Physica B 413 (2013) 73–81

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Virtual-bound, filamentary and layered states in a box-shaped quantum dot of square potential form the exact numerical solution of the effective mass Schrödinger equation

A. Luque *, A. Mellor, I. Tobías, E. Antolín [1], P.G. Linares, I. Ramiro, A. Martí

Instituto de Energía Solar, Universidad Politécnica de Madrid, Spain

ARTICLE INFO

Article history:
Received 31 October 2012
Received in revised form
7 December 2012
Accepted 21 December 2012
Available online 4 January 2013

Keywords:
Quantum dots
Energy spectrum
Modeling

ABSTRACT

The effective mass Schrödinger equation of a QD of parallelepipedic shape with a square potential well is solved by diagonalizing the exact Hamiltonian matrix developed in a basis of separation-of-variables wavefunctions. The expected below bandgap bound states are found not to differ very much from the former approximate calculations. In addition, the presence of bound states within the conduction band is confirmed. Furthermore, filamentary states bounded in two dimensions and extended in one dimension and layered states with only one dimension bounded, all within the conduction band—which are similar to those originated in quantum wires and quantum wells—coexist with the ordinary continuum spectrum of plane waves. All these subtleties are absent in spherically shaped quantum dots, often used for modeling.

1. Introduction

Quantum dots (QDs) are mesoscopic structures for which ab initio modeling, often used for bulk crystals, is difficult to apply [1] because they require extensive utilization of computational resources. The k·p method may [2–4] provide a procedure for dealing approximately with these problems. However, this method can also be very costly in the use of computational resources [5] when considering mesoscopic structures. Although the cooperation of specialists in quantum calculations and device technology is very desirable, and is sometimes achieved [6,7], the development of simple models, easier to use by experimentalists assists technological progress effectively.

In this regard, the use of the effective mass approximation (actually a 1-band variant of the k·p method) may be interesting for devices where the optical interaction between the QD bound states and the conduction band (CB) is essential. This is, among others, the case for intermediate band solar cells (IBSC) [8–11] and QD infrared photodetectors [12,13].

The simplicity of the model is still increased, and widely used, if square well potentials are considered. These potentials are usually the band offset (corrected by strain) between the different semiconductors forming the nanostructure, which for this purpose are considered of sharp edges. In this paper we want to show how despite this simplicity the solutions can present high complexity whose full discussion is facilitated by the simplicity of the basic model. In particular we want to show the appearance in QDs of virtual bound states (confined states within the CB) already discussed by several authors [5,14–16], filamentary and layered states.

In this context, QDs have often been modeled as spherical potential wells [17,18], in particular when the actual QDs have this shape. Spherical symmetry has also been used to determine the optimal size of the QDs in IBSC [19] in which the electron confinement was produced by the band offset. Since the spherical geometry permits analytical solutions which are textbook exercises in quantum mechanics [20], it has also been used even if the symmetry was known not to be spherical [21,22]. However, in many other cases, and in particular when the QDs are grown by molecular beam epitaxy (MBE) in the Stranski-Krastanov mode, e.g., in the commonly used InAs QDs grown in GaAs, the QDs take the shape of short quadrangular truncated pyramids that may be approximated as a parallelepipedic box [23–27] (of dimensions $2a \times 2a \times 2c$ in this paper).

The use of the box shape in the QD allows approximate solution of the time independent Schrödinger equation (TISE) by separation-of-variables: the eigenfunctions—$\Phi(x,y,z)=\xi(x)\psi(y)\zeta(z)$—are the product of three one-dimensional functions, each one being eigenfunctions of a one-dimensional Hamiltonian, in which the QD is characterized by a square potential well.

This model is useful not only to describe the CB electrons but also to determine, by application of the appropriate effective masses and band offsets, the energies of VB electrons in all the

* Corresponding author. Tel.: +34 913367229; fax: +34 915446341.
E-mail addresses: a.luque@upm.es, luque@ies-def.upm.es (A. Luque).
[1] Currently at: Instituto de Microelectrónica de Madrid (CSIC).

0921-4526/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.12.047

three bands (heavy holes, light holes and split-off band) [27] that characterize these electrons. For the CB, the method provides a reasonable approximation of the eigenfunctions and thus it can be directly applied (much more easily than in spherical symmetry) to the determination of the intraband photon absorption matrix elements [25,26,28]. In the case of the VB, a four-band k·p solution, still based in the box shaped symmetry, is necessary [27,29] for determination of the eigenfunctions and the interband absorption coefficient.

However, the separation-of-variables solutions are only an approximation [25]. In this paper we shall use these solutions as a basis for the development of the described Hamiltonian so obtaining the exact eigenvalues and eigenfunctions; exact, of course, in the limits of our geometrical description of the QD, its square potential and in the frame of the one-electron treatment and the effective mass approximation.

Section 2 presents the exact Hamiltonian we want to solve and describes how it is modified to accept separation-of-variables solutions. A perturbation Hamiltonian is then defined that transforms the latter into the former. Section 3 analyzes the nature of the eigenvectors and eigenvalues, describing the modalities of the discrete spectrum and the different continua spectra found and finally calculates the eigenfunctions and eigenvectors for each modality. Section 4 studies the density of states associated to each discrete or continuum spectrum modality. Section 5 compares the spherical symmetry solutions to the box shaped symmetry used in this paper. Finally Section 6 draws some conclusions.

