_{\varphi\varphi}^{(i)}. \tag{12}$$

Determining the deformations in the core and shell of QD is necessary for researching the influence of pulsed laser irradiation on the optical properties of QDs, in particular, their spectral characteristics. Laser radiation, which is absorbed by the QD core, generates acoustic oscillations [21], which lead to the deformation of individual layers of the heterostructure and, accordingly, to the shift of the edges of allowed bands. This, in turn, leads to a change in the energy spectrum of charge carriers.

In Fig. 2, 3 shows the dependence of the amplitude of deformation at the boundary between the CdSe core and the ZnS shell of QD in the CdSe (Fig. 2) and the ZnS (Fig. 3) material on the frequency of the acoustic wave, at different sizes of the QD core and at different shell thicknesses, at $\sigma_0 = 10\ bar$. Such dependencies have a non-monotonic character. The position of the maxima amplitude of deformation in the QD core depends significantly on its radius, and practically does not depend on the shell thickness (Fig. 2). When the radius of the QD core increases, a shift of the deformation maxima towards lower frequencies is observed, which is caused by a decrease in the frequency of natural oscillations [21] of the atoms of QD. Also, an increase in the QD core radius leads to a monotonic decrease in comprehensive deformation. This is explained by the fact that QDs with a smaller core are more sensitive to the influence of external mechanical strain [22]. On the contrary, an increase in the thickness of the ZnS shell leads to an increase in the deformation of the QD core (Fig. 2).

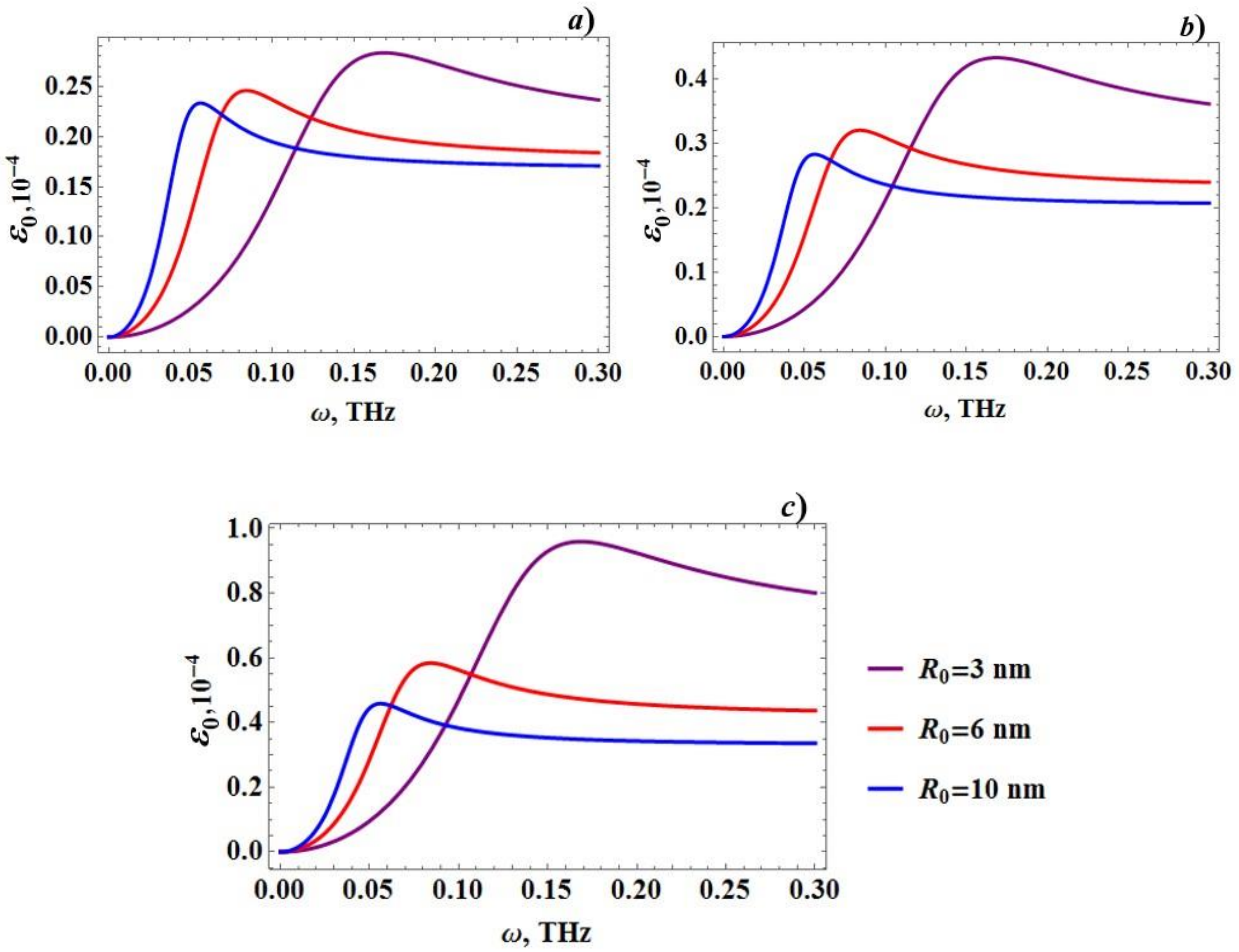

Fig. 2. The dependence of the amplitude of the acoustic deformation at the boundary between the CdSe core and the ZnS shell of QD in the CdSe material, at different core radii and shell thicknesses: $d_1 = 2a^{(ZnS)}$ (***a***); $d_1 = 6a^{(ZnS)}$ (***b***); $d_1 = 20a^{(ZnS)}$ (***c***)

