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**ELECTRONIC AND OPTICAL PROPERTIES
OF SEMICONDUCTOR QUANTUM WIRES AND DOTS**

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V. Pleșca

GENERAL DESCRIPTION OF THE WORK

Actuality of the topic. The envelope-function approximation is widely employed for the investigation of semiconductor heterostructures because of its straightforward applicability and its limited computational effort. In most cases the envelope-function approximation is implemented as an effective-mass equation for the whole heterostructure, which also holds across abrupt interfaces. Away from them, equations reduce to the usual bulk form. This description was originally based on heuristic arguments, but was formalized into an exact envelope-function theory by Burt a few years ago. Envelope-function components are continuous everywhere and boundary conditions for their derivatives can be obtained by integration of the effective-mass equation across the heterointerface. Another approximation widely used for the theoretical analysis of quantum structures is the parabolic (one-band) approximation for the conduction and valence bands. However, most of the semiconductors do not have such simple conduction and valence bands. The parabolic band approximation is useful only for obtaining a qualitative understanding and not for a quantitative description of electronic and optical properties of real semiconductors. Therefore, the real multi-band structure of these semiconductors must be taken into account. Following Burt's guidelines, Foreman has derived a multi-band effective-mass Hamiltonian for heterostructures with one-dimensional confinement (quantum-well heterostructures). However, the derivation of a multi-band effective-mass Hamiltonian for heterostructures with two-dimensional or three-dimensional confinement (quantum-wire or quantum-dot heterostructures) has been lacking until now.

The investigation of low-dimensional semiconductor structures, such as quantum wires, has attracted much attention in recent years, because they not only demonstrate interesting electronic and optical properties, but also show promise for their application to electronic and optoelectronic devices. In quantum wires, carriers and excitons move freely in one direction but are confined in two others. This results in prominent exciton features such as large binding energies and oscillator strengths: the restriction of motion reduces the distance between an electron and a hole, thus enhancing their effective Coulomb attraction. So far, quantum wires with various cross-section forms have been fabricated and their successful application to quantum-wire lasers has been achieved. In the valence band of quantum wires, a reduction of the dimensionality enhances the heavy hole and light hole mixing and increases the nonparabolicities compared with those of quantum wells. Therefore, for optimal design of quantum-wire optical devices, it is quite important to

analyze the electronic and optical properties of quantum wires using accurate theoretical models.

Semiconductor quantum dots (also termed as artificial atoms) have been of major interest in recent years. They can be characterized as systems where the carriers are confined in all three spatial directions. The consequence of such confinement is that the lowest part of the electronic structure of quantum dots represents a series of discrete levels, contrary to the continuous density of states of bulk semiconductors, or to their higher dimensional relatives, such as quantum wells and quantum wires. Semiconductor nanocrystals synthesized in colloidal solutions are the smallest quantum dots with the strongest three-dimensional confinement. Their sizes can vary from 1 to 10 nm. They have symmetrical shapes and can be fabricated as multi-shell structures, i.e., built of concentric layers (shells) of different semiconductors with the shell thickness down to a single monolayer. The size of the nanocrystals and the composition of layers can be easily manipulated in the process of fabrication, which makes it possible to tailor to a large extent their discrete energy spectra. This makes them attractive for applications in novel optoelectronic devices. Some of the important issues in the physics of quantum dots are shape and dielectric mismatch effects. Usually quantum dots of a given semiconductor material are embedded in a matrix of a different semiconductor or dielectric material, whose dielectric properties are quite different as compared with the quantum dot material. This dielectric mismatch at the quantum dot interface has important consequences, as in the presence of charged particles inside the quantum dot (electrons, holes, impurities, etc.) they induce superficial charges at the boundaries. These induced charges interact in turn with the particles. Such interactions must be taken into account because they are often of the same magnitude as the Coulomb interaction between the real particles. The calculation of electron and hole energy spectra and wave functions in quantum dots of arbitrary shape is a considerably more difficult and computationally intensive task than that for a quantum well structure, where quantization occurs only along one direction. The theoretical study of GaN quantum dots is now of major interest, both to interpret existing data and to guide future developments. To compute quantum states in GaN quantum dots, three-dimensional distributions of strain and piezoelectric fields are also necessary.

Goal of the work. The main goal of present work is development and application of a modern accurate theory to study electronic and optical properties of practically important semiconductor quantum wires and dots. To achieve this goal, the following objectives are addressed:

- ✓ Development of multi-band theory valid for quantum heterostructures of different size, shape, and material content;

- ✓ Rigorous detailed investigation of electronic and optical properties of single and multiple rectangular quantum wires;
- ✓ Rigorous detailed investigation of electronic and optical properties of spherical and non-spherical quantum dot heterostructures.

Scientific novelty of the work. The scientific novelty of main results of present thesis is reflected in the following research, which has been carried out for the first time.

- Eight-band Hamiltonian applicable to quantum-wire and quantum-dot heterostructures is derived in the envelope function representation.
- Analytical expressions for the energy spectrum and wave functions of charge carriers confined in spherical quantum-dot heterostructures are obtained within the eight-band theory.
- An efficient numerical procedure is proposed to calculate electron states in single and multiple rectangular quantum wires.
- Electron states in finite and infinite lattices of rectangular quantum wires are considered; edge quantum states are revealed in the finite lattice.
- Exciton and impurity states in rectangular quantum wires are calculated using Coulomb potential energy of interaction between charges that properly takes into account dielectric mismatch.
- Electron and hole states in quantum-dot quantum wells are computed within the developed eight-band theory.
- Donor and acceptor states in quantum-dot quantum wells are found within the developed 8-band theory as a function of the impurity position.
- Exciton states in a typical quantum-dot quantum wells are calculated; absorption spectrum is obtained within the non-adiabatic theory.
- Finite difference method is applied to calculate electron and hole states in quantum dots of arbitrary shape.
- Potential energy of the electron-hole system that also includes electron and hole self-action energies is computed for quantum dots of arbitrary shape.
- Oscillator strengths are investigated for quantum dots of arbitrary shape.
- A theoretical investigation of GaN quantum dots of different shape and crystallinity is carried out.

Practical significance. The practical importance of obtained in present thesis results follows from the fact that a number of significant theoretical issues listed below have been brought to practice.