2. The exact and separation-of-variables potentials

2.1. The Schrödinger equation

The time-independent Schrödinger equation (TISE) is

$$\frac{\hbar^2}{2m^*}\frac{\nabla^2\Psi}{\Psi}+E=V(\boldsymbol{r}) \tag{1}$$

where the right side term is the band edge position (with changed sign if it refers to holes). The asterisk indicates that an effective mass is used. The energy origin is arbitrary and for the calculations the zero is set at the bottom of the potential well inside the QD (which is at the dot material conduction band edge) and U outside it. In symbolic language ($\forall$=for all, $\wedge$=and, $\vee$=or),

$$V(\boldsymbol{r})=\begin{cases} 0\ \forall\ \ |x|<a\wedge|y|<a\wedge|z|<c \\ U\ \ \forall\ \ |x|\geq a\vee|y|\geq a\vee|z|\geq c \end{cases} \tag{2}$$

However, for presentation purposes, the zero shall be set at the barrier material conduction band edge, which means that U must be subtracted from all the energy results. The reason for taking the origin of potential at the QD CB bottom is explained in the two following sections.

2.2. One dimensional solutions

The functions $\xi(x)$, $\psi(y)$, $\zeta(z)$ are defined by

$$\frac{\hbar^2}{2m^*}\frac{d^2\xi/dx^2}{\xi}+E_x=\begin{cases} 0 & \forall|x|<a \\ U & \forall|x|\geq a \end{cases} \tag{3}$$

and similarly for $\psi(y)$, $\zeta(z)$ (in the latter case using c instead of a as the well boundary).

The position of the origin of potential at the QD CB bottom is common in textbooks for one dimensional square potential wells. It also fits with our choice in the last section.

Finding the solutions for $\xi(x)$ (or for $\psi(y)$, $\zeta(z)$) constitutes a simple exercise of differential equations. In this context, a discussion is provided e.g. in [25]. For $E<U$ (the subindex x is dropped in this subsection) bounded solutions, different from the trivial $\xi(x)\equiv 0$, are even ($\cos(kx)$) or odd ($\sin(kx)$)harmonic functions inside the well flanked by fading exponential functions outside it ($\exp(-\kappa x)\ \forall\ x\geq a$). Solutions may only exist for certain values of the wavenumber k_n for which the non-fading exponential solution is canceled. The energy E_n, fading coefficient κ_n and k-values are related by

$$E_n=\hbar^2k_n^2/2m^*=U-\hbar^2\kappa_n^2/2m^* \tag{4}$$

The index n denotes the different permitted energies in increasing order. It is a quantum number (QN). Odd QNs correspond to even functions and vice versa.

Table 1 presents the values of k for the different QNs and the one-dimensional energy. The CB offset and QD dimensions are those in [28] and are derived from the data of a prototype IBSC in [30] (sample SB).

Although the effective mass is different for the dot (InAs) and barrier (GaAs) material, we use the dot material value across this paper. A straightforward modification of Eq. (1) where m^* is position-variable would lead to a non-hermitical Hamiltonian [31]. There are several possible modifications but their discussion are beyond the scope of this paper. This effective mass choice is accurate for low QNs and less so for the extended states to be studied below, but still very meaningful qualitatively.

For $E\geq U$, the solution is harmonic with wavenumber k inside the potential well and also harmonic, even or odd, outside it but with a different value of the wavenumber k_e and a phase term. That is, they are of the form $\cos(k_ex-\theta)$ or $\sin(k_ex-\theta)$. Details can be found, e.g. in [28]. In this case,

$$E_n=U+\hbar^2k_e^2/2m^*=\hbar^2k^2/2m^* \tag{5}$$

and

$$\begin{aligned}(k_e/k)\cot(ka)&=\cot(k_ea-\theta)\\ (k_e/k)\tan(ka)&=\tan(k_ea-\theta)\end{aligned} \tag{6}$$

respectively for the even and odd functions.

For $E\geq U$, k_e can take any value and therefore it leads to a continuum spectrum of energies. Since the mathematics of continuum spectra is rather complicated, it is common to assume that the wavefunctions are restricted to a large but finite region (a segment of length $2L$, with large L, for one-dimensional cases, or a big parallelepiped for three-dimensional ones) and assume periodic conditions there. This leads [28] to

$$k_eL-\theta=\tilde{n}\pi/2 \tag{7}$$

where $\tilde{n}$ is an integer, odd for the even solutions and even for the odd solutions.

Neglecting the variation of θ the permitted values of k_{ex} are separated $\Delta k_e\cong\pi/2L$ that is small as long as L is big (with respect to a or c). However, only a numerable set of k_e-values are now permitted and the new QN, $\tilde{n}$, has now appeared.

Table 1
Values of k (multiplied by the potential well half-width) and one-dimensional energy for the CB offset and QD dimensions in [28]. Energies are with respect to the barrier material CB bottom.

n	x-,y-eigenfunctions				z-eigenfunctions	
	1	2	3	4	1	2
$k_{\times}a$, k_zc	1.299	2.579	3.806	4.810	0.968	1.695
E_0 (eV)	−0.439	−0.338	−0.180	−0.0045	−0.338	−0.059

U=0.473 eV; m^*=0.0294m_e; a=8 nm; c=3 nm.