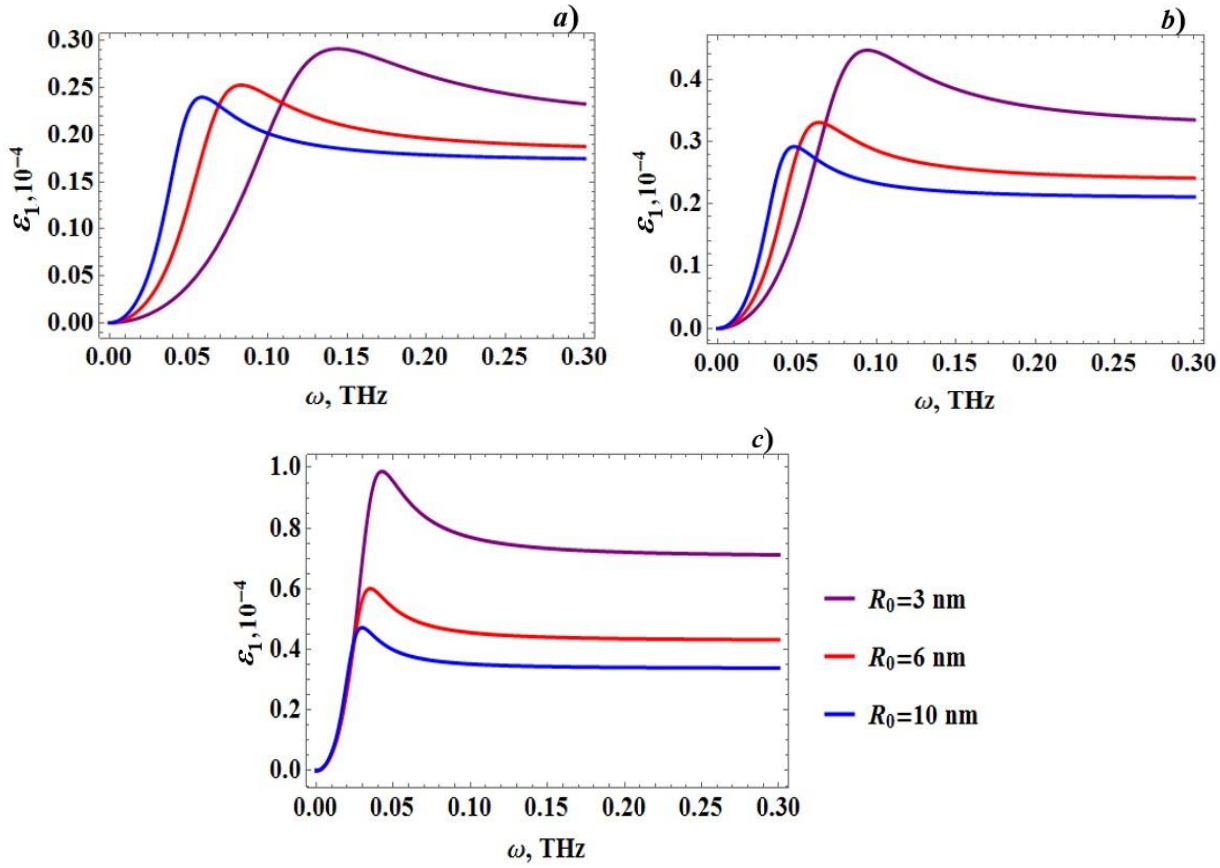

Fig. 3. The dependence of the amplitude of the acoustic deformation at the boundary between the CdSe core and the ZnS shell of QD in the ZnS material, at different core radii and shell thicknesses: $d_1 = 2a^{(ZnS)}$ (***a***); $d_1 = 6a^{(ZnS)}$ (***b***); $d_1 = 20a^{(ZnS)}$ (***c***)

Similarly, the deformation of shell decreases with an increase in the core radius and with a decrease in the shell thickness (Fig. 3). For thick shells (Fig. 3, c), the maximum amplitude of deformation practically does not depend on the core radius.

In Fig. 4, 5 shows the dependence of the amplitude of deformation at the boundary between the CdSe core and the ZnS/CdS shell of QD in the CdSe core material (Fig. 4) and in the ZnS layer material of shell (Fig. 5) on the frequency of the acoustic wave, at different sizes of the QD core and different thicknesses of the ZnS and CdS layers of shell.

In Fig. 6 shows a similar dependence in the material of the CdS layer at the boundary between the ZnS and CdS layers of shell. An increase in the number of the layers of shell leads to an increase in the amplitude of the acoustic deformation in the QD core (Fig. 4), and, on the contrary, to the reduction of deformation in the ZnS layer (as can see, comparing Fig. 5 and Fig. 3). This is due to the redistribution of mechanical strains between individual layers of the heterosystem. The frequency at which the maximum amplitude of the acoustic deformation in the ZnS layer is observed shifts to higher frequencies.

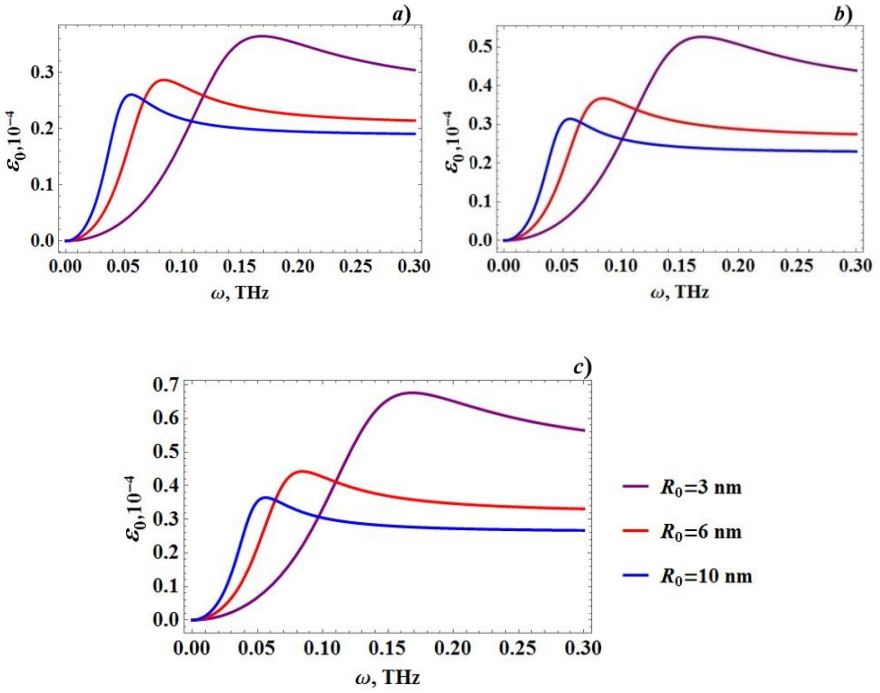

Fig. 4. The dependence of the amplitude of the acoustic deformation at the boundary between the CdSe core and the ZnS/CdS shell of QD in the CdSe material, at different core radii and shell layer thicknesses: $d_1 = 2a^{(ZnS)}$, $d_2 = 2a^{(CdS)}$ (***a***); $d_1 = 2a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***b***); $d_1 = 6a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***c***)