- ◆ Developed eight-band theory allows application of the envelope-function (effective-mass) method to find precise energy spectrum and wave functions in quantum-wire and quantum-dot heterostructures of any size and with arbitrary value of the band gap.
- ◆ Almost analytical solution of the multiband envelope-function equations for multilayer spherical quantum dots opens an easy way to investigate such systems.
- ◆ Electronic states in quantum-dot quantum wells can be easily calculated.
- ◆ Tuning the height of the exterior potential barrier in a finite array of quantum wires allows modulation of the electron density distribution across the array.
- ◆ Dielectric mismatch at the boundaries of quantum heterostructures can be rigorously taken into account.
- ◆ Semimetal nature of HgS and HgTe can be easily taken into account when considering quantum-dot quantum wells.
- ◆ Due to the almost analytical solution for the Coulomb potential in quantum-dot quantum wells, exciton and impurity problems are greatly simplified.
- ◆ In principle, the position of an impurity in quantum-dot quantum wells can be theoretically estimated.
- ◆ Accurate excitonic spectra allow direct comparison with experimental luminescence and absorption spectra.
- ◆ An important factor of shape of quantum dots must be included in both qualitative and quantitative description of electronic and optical properties of quantum dots.
- ◆ Dielectric continuum model can be used to study quantum heterostructures of arbitrary shape.
- ◆ Based on oscillator strengths, it is possible to compare optical properties of quantum dots with different shapes.
- ◆ The influence of confinement, strain, and piezoelectric effect on the optical properties of GaN quantum dots can be taken into account.

The general principles advanced for the defense:

1. Eight-band effective-mass Hamiltonian for quantum-dot heterostructures in Burt's envelope-function representation is derived. The eight-band radial Hamiltonian and the boundary conditions for the Schrödinger equation are obtained for spherical quantum-dot heterostructures. Electron and hole energy spectra in three spherical quantum dots: HgS/CdS, InAs/GaAs, and GaAs/AlAs are calculated as a function of the quantum dot radius within

the approximate symmetrized and exact nonsymmetrized eight-band models. The parameters of dissymmetry are shown to influence the energy levels and the wave functions of an electron and a hole and, consequently, the energies of both intraband and interband transitions.

2. Electron and hole states are studied in quantum wires with rectangular cross-section. A theoretical approach is developed, within which the electronic properties of a single quantum wire as well as of finite and infinite planar lattices of quantum wires are analyzed. A six-wire lattice is studied in detail. Edge states, which can be observed in optical spectra, are revealed, when the barrier heights are different inside and outside the lattice. The structure of minibands is investigated for an infinite lattice of quantum wires. Impurity and exciton states in rectangular quantum wires are studied. The calculated excitonic energies are in a good agreement with the experimental data on photoluminescence in GaInAs/InP quantum wires.

3. Electron, hole, exciton, and impurity states in spherical CdS/HgS/CdS and CdTe/HgTe/CdTe quantum-dot quantum-wells are calculated. An investigation of electron, hole, and exciton energy spectra as well as oscillator strengths of optical transitions in colloidal CdS quantum dots with spherical and tetrahedral shape is carried out. Coulomb potential energy of the electron-hole system is treated taking into account the dielectric mismatch at the quantum dot boundaries. Excitonic states and oscillator strengths of optical transitions in GaN quantum dots characterized by different size, shape, interface, and substrate are theoretically investigated. Piezoelectric field-induced red shift of excitonic ground state transition in GaN/AlN quantum dots is determined.

Approbation of the work. The materials of the work were presented at the following scientific conferences: *Spring meeting of the German Physical Society* (Münster, Germany, March 22-26, 1999); *March Meeting of the American Physical Society* (Minneapolis, Minnesota, March 20-24, 2000); *Spring meeting of the German Physical Society* (Regensburg, Germany, March 27-31, 2000); *44th Electronic Materials Conference* (Santa Barbara, California, June 26-28, 2002); *5th International Conference on Excitonic Processes in Condensed Matter EXCON'02* (Darwin, Australia, July 22-26, 2002); *26th International Conference on the Physics of Semiconductors* (Edinburgh, UK, July 29 - August 2, 2002); *XVI Jahn-Teller Conference* (Leuven, Belgium, August 26 - September 1, 2002).

Publications. The principle results of the thesis were presented in 20 scientific works, which are listed at the end of the abstract.

Volume and structure of the work. The thesis consists of the abstract, five chapters, bibliography (145 items), and acknowledgment. The volume of the thesis is 142 pages, 45 figures, and 4 tables.

CONTENTS OF THE WORK

I. Introduction

In the first chapter the actuality of the topic is motivated, the goal is formulated, scientific novelty, practical importance, the general principles advanced for the defense, and content of the work in chapters are presented.

II. Development of a multi-band theory for quantum heterostructures

In the second chapter the eight-band effective mass theory for quantum-wire and quantum-dot heterostructures is developed in the Burt's envelope-function representation. The chapter consists of four sections.

II.A. Peculiarities of application of a multi-band theory for quantum heterostructures

Recent literature is analyzed regarding the use of multiband Hamiltonians to describe electronic spectra of quantum nanostructures. At the heterointerfaces of the multilayer nanostructures, there occurs an abrupt change of effective-mass parameters from their values in one material to those in the adjacent material. Therefore, the ordering of the differential operators and coordinate-dependent effective-mass parameters in the multiband Hamiltonian becomes crucial. The Burt's envelope-function equations and the application of the connection rules and of the boundary conditions to find envelope wave functions in quantum heterostructures are discussed.