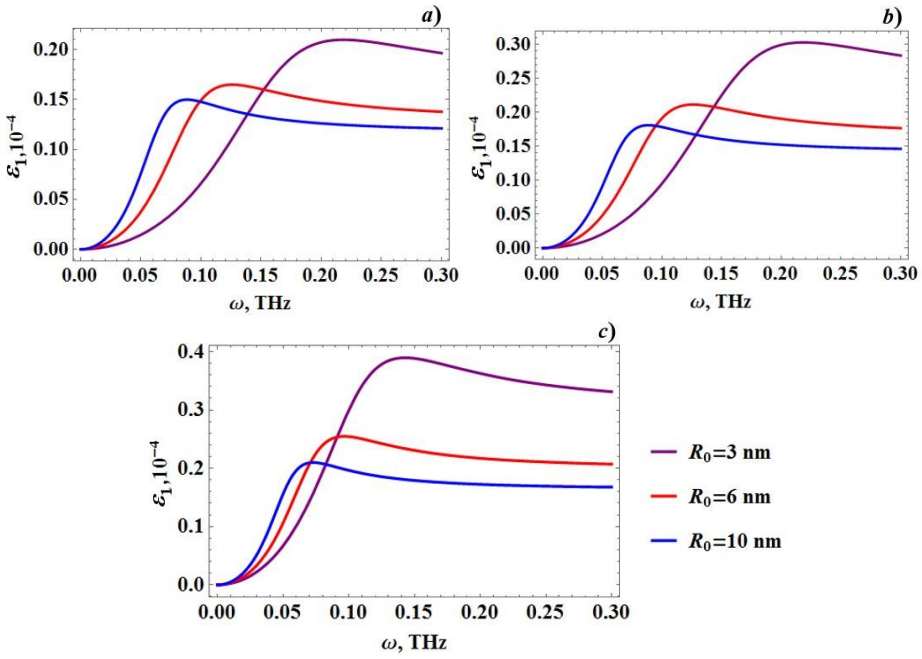

Fig. 5. The dependence of the amplitude of the acoustic deformation at the boundary between the CdSe core and the ZnS/CdS shell of QD in the ZnS material, at different core radii and shell layer thicknesses: $d_1 = 2a^{(ZnS)}$, $d_2 = 2a^{(CdS)}$ (***a***); $d_1 = 2a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***b***); $d_1 = 6a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***c***)

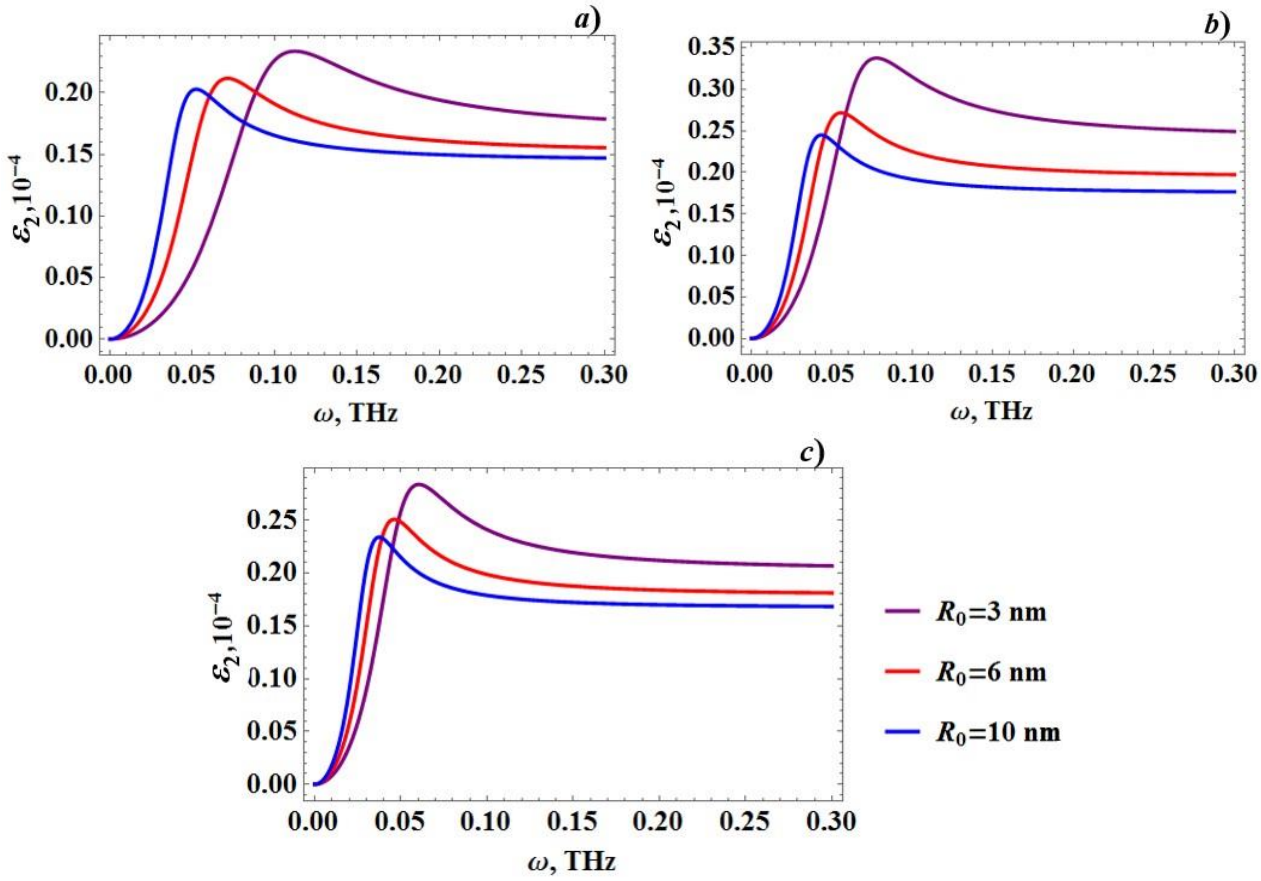

Fig. 6. The dependence of the amplitude of the acoustic deformation at the boundary between the layers of ZnS/CdS shell in the CdS material, at different core radii and shell layer thicknesses: $d_1 = 2a^{(ZnS)}$, $d_2 = 2a^{(CdS)}$ (***a***); $d_1 = 2a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***b***); $d_1 = 6a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***c***)

As in the case of a single-layer shell, the maximum amplitude of deformation in the outer CdS layer practically does not depend on the core radius for the case of a thick shell (Fig. 6, c).

An increase in the thickness of layers of the ZnS/CdS shell leads to an increase in the deformation of the QD core and the inner ZnS layer of shell. For the outer CdS layer, this dependence has a non-monotonic character. At large thicknesses of the shell layers, their further increase leads to a decrease in the deformation of the outer CdS layer (Fig. 6).

A similar pattern is observed for shell materials of the CdSe-core / ZnS/CdS/ZnS-shell QD (the QD with a three-layer shell). In this case, the deformation of the inner CdS layer of shell practically does not depend on the core radius and the thickness of the shell layers.

The frequency dependence of deformation of the CdSe core (Fig. 7) is slightly different from the previous cases. This difference is especially noticeable with small core radii and a thick shell (Fig. 7, c). In this case, another maximum appears at lower frequencies (around 40 *GHz*).