II.B. Derivation of an eight-band Hamiltonian for quantum heterostructures

The eight-band Hamiltonian for envelope functions has been obtained in the following form (Bloch function basis is indicated on the right side),

$$\hat{H} = \frac{\hbar^2}{2m_0} \begin{pmatrix} \varepsilon_c + T & 0 & iV_1 & \sqrt{\frac{2}{3}}V_0 & \frac{i}{\sqrt{3}}V_{-1} & 0 & \frac{i}{\sqrt{3}}V_0 & \sqrt{\frac{2}{3}}V_{-1} \\ 0 & \varepsilon_c + T & 0 & \frac{-1}{\sqrt{3}}V_1 & i\sqrt{\frac{2}{3}}V_0 & -V_{-1} & i\sqrt{\frac{2}{3}}V_1 & \frac{-1}{\sqrt{3}}V_0 \\ -iV_1^\dagger & 0 & \varepsilon_v - P - Q & -S & -R & 0 & \frac{-i}{\sqrt{2}}S & i\sqrt{2}R \\ \sqrt{\frac{2}{3}}V_0^\dagger & \frac{-1}{\sqrt{3}}V_1^\dagger & -S^\dagger & \varepsilon_v - P + Q & -C & -R & i\sqrt{2}Q & -i\sqrt{\frac{3}{2}}\Sigma \\ \frac{-i}{\sqrt{3}}V_{-1}^\dagger & -i\sqrt{\frac{2}{3}}V_0^\dagger & -R^\dagger & -C^\dagger & \varepsilon_v - P^* + Q^* & S^\dagger & i\sqrt{\frac{3}{2}}\Sigma^* & i\sqrt{2}Q^* \\ 0 & -V_{-1}^\dagger & 0 & -R^\dagger & S^\dagger & \varepsilon_v - P^* - Q^* & i\sqrt{2}R^* & \frac{i}{\sqrt{2}}S^* \\ \frac{-i}{\sqrt{3}}V_0^\dagger & -i\sqrt{\frac{2}{3}}V_1^\dagger & \frac{i}{\sqrt{2}}S^\dagger & -i\sqrt{2}Q & -i\sqrt{\frac{3}{2}}\Sigma^\dagger & -i\sqrt{2}R & \varepsilon_v^* - P & C \\ \sqrt{\frac{2}{3}}V_{-1}^\dagger & \frac{-1}{\sqrt{3}}V_0^\dagger & -i\sqrt{2}R^\dagger & i\sqrt{\frac{3}{2}}\Sigma^\dagger & -i\sqrt{2}Q^\dagger & \frac{-i}{\sqrt{2}}S^\dagger & C^\dagger & \varepsilon_v^* - P^* \end{pmatrix} \begin{matrix} |S \uparrow\rangle \\ |S \downarrow\rangle \\ \frac{1}{\sqrt{2}}(|X \uparrow\rangle + i|Y \uparrow\rangle) \\ \frac{i}{\sqrt{6}}(|X \downarrow\rangle + i|Y \downarrow\rangle) - 2|Z \uparrow\rangle \\ \frac{1}{\sqrt{6}}(|X \uparrow\rangle - i|Y \uparrow\rangle) + 2|Z \downarrow\rangle \\ \frac{i}{\sqrt{2}}(|X \downarrow\rangle - i|Y \downarrow\rangle) \\ \frac{1}{\sqrt{3}}(|X \downarrow\rangle + i|Y \downarrow\rangle) + |Z \uparrow\rangle \\ \frac{-i}{\sqrt{3}}(|X \uparrow\rangle - i|Y \uparrow\rangle) - |Z \downarrow\rangle \end{matrix} \quad (1)$$

where daggers (\dagger) denote the hermitian conjugation, i.e. $A^\dagger \equiv (A^T)^*$;

$$\begin{aligned}
\varepsilon_v^* &= \varepsilon_v - \delta, & \hat{\mathbf{k}} &= -i\nabla, & \hat{k}_+ &= \frac{\hat{k}_x + i\hat{k}_y}{\sqrt{2}}, & \hat{k}_- &= \frac{\hat{k}_x - i\hat{k}_y}{\sqrt{2}}, \\
V_1 &= \frac{1}{2}((v+\xi)\hat{k}_+ + \hat{k}_+(v-\xi)), & V_{-1} &= \frac{1}{2}((v+\xi)\hat{k}_- + \hat{k}_-(v-\xi)), \\
V_0 &= \frac{1}{2}((v+\xi)\hat{k}_z + \hat{k}_z(v-\xi)), & T &= \hat{k}_+\alpha\hat{k}_- + \hat{k}_-\alpha\hat{k}_+ + \hat{k}_z\alpha\hat{k}_z, \\
P &= \hat{k}_+(\gamma_1 - 2\chi)\hat{k}_- + \hat{k}_-(\gamma_1 + 2\chi)\hat{k}_+ + \hat{k}_z\gamma_1\hat{k}_z, & Q &= \hat{k}_+(\gamma_2 - \chi)\hat{k}_- + \hat{k}_-(\gamma_2 + \chi)\hat{k}_+ - 2\hat{k}_z\gamma_2\hat{k}_z, \\
R &= \sqrt{3}(\hat{k}_+(\gamma_2 - \gamma_3)\hat{k}_+ + \hat{k}_-(\gamma_2 + \gamma_3)\hat{k}_-), & S &= -i\sqrt{6}(\hat{k}_-(\gamma_3 + \chi)\hat{k}_z + \hat{k}_z(\gamma_3 - \chi)\hat{k}_-), \\
\Sigma &= -i\sqrt{6}\left(\hat{k}_-\left(\gamma_3 - \frac{\chi}{3}\right)\hat{k}_z + \hat{k}_z\left(\gamma_3 + \frac{\chi}{3}\right)\hat{k}_-\right), & C &= -i2\sqrt{2}(\hat{k}_-\chi\hat{k}_z - \hat{k}_z\chi\hat{k}_-).
\end{aligned}$$

In addition to the eight-band effective-mass parameters ε_c , ε_v , δ , ν , α , γ_1 , γ_2 , and γ_3 , parameters of dissymmetry ξ and χ have been introduced in the developed theory.

II.C. Eight-band Hamiltonian and boundary conditions for a multi-layer spherical quantum dot

To study the electronic structure of spherical quantum dots, the spherical approximation $\gamma_2 = \gamma_3 \equiv \gamma$ has been applied. In spherical quantum dots, where all effective-mass parameters depend only on the absolute value r of the radius-vector, electron and hole states are eigenfunctions of the total angular momentum j , its z -component $m \equiv j_z$, and of the parity p . Therefore, the envelope wave function of the Hamiltonian (1) can be found as a combination of spherical harmonics and of radial envelope functions. Integrating over angular variables θ and ϕ , the radial Hamiltonian that corresponds to the radial Schrödinger equation has been obtained. The radial Hamiltonian does not depend on m , therefore the energy spectrum in the spherical approximation is degenerate with respect to m . In order to find solutions of the radial Schrödinger equation inside each spherical layer, one can use the bulk radial Hamiltonian. When the wave functions inside each spherical layer are known, the boundary conditions should be applied to match the wave functions from two adjacent layers. When considering the multiband models, the boundary conditions for the wave function are obtained by integrating the Schrödinger equation across the heterointerface and assuming the continuity of the wave-function envelopes. Such boundary conditions have been compared with the commonly used connection rules that the wave function and the normal component of the velocity are continuous at the heterointerface.

II.D. Practical importance of the developed multi-band theory

In this section the electronic structure of three spherical quantum heterostructures with different values of the band gap: HgS/CdS, InAs/GaAs, and GaAs/AlAs are investigated. The section consists of four subsections.

II.D.1. *Electron energy levels*

All the discrete electron energy levels have been calculated as a function of the quantum dot radius a for HgS/CdS (see Fig. 1), InAs/GaAs, and GaAs/AlAs spherical quantum dots.

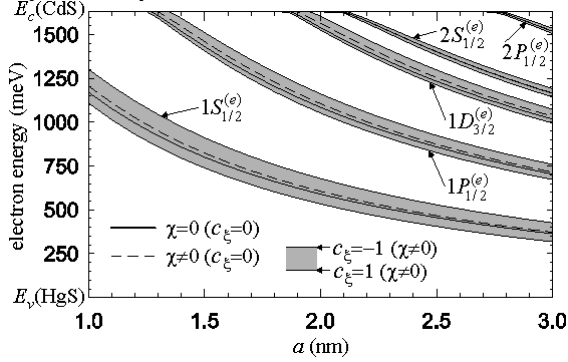


FIG. 1. All the discrete electron energy levels in the HgS/CdS quantum dot as a function of the quantum dot radius. The $P_{3/2}^{(e)}$ and $D_{5/2}^{(e)}$ energy levels are not shown because in the chosen scale they coincide with the levels $P_{1/2}^{(e)}$ and $D_{3/2}^{(e)}$, correspondingly. Dissymmetry parameter ξ is chosen as $\xi = c_\xi v$ and the dissymmetry parameter χ is defined as $\chi = [2\gamma_2 + 3\gamma_3 - \gamma_1 - 1]/3$. Solid lines represent the result of the symmetrized 8-band model ($c_\xi = 0, \chi = 0$). With the nonsymmetrized valence band part of the Hamiltonian ($\chi \neq 0$), dashed lines show the case $c_\xi = 0$ while gray bands represent the continuous change of c_ξ from 1 to -1 . The insert with inscriptions $c_\xi = -1$ and $c_\xi = 1$ shows to which values of c_ξ the edges of the gray bands are related.

II.D.2. *Hole energy levels*

All the discrete energy levels of S - and P -types of a hole in the HgS/CdS quantum dot and discrete energy levels with $j=3/2$ of InAs/GaAs and GaAs/AlAs quantum dots have been calculated as a function of the quantum dot radius a .

II.D.3. *Electron and hole wave functions and pair energies*

The S -component of the radial wave functions of electron ground state ($1S_{1/2}^{(e)}$) and hole ground state ($1S_{3/2}^{(h)}$) is investigated for HgS/CdS ($a = 2$ nm), InAs/GaAs ($a = 4$ nm), and GaAs/AlAs ($a = 3$ nm) quantum dots. The lowest electron-hole pair energies are presented as a function of c_ξ for all considered quantum dots.

II.D.4. *Summary of the developed multi-band theory*

The exact nonsymmetrized eight-band effective-mass Hamiltonian for a three-dimensional heterostructure has been obtained using the Burt's envelope-function representation. Within the spherical approximation, the 8×8 radial Hamiltonians and the necessary boundary conditions have been derived for multilayer spherical quantum dots. It has been shown that the connection rules, which are commonly used to match the solutions of the appropriate bulk $\mathbf{k} \cdot \mathbf{p}$ Hamiltonians, coincide with boundary conditions for the symmetrized Hamiltonians. The parameters of dissymmetry $\chi(\mathbf{r})$ and $\xi(\mathbf{r})$, giving nonzero contribution to the multiband Hamiltonians only at the heterointerfaces, have a strong effect on the electron and hole spectra. Thus, for practically important cases of relatively small quantum-dot heterostructures with noticeably different effective-mass parameters of the constituent materials, the use of the obtained Hamiltonian is necessary for the adequate description of experiment.

III. Electronic and optical properties of single and multiple rectangular quantum wires

In the third chapter, electron, hole, exciton, and impurity states are studied for quantum wires with a rectangular cross-section and for the lattices of such wires. The chapter consists of four sections.

III.A. Quantum wires as an object of physical research

Recent literature is analyzed regarding the fabrication and investigation of physical properties of semiconductor quantum wires with nanometer dimensions. It was proved that transistors and lasers made of quantum wires demonstrate excellent characteristics.

III.B. Effective method of calculation of quantum states in single rectangular quantum wires and lattices of such wires

Rectangular quantum wires layered out along one plane and parallel to each other are considered (see Fig. 2). A theoretical method is developed to calculate electron states in single quantum wires and in finite and infinite lattices of such wires.

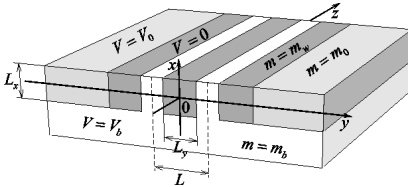


FIG. 2. A schematic picture of the lattice of quantum wires. Three quantum wires (dark gray), edge barrier (light gray), and barrier region (white) are shown. The structure is covered ($x > L_x/2$) by the same substance as its substrate ($x < -L_x/2$).

III.C. Electron and hole states in rectangular quantum wires and lattices of such wires

Electron and hole states are studied in quantum wires with a rectangular cross-section. It has been demonstrated that the ratio of effective masses in well and barrier regions influences the dispersion law of electron's motion along the wire axis. The lattice of six wires is studied in detail. Edge

states are revealed when the heights of the potential barrier are different inside and outside the lattice. The miniband structure is investigated for an infinite lattice of quantum wires. The evolution of electron states is analyzed when the number of wires in the lattice increases.

III.D. Exciton and impurity states in rectangular quantum wires

Exciton and impurity states in rectangular quantum wires are studied. It has been found that the lowest absolute value of impurity ground state energy is achieved when the impurity is located in the center of the rectangular quantum wire. The calculated exciton energies are in good agreement with the experimental data on photoluminescence in $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}/\text{InP}$ quantum wires.