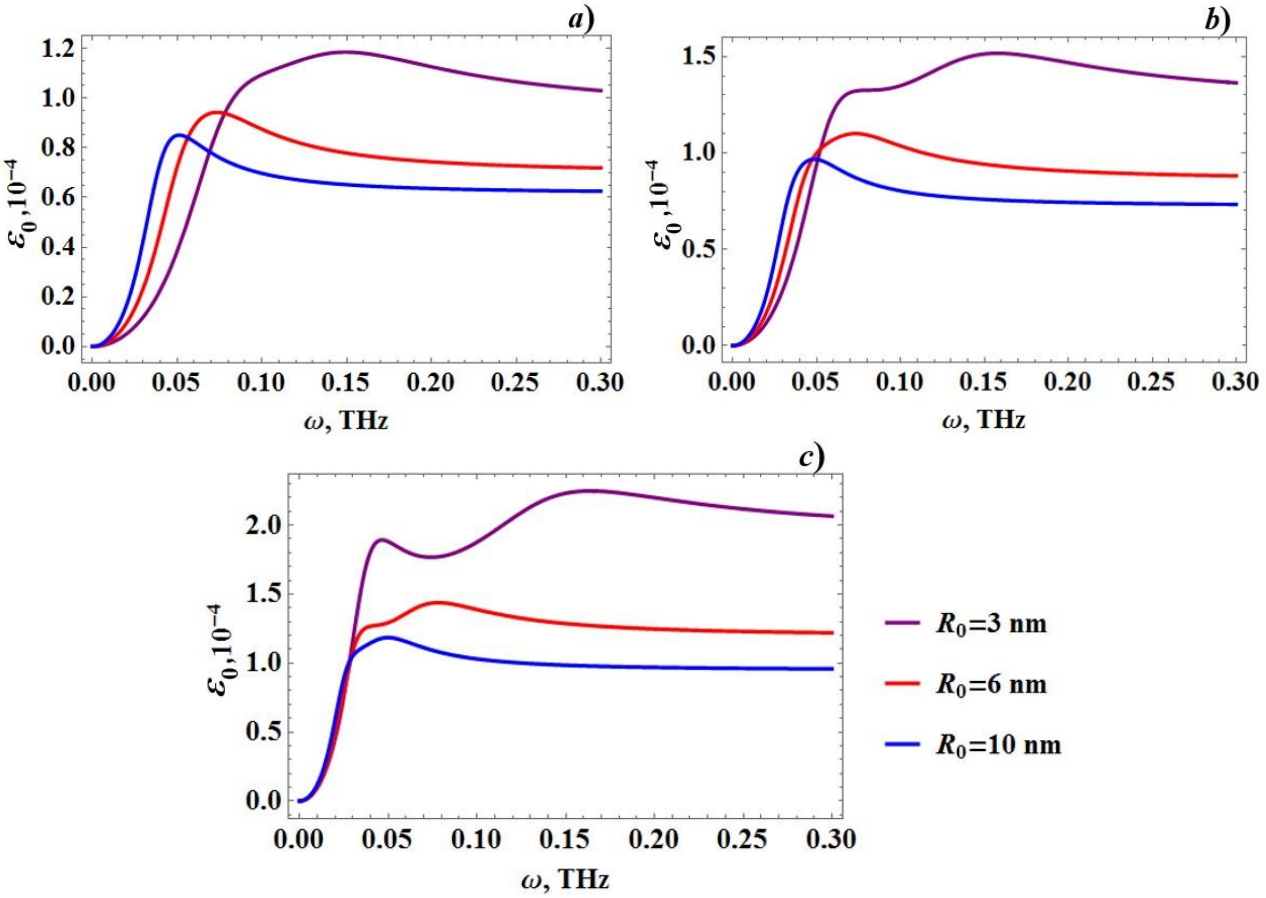

Fig. 7. The dependence of the amplitude of the acoustic deformation at the boundary between the CdSe core and the ZnS/CdS/ZnS shell of QD in the CdSe material, at different core radii and shell layer thicknesses: $d_1 = d_3 = 2a^{(\mathrm{ZnS})}$, $d_2 = 2a^{(\mathrm{CdS})}$ (***a***); $d_1 = d_3 = 2a^{(\mathrm{ZnS})}$, $d_2 = 6a^{(\mathrm{CdS})}$ (***b***); $d_1 = d_3 = 6a^{(\mathrm{ZnS})}$, $d_2 = 6a^{(\mathrm{CdS})}$ (***c***)

3 Modulation of the energy of radiation quantum of the QD with a multilayer shell

The energy and wave functions of electron and hole in QD with a multilayer shell are found from the non-stationary Schrödinger equation

$$\hat{H}_{e,h}(r,\theta,\varphi,t)\Psi^{(\mathrm{e,h})}(r,\theta,\varphi,t) = -\frac{\hbar}{i}\frac{d\Psi^{(e,h)}}{dt}(r,\theta,\varphi,t) \tag{13}$$

with the Hamiltonian

$$\hat{H}(r,\theta,\varphi,t)_{e,h} = -\frac{\hbar^2}{2}\vec{\nabla}\frac{1}{m^{(e,h)}(r)}\vec{\nabla} + W^{(e,h)}(r) + \Delta W^{(e,h)}(r,t),$$

where the potential energies $W^{(e,h)}(r, t)$ in the CdSe-core / ZnS/CdS/ZnS-shell QD are determined by formula (9) from work [8] taking into account the additional acousto-electron non-stationary potential:

$$\Delta W^{(e)}(r,t) = -a_c^{(0)}\varepsilon^{(0)}(r,t) + a_c^{(i)}\varepsilon^{(i)}(r,t),\ \Delta W^{(h)}(r,t) = a_\upsilon^{(0)}\varepsilon^{(0)}(r,t) - a_\upsilon^{(i)}\varepsilon^{(i)}(r,t).$$

Here $a_c^{(i)}$, $a_\upsilon^{(i)}$ are the constants of hydrostatic deformation potential of the conduction band and valence band, respectively.

Assuming that the Hamiltonian varies slowly with time, then the approximate solution of the Schrödinger equation is the stationary eigenfunctions of the energy operator calculated at fixed time (adiabatic approximation). That is, the wave function found at a certain moment in time continuously changes into the corresponding function for a later moment in time [23]. This approximation can be used when

$$\frac{1}{\hbar}\left|\frac{\partial H}{\partial t}\frac{1}{\omega_{kn}^2}\right| << 1, \tag{14}$$

where ω_{kn} is the radiation frequency of the transition between the corresponding energy levels.

The solution of the stationary Schrödinger equation for a mechanically deformed QD with a multilayer shell is found in [8]. Criterion (14) is determined by the relation between the frequency of the acoustic wave and ω_{kn}, and between the deformation potential and the energy gap between the ground $E_0^{(e,h)}$ and excited $E_1^{(e,h)}$ states of electron and hole. Calculations show that $\omega << \omega_{kn}$ and $a_{c,\upsilon}^{(i)}\varepsilon^{(i)} << E_1^{(e,h)} - E_0^{(e,h)}$.

In the future, we will use perturbation theory. An acoustic wave leads to a change in the energy of electron or hole by the amount (in the first approximation):

$$E_{1n}^{(e,h)} = \int_V \psi_n{}^{*(e,h)}(r)\Delta W^{(e,h)}(r,t)\psi_n{}^{(e,h)}(r)dV\,. \tag{15}$$

Then, the periodic change in the energy of radiation quantum which corresponds to the transition between the electron and hole ground states in the CdSe-core / ZnS/CdS/ZnS-shell quantum dot is determined as follows:

$$\Delta E(t) = E_{10}^{(e)}(t) + E_{10}^{(h)}(t) + \Delta E_g(t)\,, \tag{16}$$

where $\Delta E_g = a_c^{(0)}\varepsilon^{(0)} - a_\upsilon^{(0)}\varepsilon^{(0)}$ is the change in the band gap width of the QD core under the action of an acoustic wave. That is, the acousto-electron interaction leads to the modulation of the energy of radiation quantum of the QD with a multilayer shell.

In Fig. 8 shows the results of calculations of the dependence of the modulation amplitude of the energy of radiation quantum ΔE of the CdSe/ZnS QD, which corresponds to the recombination transition between the electron and hole ground states, on the frequency of the acoustic wave. The parameters of the corresponding materials are given in [8].

Such dependence for QD with a small core but a thick shell has a non-monotonic character with two maxima (Fig. 8, c). This is due to the fact that the radiation energy is determined by the energy shift of the edges of allowed bands in both the core and the shell under the influence of an acoustic wave. And for such QDs, the maxima of acoustic deformation in the core and shell are significantly shifted (Fig. 2, c and Fig. 3, c).

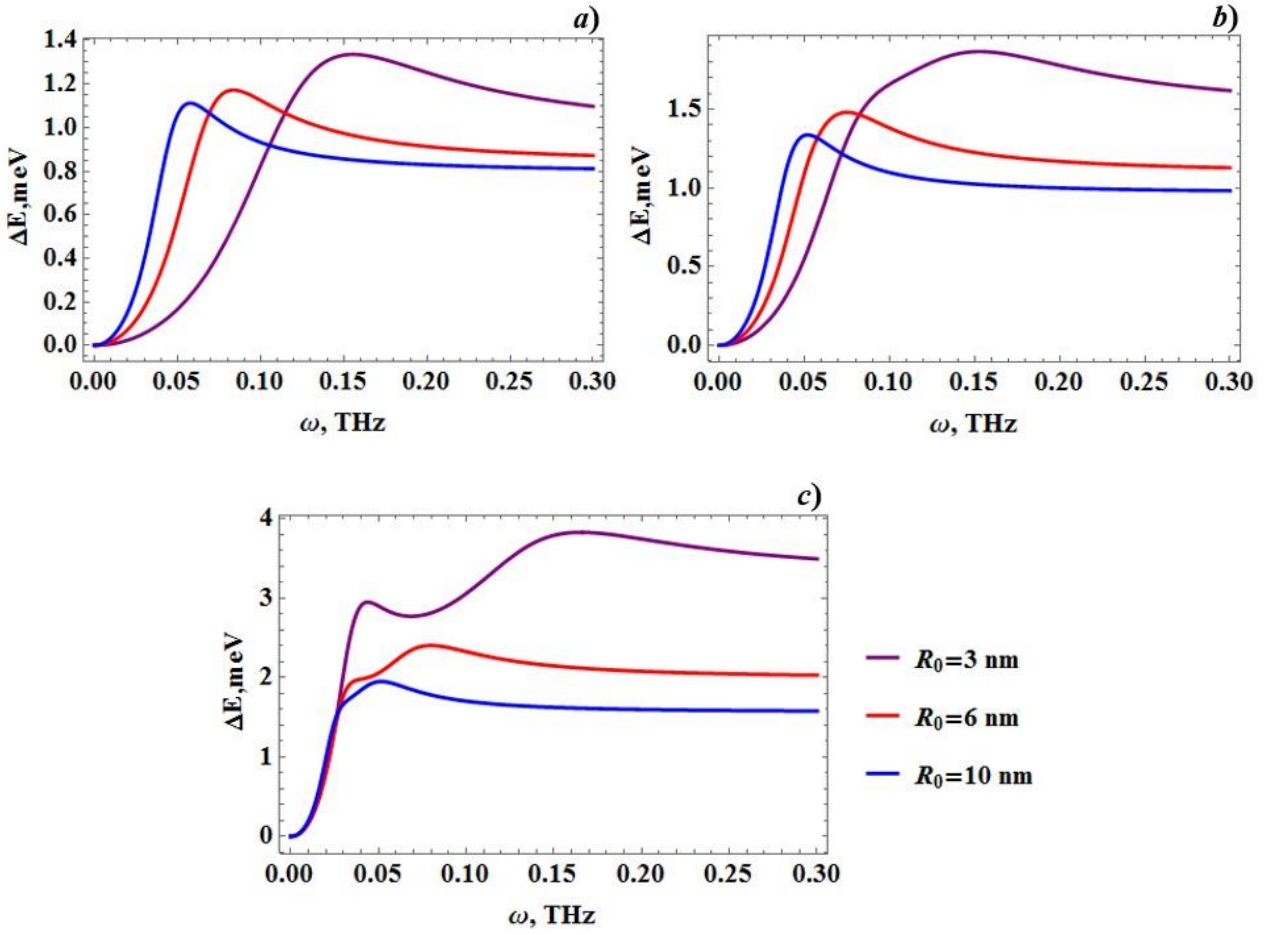

Fig. 8. The dependence of the modulation amplitude of the energy of radiation quantum of the CdSe/ZnS QD, which corresponds to the recombination transition between the electron and hole ground states, on the frequency of the acoustic wave, at different core radii and shell thicknesses:
$d_1 = 2a^{(ZnS)}$ (***a***); $d_1 = 6a^{(ZnS)}$ (***b***); $d_1 = 20a^{(ZnS)}$ (***c***)

In Fig. 9 shows a similar dependence for the QD with a three-layer shell. In this case, the change in radiation energy due to the acoustic wave is almost completely determined by the character of deformation in the core (Fig. 7) and is practically independent of the deformation of the shell layers.

Also, an increase in the number of the layers of shell leads to a more significant change in the radiation energy due to the acoustic wave. Thus, for a single-layer shell, even with its thickness of $20a^{(ZnS)}$, the maximal change in radiation energy does not exceed 3.8 *meV* (Fig. 8, c). Whereas for a three-layer shell, which in total is thinner ($6a^{(ZnS)}+6a^{(CdS)}+6a^{(ZnS)}$), the similar energy change reaches 5.6 *meV*.