IV. **Electronic and optical properties of spherical and non-spherical quantum dot heterostructures**

In the fourth chapter, electron, hole, exciton, and impurity states and oscillator strengths are studied for quantum-dot quantum wells, colloidal CdS quantum dots, and strained GaN quantum dots of different shapes. The chapter consists of four sections.

IV.A. Quantum dots as an object of physical research

Recent literature is analyzed regarding the fabrication and investigation of physical properties of semiconductor quantum dots with nanometer dimensions. A significant attention has been attracted to quantum dots due to their promises for applications as basic elements for semiconductor lasers, nonlinear transformers of light, computer memory, and elements of quantum logic.

IV.B. Electron, hole, exciton, and impurity states in a quantum-dot quantum well

In this section electronic and optical properties of CdS/HgS/CdS and CdTe/HgTe/CdTe quantum-dot quantum wells (see Fig. 3) are investigated using the developed eight-band theory. The section consists of four subsections.

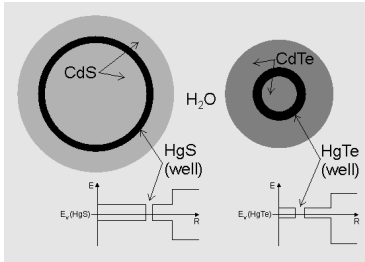


FIG. 3. A schematic picture of typical CdS/HgS/CdS (left-hand-side panel) and CdTe/HgTe/CdTe (right-hand side panel) quantum-dot quantum wells in H_2O . Diameters of the considered quantum-dot quantum wells are 6.8 nm and 4.7 nm correspondingly. The band structure of each quantum dot is shown below.

IV.B.1. *Electron and hole states*

Radial components of the wave functions of the lowest electron and hole states are presented. It is shown that in the CdS/HgS/CdS/ H_2O quantum dot holes in the lowest states are strongly localized in the well region (HgS).

On the contrary, electrons in this quantum dot and both electrons and holes in the CdTe/HgTe/CdTe/H₂O quantum dot are distributed through the entire dot.

IV.B.2. *Coulomb potential energy of interaction between charges*

The potential energy of the electron-impurity or hole-impurity or electron-hole interaction is found as an almost analytical solution of the Poisson equation taking into account a spatial variation of the dielectric constant.

IV.B.3. *Donor and acceptor states*

Donor and acceptor states are investigated as a function of impurity position in quantum dot. All donor energy levels inside the quantum dot are practically constant and on the contrary, few lowest acceptor energy levels decrease rapidly, when the acceptor approaches the HgS layer. It is due to the fact, that the hole and, therefore, the acceptor are mainly present in this layer.

IV.B.4. *Excitonic states and absorption spectrum*

The fine structure of the exciton spectrum is found taking into account the electron-hole exchange interaction in addition to the electron-hole Coulomb interaction. Frölich-like Hamiltonian of exciton-phonon interaction, adapted for multilayer spherical quantum dots is used to calculate absorption spectrum in CdS/HgS/CdS quantum dot.

IV.C. Exciton states and optical transitions in colloidal CdS quantum dots

In this section electronic and optical properties of colloidal CdS quantum dots with different shapes are investigated taking into account the dielectric mismatch. The section consists of four subsections.

IV.C.1. *Electron and hole states in quantum dots of different shapes*

In order to obtain the electron and hole states in quantum dots of arbitrary shape, the differential equations for the corresponding envelope functions have been solved using the finite difference numerical method.

IV.C.2. *Potential energy of the electron-hole system in quantum dots of different shapes*

The Coulomb potential energy of the electron-hole system in quantum dots of different shapes is treated accounting for the dielectric mismatch at the quantum dot boundaries as well as for the self-action energy of an electron and a hole.

IV.C.3. *Exciton states and oscillator strengths in quantum dots of different shapes*

Electron and hole states and electron-hole potential energy described above are used here to find the exciton states and oscillator strengths in quantum dots of different shapes.

IV.C.4. Similarities and distinctions in electronic and optical properties of spherical and tetrahedral CdS quantum dots

Exciton states and oscillator strengths for spherical and tetrahedral quantum dots have been calculated. In both quantum dots, a regularity is observed that the exciton ground state has large oscillator strength which is practically unchanged with varying the quantum dot size. The exciton ground state energies as a function of quantum dot size for spherical and tetrahedral CdS quantum dots calculated in the present work are compared with the results obtained in recent theoretical and experimental studies. A clear distinction in the optical properties of tetrahedral and spherical quantum dots has been revealed.

IV.D. Interplay of confinement, strain, and piezoelectric effect in optical spectra of GaN quantum dots

Excitonic states and oscillator strengths of optical transitions in GaN quantum dots characterized by different size, shape, interface, and substrate (see Fig. 4) are investigated. It has been determined that the piezoelectric field-induced red shift of the ground state transition, observed in recent experiments, can manifest itself only in strained GaN/AlN quantum dots with the dot height larger than 3 nm. It was also established that the oscillator strength of the red-shifted transitions is small (<0.05) and decreases fast with increasing the quantum dot size, while the strength of ground state transitions in GaN(cubic)/AlN(cubic) and GaN/dielectric quantum dots is large ($\sim 0.4-0.7$) and almost independent of the quantum dot size.

V. Conclusions

In the fifth chapter the principle results and conclusions are presented.

PRINCIPLE RESULTS AND CONCLUSIONS

Nonsymmetrized eight-band Hamiltonian valid for an arbitrary three-dimensional heterostructure has been rigorously derived using the Burt's envelope-function representation. Parameters of dissymmetry, introduced during the derivation, give nonzero contribution to the multiband Hamiltonians only at the heterointerfaces, but, nevertheless, have a strong effect on the

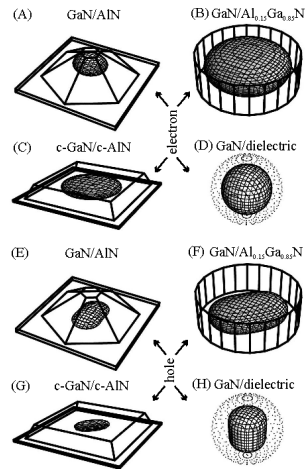


FIG. 4. Shape of GaN quantum dots of four different types with the height $H=3$ nm and iso-surfaces of probability density 0.8 for electron (A-D) and hole (E-H) ground states.

electron and hole energy spectra. It has been proven that for all practically important cases of quantum-wire and quantum-dot heterostructures with (i) noticeably different effective-mass parameters of constituent materials, (ii) hetero-layers as thin as few unit cells, and (iii) narrow-bandgap semiconductor or semimetal constituents, the obtained eight-band Hamiltonian represents the most effective tool and the only accurate method, within the envelope-function representation, for the adequate description of electronic and optical properties in quantum heterostructures.

Within the spherical approximation, the eight-band radial Hamiltonian has been derived for spherical quantum-dot heterostructures consisted of a spherical core and co-central spherical shells of different materials. In each particular spherical layer, an analytical solution of the eight-band Schrödinger equation for both electrons and holes has been found and the boundary conditions, necessary to match the obtained analytical solutions at the spherical heterointerfaces, have been extracted from the derived eight-band Hamiltonian. The boundary conditions for radial symmetrized and nonsymmetrized Hamiltonians are different and lead, therefore, to different energy levels and wave functions of charge carriers. It has been shown, that connection rules, which are commonly used to match the solutions of the appropriate bulk multi-band Hamiltonians are inaccurate, because they coincide with boundary conditions for the symmetrized Hamiltonians.

As a practical illustration of the importance of the developed multi-band theory, energy levels and wave functions resulting from the nonsymmetrized eight-band Hamiltonian have been calculated as a function of the quantum dot radius for three spherical quantum dots: a zero-bandgap semiconductor embedded into a wide-bandgap semiconductor (HgS/CdS), a narrow-bandgap semiconductor embedded into a medium-bandgap semiconductor (InAs/GaAs), and a medium-bandgap semiconductor embedded into a wide-bandgap semiconductor (GaAs/AlAs). Direct comparison with the results obtained using the symmetrized eight-band Hamiltonian allowed us to discover the role of each parameter of dissymmetry taken separately. The above fact, in its turn, allowed us to find a theoretical estimate for the value of the energy difference between the energy levels resulting from accurate nonsymmetrized and inaccurate symmetrized Hamiltonians as a function of aforementioned dissymmetry parameters.

Using a one-dimensional series expansion technique, an efficient numerical method has been developed to solve one-band Schrödinger equation for heterostructures consisted of quantum wires with rectangular cross-section. This method allowed us to get an insight into the electronic properties of a single rectangular quantum wire as well as of finite and infinite planar lattices

of such quantum wires. The main outcome of this method is stated in the three following paragraphs.

(i) Investigating the dependence of the electron energy spectrum and wave functions of a single quantum wire on the wave number k_z of electron's free motion along the wire axis, it has been found that in a practically important case when the electron effective mass inside the quantum wire is less than that outside the quantum wire, the electron wave function penetrates deeper into the barrier as the wave number k_z increases. Thus, the ratio of effective masses in the well and in the barrier has been shown to influence the electron transport along the wire axis.

(ii) Electron quantum states in the finite planar lattice of quantum wires are formed as a modulation of quantum states of each particular quantum wire constituting the lattice. Edge quantum states have been discovered when the height of the external potential barrier (outside the lattice) differs from that of the internal potential barrier (between the quantum wires). The wave function of an edge quantum state is localized near the lattice edges, while the wave functions of the rest quantum states are expelled from the edges.

(iii) In the absence of electron's motion along the quantum wire, the energy spectrum of an infinite planar lattice of quantum wires has a miniband structure. Each miniband corresponds to a quasi-discrete energy level of a single quantum wire. It has been shown that the deeper wave function of a single quantum wire constituting the superlattice penetrates into the barrier region in the in-plane direction, the wider corresponding minibands of the infinite lattice of quantum wires are.

Donor, acceptor, and exciton energy levels in a single rectangular quantum wire have been analyzed. Four-band Hamiltonian has been used to calculate hole, acceptor, and exciton states. It has been shown that the use of one-band electron and four-band hole Hamiltonians is justified for unstrained $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}/\text{InP}$ single quantum wires, because the calculated excitonic energies are in a good agreement with the experimental data on photoluminescence in these quantum wires. It is also found that the lowest absolute value of impurity ground state energy is achieved when the impurity is located in the center of the rectangular quantum wire.

Using the accurate eight-band theory developed here, electron and hole energy spectra and the corresponding wave functions for typical spherical quantum-dot quantum wells have been examined. While in the $\text{CdS}/\text{HgS}/\text{CdS}/\text{H}_2\text{O}$ quantum-dot quantum well holes in the lowest states are strongly localized in the well region, in the $\text{CdTe}/\text{HgTe}/\text{CdTe}/\text{H}_2\text{O}$ quantum-dot quantum well holes are distributed through the entire quantum dot. At the same time, electrons in both types of quantum-dot quantum wells are not localized in the quantum well.

The aforementioned conclusions about the properties of the electron and hole spectra are a consequence of one-monolayer thickness of the HgS (HgTe) well and of the semimetal character of the well material. Once again we have made it certain that the symmetrized eight-band model is not capable to describe electronic states in quantum dots composed of materials with very dissimilar effective-mass parameters. It has been also shown that the obtained results do not depend critically on the actual value of the well band gap.

In order to analyze donor, acceptor, and excitonic states in quantum-dot quantum wells, Coulomb potential energy of interaction between charges for a multi-layer spherical structure has been derived. The donor and acceptor energy spectra have been obtained for a typical CdS/HgS/CdS/H₂O quantum-dot quantum well as a function of the impurity position. It has been shown that all donor energy levels do not practically depend on the impurity position when the impurity is inside the quantum dot. A strong decrease of the absolute value of acceptor ground state energy has been found when the acceptor is near HgS layer. The donor is mainly concentrated in the CdS core even if the impurity is located in the HgS layer. The acceptor is almost entirely localized in the closest to the impurity region of the HgS layer.