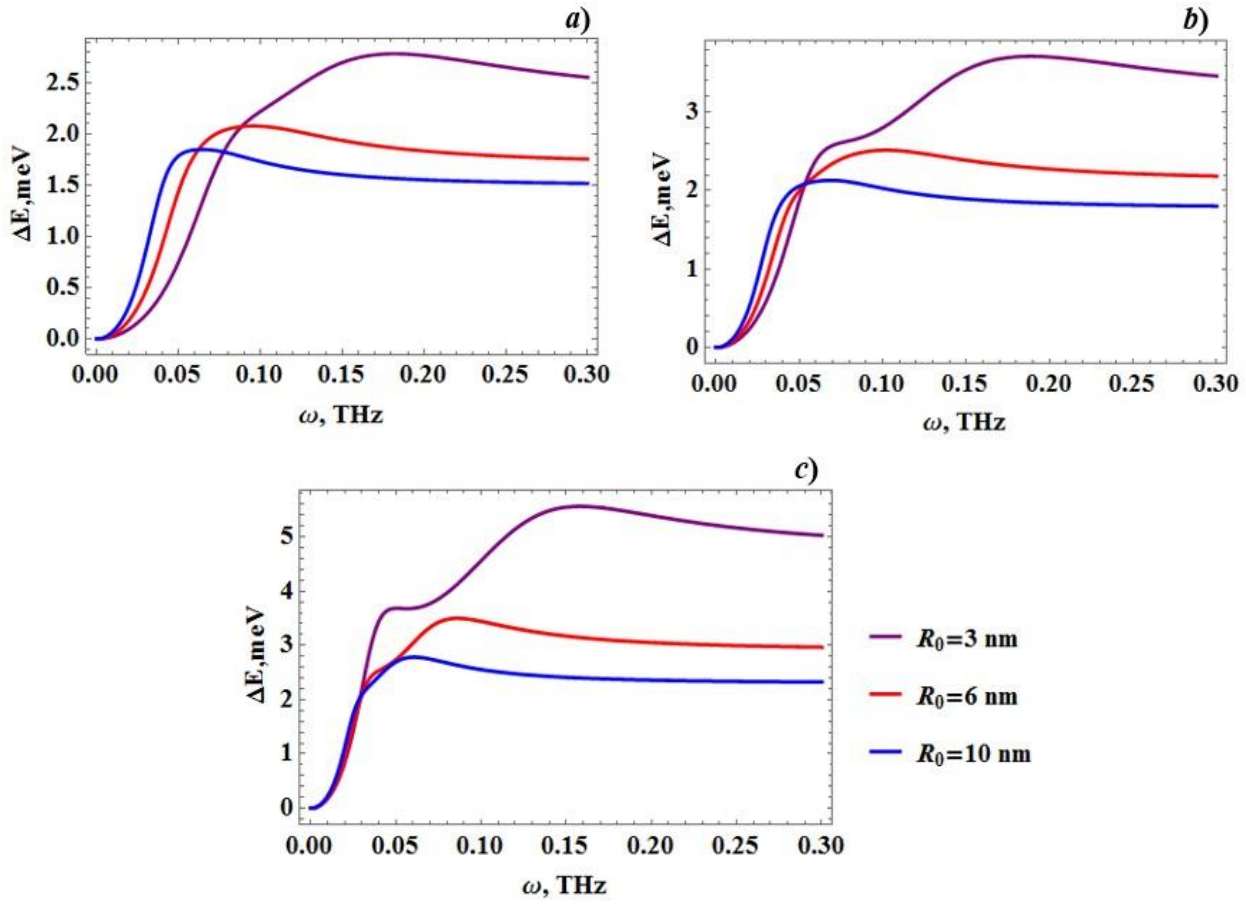

Fig. 9. The dependence of the modulation amplitude of the energy of radiation quantum of the CdSe / ZnS/CdS/ZnS QD, which corresponds to the recombination transition between the electron and hole ground states, on the frequency of the acoustic wave, at different core radii and shell layer thicknesses:
$d_1 = d_3 = 2a^{(ZnS)}$, $d_2 = 2a^{(CdS)}$ (***a***); $d_1 = d_3 = 2a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***b***);
$d_1 = d_3 = 6a^{(ZnS)}$, $d_2 = 6a^{(CdS)}$ (***c***)

4 Acousto-electron effects in the bionanocomplex based on QD during the propagation of an ultrasonic wave

Fluorescent A^2B^6 QDs of the core/shell type have found wide use in medical diagnosis and treatment [24]. Conducting ultrasound diagnostics in such conditions requires accurate information about the energy spectrum of charge carriers and the energy of radiation quantum.

An important research area of QDs for their medical applications is establishing regularities of their interaction with proteins, in particular with human serum albumin (HSA) [24, 25]. In works [26, 27] the stable biocomplexes of the core/shell QD – HSA type were obtained with the use of ultrasound. In [28] it is shown that the complex use of ultrasound and biocomplexes QD – HSA have a perspective for drug delivery and

complex chemo- and photoacoustic therapy.

As a result of the electrostatic interaction between QDs and albumin molecules (their attraction), the mechanical pressure occurs on the QD surface, which, as a result of self-consistent electron-deformation interaction, leads to a change in band structure of QD [29].

Let's consider the bionanocomplex of QD of spherical shape exposed to ultrasound. The propagation of ultrasound leads to a decrease in the pressure of HSA molecules on the QD surface along the direction of wave propagation and, accordingly, to an increase in the QD radius in this direction.

Let us assume that the ultrasonic wave propagates along the Oz axis. Then, along the direction of acoustic wave propagation, the radius of the QD core will increase and will be

$$R_{0z} = b = R_0\left(1 + \Delta\varepsilon^{(0)}\right), \tag{17}$$

where $\Delta\varepsilon^{(0)}$ is the amount of reduction in compressive deformation of QD due to ultrasound; R_0 is the radius of the spherical QD (before the action of ultrasound). In directions perpendicular to the propagation of ultrasound, the QD will undergo compression deformation, and its sizes will be [30]

$$R_{0x} = R_{0y} = a = R_0(1 - \nu^{(0)}\Delta\varepsilon^{(0)}), \tag{18}$$

where $\nu^{(0)}$ is the Poisson's ratio of the QD core material.

Similarly, the thicknesses of the shell layers will change in the corresponding directions:

$$d_{iz} = d_i\left(1 + \Delta\varepsilon^{(i)}\right),$$
$$d_{ix} = d_{iy} = d_i\left(1 - \nu^{(i)}\Delta\varepsilon^{(i)}\right).$$

4.1 The influence of shape distortion of QD on the ground state energy of electron and hole

Let's determine the energies of the ground state of electron and hole in the QD which is exposed to ultrasound.