Excitonic states and absorption spectrum for a typical CdS/HgS/CdS/H₂O quantum-dot quantum well have been obtained. To find the fine structure of excitonic spectrum, which is important for the analysis of the absorption spectrum, in addition to electron-hole Coulomb interaction, electron-hole exchange interaction has been taken into account. It is shown that four lowest exciton states in the spherical quantum-dot quantum well are passive. Frölich-like Hamiltonian of exciton-phonon interaction, adapted for multilayer spherical quantum dots has been used to calculate the absorption spectrum. It is demonstrated that within the nonadiabatic theory, phonon-assisted contributions to the absorption spectrum are much larger than those given by the adiabatic approximation. In the adiabatic approximation, the one-phonon sidebands appear only for optically allowed transitions. As distinct from that, in the nonadiabatic theory, the one-phonon sidebands appear for both allowed and forbidden exciton transitions.

The multi-band theory of electron, hole, and exciton states in spherical and tetrahedral CdS quantum dots has been developed. Exciton energy spectra have been calculated using the Coulomb potential energy of the electron-hole system accounting for the dielectric mismatch between the quantum dot and the surrounding medium as well as for the self-action energy of an electron and a hole. The finite difference method and the scalability of the corresponding differential equations have been employed to calculate the size-dependence of electron, hole, and exciton states as well as potential energies

and oscillator strengths in quantum dots of arbitrary shape in the infinite confinement approximation for the charge carriers.

In contrast to spherical quantum dots, lowest electron-hole pair energies in tetrahedral quantum dots are optically active. Unlike electron-hole pair levels, exciton energy levels in spherical and tetrahedral quantum dots have many similar features. For example, exciton ground states in a tetrahedral quantum dot of any size and in a spherical quantum dot of almost any radii are optically active. The ground states in both quantum dots have large oscillator strengths, which are practically unchanged with varying the quantum dot size.

The dielectric mismatch at the CdS/H₂O boundary leads to the enhancement of the exciton binding energy by a factor of about two in both spherical and tetrahedral quantum dots. Calculated exciton ground state energies for spherical and tetrahedral CdS quantum dots have been compared with the results obtained in recent theoretical and experimental studies. A satisfactory agreement with the experimental data has been found. A clear distinction in the optical properties of tetrahedral and spherical quantum dots has been revealed. Therefore, the real shape of quantum dots and the dielectric mismatch at the quantum dot boundary are essential for theoretical interpretation of exciton optical spectra.

Investigation of confinement, strain, and piezoelectric field effects on optical spectrum of GaN quantum dots has been carried out on the basis of our multi-band theory. To separate the effects and elucidate their relative strengths, we have considered four different types of GaN quantum dots, which have been reported in literature. We have shown that the interplay of quantum confinement and piezoelectric field allows one to fine-tune the energy and strength of optical transitions in GaN quantum dots by smart choice of crystallinity, shape, and interface of the quantum dots.

The principle results of the thesis were published in the papers:

1. V. A. Fonoberov and E. P. Pokatilov, "Size-Quantized Electron States in Rectangular Quantum Dot" (in Russian), *Rezumatele comunicărilor* (Conferința științifică studentească, Ediția a III-a, Universitatea de Stat din Moldova, April 7-10, 1998), p. 60 (1998). – **Awarded with the 3rd prize.**
2. E. P. Pokatilov, S. N. Balaban, V. A. Fonoberov, and V. M. Fomin, "Electron States in an Array of Rectangular Quantum Wires", *Verhandlungen der Deutschen Physikalischen Gesellschaft* **34**, p. 718 (1999) [Spring meeting of the German Physical Society, Münster, Germany, March 22-26, 1999].
3. V. A. Fonoberov and E. P. Pokatilov, "Electron States in Rectangular Quantum Well Wires (Single Wires, Finite and Infinite Lattices)" (in Russian), *Rezumatele comunicărilor* (Conferința științifică studentească, Ediția a IV-a,

Universitatea de Stat din Moldova, April 28 - May 3, 1999), p. 56 (1999). – **Awarded with the 1st prize.**

4. V. A. Fonoberov, “Electron States in Rectangular Quantum Well Wires (Single Wires, Finite and Infinite Lattices)” (in Russian), *Anale Științifice ale Universității de Stat din Moldova* (Seria “Lucrări Studentești”, Chișinău, 1999), pp. 141-146 (1999).

5. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, S. N. Klimin, and J. T. Devreese, “Exciton and Impurity Energy Spectrum in Quantum Dot Quantum Wells”, *Bulletin of American Physical Society* **45**, p. 988 (2000) [March Meeting of the American Physical Society, Minneapolis, Minnesota, March 20-24, 2000].

6. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, S. N. Balaban, and D. L. Nica, “Exciton and Impurity States in Rectangular Quantum Well Wires”, *Verhandlungen der Deutschen Physikalischen Gesellschaft* **35**, p. 501 (2000) [Spring meeting of the German Physical Society, Regensburg, Germany, March 27-31, 2000].

7. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, and S. N. Balaban, “Edge States in the Lattice of Rectangular Quantum Well Wires”, *Verhandlungen der Deutschen Physikalischen Gesellschaft* **35**, p. 516 (2000) [Spring meeting of the German Physical Society, Regensburg, Germany, March 27-31, 2000].

8. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, S. N. Klimin, and J. T. Devreese, “Exciton and Impurity Energy Spectrum in Quantum Dot Quantum Wells” (in Russian), *Rezumatetele comunicărilor în științe fizico-matematice* (Conferința a corpului didactico-științific ale Universității de Stat din Moldova, September 27 - October 2, 2000), pp. 208-209 (2000).

9. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, S. N. Balaban, and D. L. Nica, “Exciton and Impurity States in Rectangular Quantum Well Wires” (in Romanian), *Rezumatetele comunicărilor în științe fizico-matematice* (Conferința a corpului didactico-științific ale Universității de Stat din Moldova, September 27 - October 2, 2000), pp. 210-211 (2000).

10. E. P. Pokatilov, V. A. Fonoberov, S. N. Balaban, and V. M. Fomin, “Electron States in Rectangular Quantum Well Wires (Single Wires, Finite and Infinite Lattices)”, *Journal of Physics: Condensed Matter* **12**, pp. 9037-9052 (2000).

11. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, and J. T. Devreese, “Development of an Eight-Band Theory for Quantum Dot Heterostructures”, *Physical Review B* **64**, 245328 (2001) (16 pages) [cond-mat/0109275].

12. E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, and J. T. Devreese, “Electron and Hole States in Quantum Dot Quantum Wells within a Spherical

Eight-Band Model”, *Physical Review B* **64**, 245329 (2001) (7 pages) [cond-mat/0109277].