Let's write down the Hamiltonian of an isolated QD:

$$\hat{H}^{(e,h)} = -\frac{\hbar^2}{2m^{(e,h)}}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{U}, \tag{19}$$

where $m^{(e,h)}$ is the effective mass of electron (hole) inside an isolated nanocrystal in the form of an ellipsoid of rotation; $\hat{U}$ is the potential energy of charge carrier inside an isolated nanocrystal in the form of an ellipsoid of rotation:

$$\hat{U}(x,y,z)=\begin{cases}0, & \dfrac{x^2+y^2}{a^2}+\dfrac{z^2}{b^2}\le 1;\\ V_i^{(e,h)}, & \dfrac{x^2+y^2}{a^2}+\dfrac{z^2}{b^2}\ge 1, \quad \dfrac{x^2+y^2}{\left(a+\sum\limits_{k=1}^{i}d_{kx}\right)^2}+\dfrac{z^2}{(b+\sum\limits_{k=1}^{i}d_{kz})^2}\le 1;\end{cases} \tag{20}$$

where $V_i^{(e,h)}$ are defined in [8].

In order to investigate the influence of the distortion of the spherical shape of QD by the action of ultrasound on the shift of the energy level of the ground state of a quasiparticle (electron or hole), we will replace the variables:

$$x=x',\ y=y',\ z'=\frac{a}{b}z\,. \tag{21}$$

Taking into account the substitution (20), the Hamiltonian (19) will take the form:

$$\hat{H}^{(e,h)}=-\frac{\hbar^2}{2m^{(e,h)}}\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{a^2}{b^2}\frac{\partial^2}{\partial z'^2}\right)+\hat{U}\,. \tag{22}$$

Now let's represent (22) in the form:

$$\hat{H}^{(e,h)}=\hat{H}_0^{(e,h)}+\hat{V}^{(e,h)},$$

$$\hat{H}_0^{(e,h)}=-\frac{\hbar^2}{2m^{(e,h)}}\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{\partial^2}{\partial z'^2}\right)+\hat{U},$$

$$\hat{V}^{(e,h)}=-\frac{\hbar^2}{2m^{(e,h)}}\left(\left(\frac{a^2}{b^2}-1\right)\frac{\partial^2}{\partial z'^2}\right), \tag{23}$$

where $\hat{H}_0^{(e,h)}$ is the Hamiltonian operator of the unperturbed problem; $\hat{V}^{(e,h)}$ is the perturbation operator caused by the distortion of the spherical shape of QD. The distorted spherical shape of QD has the form of an ellipsoid of rotation. Substituting (17), (18) into (9), we get:

$$\hat{V}^{(e,h)}=\frac{\hbar^2\Delta\varepsilon^{(i)}(1+\nu^{(i)})}{m^{(e,h)}}\frac{\partial^2}{\partial z'^2}\,. \tag{24}$$

The eigenvalues $E_{n0}^{(e,h)}$ and eigenfunctions $\psi_{nl0}^{(e,h)}$ of the unperturbed Hamiltonian operator are found from the solution of the Schrödinger equation:

$$\hat{H}_0^{(e,h)}\psi_{nl0}^{(e,h)}(r')=E_{n0}^{(e,h)}\psi_{nl0}^{(e,h)}(r')\,.$$

Then the first-order correction $E_{11}^{(e,h)}$ to the energy of the ground state of electron or hole is equal to

$$E_{11}^{(e,h)}=\int\psi_0^{(0)*}\hat{V}\psi_0^{(0)}dV'\,.$$

In the case of the QD without a shell, the energy of the ground state $E_{10}^{(e,h)}$ and the eigenfunctions $\psi_{100}^{(e,h)}$ of the Hamiltonian operator of an isolated spherical QD, respectively, are equal to

$$E_{10}^{(e,h)} = \frac{\hbar^2 \pi^2}{2m^{(e,h)} R_0^2}, \tag{25}$$

$$\psi_0^{(0)} = \frac{1}{\sqrt{2\pi R_0} r'} \sin\left(\frac{\pi r'}{R_0}\right). \tag{26}$$

Then the first-order correction to the energy of the ground state $E_{11}^{(e,h)}$ of electron or hole is equal to

$$E_{11}^{(e,h)} = \frac{\hbar^2 \Delta\varepsilon^{(0)} (1+\nu^0)}{m^{(e,h)}} \int \psi_0^{(0)*} \frac{\partial^2}{\partial z'^2} \psi_0^{(0)} dV' = -\frac{\pi^2 \hbar^2 \Delta\varepsilon^{(0)} (1+\nu^0)}{3m^{(e,h)} R_0^2}. \tag{27}$$

As can see from formula (27), the distortion of the QD shape under the influence of ultrasound leads to a decrease in the energy of the ground state of electron and hole.

4.2 The influence of changing the QD volume on the width of its band gap

As can see from formulas (17), (18), the action of the acoustic wave not only distorts the QD shape, but also changes its volume. The relative change in the volume ε_0 of the QD core in the linear approximation is

$$\varepsilon_0 = 2\frac{a - R_0}{R_0} + \frac{b - R_0}{R_0} = \Delta\varepsilon^{(0)}\left(1 - 2\nu^{(0)}\right). \tag{28}$$

The elastic deformation of the QD material leads to the energy shift of the edges of allowed bands [8]:

$$\Delta E_c = a_c^{(0)} \varepsilon_0 = a_c^{(0)} \Delta\varepsilon_0 \left(1 - 2\nu^{(0)}\right), \tag{29}$$

$$\Delta E_\upsilon = a_\upsilon^{(0)} \varepsilon_0 = a_\upsilon^{(0)} \Delta\varepsilon_0 \left(1 - 2\nu^{(0)}\right), \tag{30}$$

where ΔE_c, ΔE_υ are the energy shift of the bottom of conduction band and the top of valence band, respectively. Then the change in the width of band gap:

$$\Delta E_g = \Delta E_c - \Delta E_\upsilon = \left(a_c^{(0)} - a_\upsilon^{(0)}\right) \Delta\varepsilon_0 \left(1 - 2\nu^{(0)}\right). \tag{31}$$

As can see from formula (31), the influence of ultrasound leads to a decrease in the width of band gap of the CdSe core of QD ($a_c < 0$).

The change in the energy of recombination radiation under the influence of ultrasound in the QD – HSA bionanocomplex can be determined as follows:

$$\Delta E = E_{11}^{(e)} + E_{11}^{(h)} + \Delta E_g .$$

In Fig. 10, 11 shows the dependence of the shift of the energy of radiation quantum of the QD – HSA bionanocomplex, which corresponds to the recombination transition between the ground states of electron and hole, under the influence of

ultrasound (at an ultrasound pressure of $\sigma_0 = 10$ *bar*), on the surface concentration of albumin, for QD with CdSe core and a single-layer shell (Fig. 10), as well as a multilayer shell (Fig. 11). An increase in the concentration of albumin leads to a monotonic decrease in the energy of radiation quantum. Moreover, this effect is more pronounced for QDs with a larger core radius and a larger shell thickness.