13. V. A. Fonoberov, E. P. Pokatilov, and A. Balandin, “Excitonic States in Self-Assembled GaN/AlN Quantum Dots”, *Proceedings of the 44th Electronic Materials Conference* (Santa Barbara, California, June 26-28, 2002), p.72 (2002).

14. V. M. Fomin, V. A. Fonoberov, E. P. Pokatilov, and J. T. Devreese, “Theory of excitons in semiconductor quantum dots”, *Program and Abstracts of the 5th International Conference on Excitonic Processes in Condensed Matter EXCON’02* (Darwin, Australia, July 22-26, 2002), p. 416 (2002) **(Invited)**.

15. V. M. Fomin, V. A. Fonoberov, E. P. Pokatilov, J. T. Devreese, “Electronic Structure of Quantum-Dot Quantum-Well Semiconductor Heterostructures”, *Abstracts of the 26th International Conference on the Physics of Semiconductors* (Edinburgh, UK, July 29 - August 2, 2002), Part III, p. 262 (2002).

16. V. A. Fonoberov, E. P. Pokatilov, and A. A. Balandin, “Exciton States and Optical Transitions in Colloidal CdS Quantum Dots: Shape and Dielectric Mismatch Effects”, *Physical Review B* **66**, 085310 (2002) (13 pages). – **Selected for the Virtual Journal of Nanoscale Science & Technology 6 (9) 2002.**

17. V. M. Fomin, V. A. Fonoberov, E. P. Pokatilov, J. T. Devreese, “Electronic Structure and Optical Properties of Quantum-Dot Quantum-Well Semiconductor Heterostructures”, *Book of Abstracts of XVI Jahn-Teller Conference* (Leuven, Belgium, August 26 - September 1, 2002), p. 40 (2002).

18. V. A. Fonoberov, “Single Particle States in Quantum Dot Quantum Wells within a Symmetrized Eight-Band Model”, *Anale Științifice ale Universității de Stat din Moldova* (Seria “Științe fizico-matematice”, Chișinău, 2002), pp. 152-158 (2002).

19. V. A. Fonoberov, “Impurity States in Quantum Dot Quantum Wells within a Symmetrized Eight-Band Model”, *Anale Științifice ale Universității de Stat din Moldova* (Seria “Științe fizico-matematice”, Chișinău, 2002), pp. 159-165 (2002).

20. V. A. Fonoberov, E. P. Pokatilov, and A. A. Balandin, “Interplay of Confinement, Strain, and Piezoelectric Effects in Optical Spectrum of GaN Quantum Dots”, *Journal of Nanoscience and Nanotechnology* (in review, submitted November 2002).

Summary

of the thesis “Electronic and Optical Properties of Semiconductor Quantum Wires and Dots”*

presented by Vladimir Fonoberov for the competition of Ph.D. degree in
Physical and Mathematical Sciences

The eight-band theory, which takes into account coupling between two electron bands, two heavy-hole bands, two light-hole bands, and two spin-orbit split-off hole bands around the Γ point of the Brillouin zone of common semiconductors, is adapted for an arbitrary three-dimensional quantum heterostructure using the envelope-function representation. It is proven that for quantum-wire and quantum-dot heterostructures with (i) noticeably different effective-mass parameters of constituent materials, (ii) thin hetero-layers, and (iii) narrow-bandgap semiconductor constituents, the derived eight-band theory represents the most effective tool and the only accurate method, within the envelope-function representation, for the adequate description of electronic and optical properties of such heterostructures. Using the developed eight-band theory and its particular cases with smaller number of bands, electronic and optical properties of (i) single and multiple rectangular quantum wires, (ii) spherical quantum-dot quantum wells, (iii) spherical and tetrahedral colloidal quantum dots, and (iv) GaN quantum dots of different shapes and crystallinity have been investigated in detail. A number of other scientific findings, such as appearance of edge states in the finite lattice of quantum wires, necessity of the nonadiabatic theory for the description of optical transitions in quantum-dot quantum wells, importance of the shape and environment for colloidal quantum dots, and the key role of piezoelectric effects for hexagonal GaN quantum dots, are made. The most powerful support for the developed here theory is the fact that it agrees very well with all present-day experimental data available for quantum wires and quantum dots.

* Translation of the thesis from Romanian into English is available at
<http://www.ee.ucr.edu/~vladimir/PhDThesis.pdf>

Аннотация

диссертации “Электронные и оптические свойства полупроводниковых квантовых нитей и точек”

представленной Владимиром Фоноберовым на соискание учёной степени кандидата физико-математических наук

Используя представление огибающих функций, восьмизонная теория, учитывающая связь между двумя зонами электрона, двумя зонами тяжелой дырки, двумя зонами лёгкой дырки и двумя зонами спин-орбитально отщеплённой дырки в окрестности Γ точки зоны Бриллюэна обычных полупроводников, адаптирована к произвольной трёхмерной квантовой гетероструктуре. Доказано, что для квантово-нитевых и квантово-точечных гетероструктур с (i) заметно различными параметрами эффективной массы составляющих материалов, (ii) тонкими гетерослоями и (iii) узкозонными полупроводниковыми составляющими, выведенная восьмизонная теория представляет собой самый эффективный инструмент и единственный точный метод, в рамках представления огибающих функций, для адекватного описания электронных и оптических свойств подобных гетероструктур. Используя развитую восьмизонную теорию и её частные случаи с меньшим количеством зон, детально исследованы электронные и оптические свойства (i) отдельных и многократных прямоугольных квантовых нитей, (ii) сферических квантово-точечных квантовых ям, (iii) сферических и тетраэдрических коллоидных квантовых точек и (iv) GaN квантовых точек с различной формой и кристалличностью. Сделано некоторое количество других научных находок, таких как появление краевых состояний в конечной решётке из квантовых нитей, необходимость неадиабатической теории для описания оптических переходов в квантово-точечных квантовых ямах, важность формы и окружающей среды для коллоидных квантовых точек и ключевая роль пьезоэлектрических эффектов для гексагональных GaN квантовых точек. Самой сильной поддержкой развитой здесь теории является тот факт, что она прекрасно согласуется со всеми современными экспериментальными данными, имеющимися в распоряжении для квантовых нитей и квантовых точек.