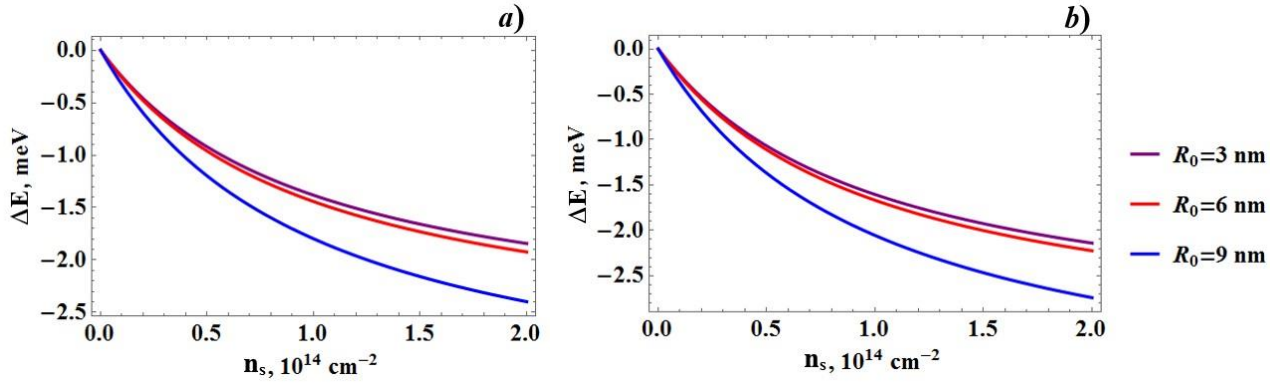

Fig. 10. The dependence of the shift of the energy of radiation quantum of the CdSe/ZnS QD – HSA bionanocomplex, which corresponds to the recombination transition between the electron and hole ground states, under the influence of ultrasound, on the surface concentration of albumin, at different core radii and shell thicknesses: $d_1 = 2a^{(ZnS)}$ (***a***); $d_1 = 6a^{(ZnS)}$ (***b***)

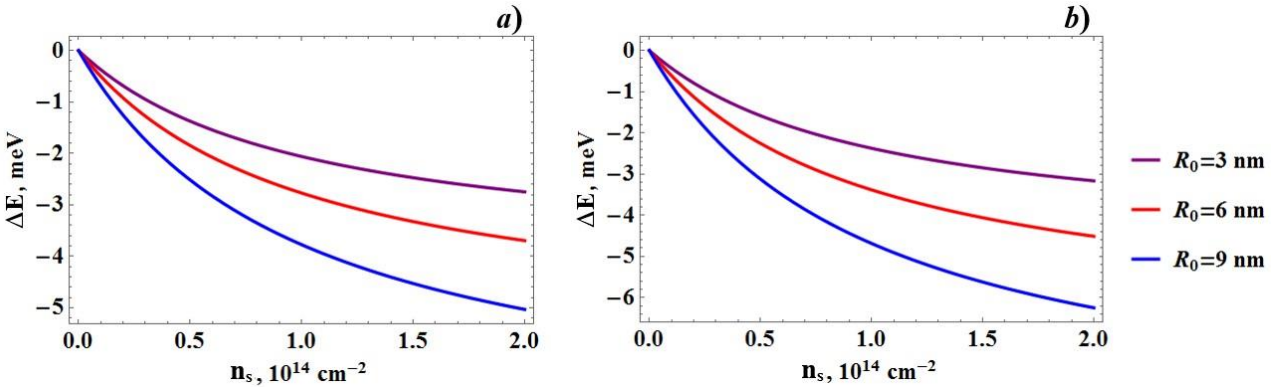

Fig. 11. The dependence of the shift of the energy of radiation quantum of the CdSe / ZnS/CdS QD – HSA bionanocomplex (***a***) and the CdSe / ZnS/CdS/ZnS QD – HSA bionanocomplex (***b***), which corresponds to the recombination transition between the electron and hole ground states, under the influence of ultrasound, on the surface concentration of albumin, at different core radii

An increase in the number of the layers of shell leads to a more significant decrease in the radiation energy of QD under the influence of ultrasound. Thus, if for CdSe/ZnS QD with the surface concentration of HAS of $2 \cdot 10^{14}$ cm^{-2}, such decrease is 2.5 *meV* (Fig. 10), then for CdSe / ZnS/CdS QD it is more than 5 *meV* (Fig. 11, a). The use of a three-layer shell leads to a slight decrease in the radiation energy of QDs under the influence of ultrasound (Fig. 11, b).

5 Discussion of results and Conclusions

In this work, the theoretical model of modulation of the radiation energy of QD with a multilayer shell under the influence of spherical acoustic wave was constructed and the influence of an ultrasonic wave on the radiation energy of the QD – HSA bionanocomplex was investigated. An acoustic wave in quantum dots can arise due to ultrasound or under the action of pulsed electromagnetic radiation. In this case, the sound arises as a result of the absorption of light by quantum dots (the width of band gap of the shell materials is greater than that of the QD core). To obtain optimal sound generation, it is necessary to choose the correct pulse duration, which depends on the sizes and structure of QD [10].

The dependence of the deformation of the CdSe core and shell materials of QD on the frequency of the acoustic wave for different sizes of the core, shell layers, and the number of shell layers was researched. It is shown that such dependence has a non-monotonic character with a maximum, the position of which depends on the core radius and the thickness of the shell layers. In the case of a three-layer ZnS/CdS/ZnS shell, the frequency dependence of deformation of the CdSe core has two maxima.

The regularities of the change in amplitude of modulation of the energy of radiation quantum of the CdSe/ZnS QD and CdSe / ZnS/CdS/ZnS QD have been established, which corresponds to the recombination transition between the electron and hole ground states, depending on the frequency of the acoustic wave and the geometric sizes of QD. These regularities are determined by the character of deformation in the QD core and individual layers of shell.

The regularities of the influence of ultrasound on the energy spectrum of the charge carriers of the QD – HSA bionanocomplex were investigated. It has been shown that ultrasound waves lead to a change in both the shape and the volume of QD. The first factor (the distortion of shape) leads to a decrease in the energy of the ground state of electron and hole, and the second factor (the change in volume) leads to a decrease in the band gap. The regularities of the change in radiation energy of QD with the CdSe core and different structure of shell depending on the surface concentration of HSA have been established.

The calculations carried out in this work are in good agreement with the results of experimental researches of the influence of the surface acoustic wave with a frequency of 3 *GHz* on QD radiation, which were obtained in work [20]. In this work, it is shown, firstly, that the acoustic wave leads to the modulation of the radiation energy (the broadening of the spectral line), and secondly, that the increase in the

intensity of the acoustic wave leads to a linear decrease in the radiation energy.

Having experimental data on the shift of radiation energy of QD under the influence of ultrasound, it is possible to solve the inverse problem of finding the deformation created by an acoustic wave.

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