



PII: S0038-1098(97)00196-8

THE SELF-CONSISTENT ELECTRONIC STRUCTURE OF SPHERICAL SEMICONDUCTOR QUANTUM DOTS INCLUDING BOUND AND FREE STATES

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(Received 21 March 1997; accepted 7 January 1997 by R. T. Phillips)

A self-consistent procedure for calculating the energy structure, wave functions and charge distribution in spherically symmetric semiconductor quantum dots is presented, that takes account of both bound and free electron states. The Schrödinger and Poisson equation are solved iteratively while using the Morse-type parametrized potential to keep the charge neutrality in each iterative step. Numerical calculations performed for $GaAs-Al_{0.3}Ga_{0.7}As$ based quantum dot indicate that bound states account for most of the charge accumulated in the dot, while including the free states is necessary only at larger doping levels to describe the depleted region outside the dot. ©1997 Elsevier Science Ltd

Keywords: A. nanostructures, A. quantum wells, D. electronic states (localized)

1. INTRODUCTION

Semiconductor quantum dots are attracting continuous research attention, particularly boosted in recent years by successes in self-organized growth of dots (e.g. Ref. [1,2]) and by the perspective development on quantum dot based single electron devices. Electronic structure of quantum dots has been considered by methods of various levels of sophistication, e.g. within simple [3] or multiband [4] effective mass approximation, etc. In some calculations the self-consistent effects of the accumulated electronic charge of bound states has also been taken into account [5,6]. However, free electronic states were not given much consideration, with the exception of non-self-consistent calculation in Ref. [7]. In analogy to the more conventional quantum well structures [8] one may expect that free electronic states in dot may also become very important in some phenomena or applications of quantum dots. Here we present a self-consistent procedure for calculating the energy structure and charge distribution in quantum dots, taking account of both the bound and free states. We choose the spherically symmetric geometry to enable the analyticity of the procedure as much as possible.

2. THEORETICAL CONSIDERATIONS

Consider a spherically symmetric quantum dot with radius R_0 embedded in bulk of another semiconductor. The envelope wave function may be written as a product of radial $R_\ell(r)$ and angular $Y_{\ell m}(\theta, \varphi)$ parts, where the former should be determined from the self-consistent procedure. Introducing, as usual, the function $\phi_\ell(k, r) = R_\ell(k, r)/r$, the effective mass Schrödinger equation that accounts for the radially dependent effective mass $m(r)$ reads

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{1}{m(r)} \frac{d}{dr} \left(\frac{\phi_\ell(k, r)}{r} \right) \right] - \frac{\ell(\ell+1)}{r^3} \frac{\phi_\ell(k, r)}{m(r)} + \frac{2}{\hbar^2} [E - U(r)] \frac{\phi_\ell(k, r)}{r} = 0 \quad (1)$$

where ℓ is the orbital quantum number, $U(r)$ the potential energy (including the built-in and the space charge electrostatic potential), and the constant k is related to energy $E = \frac{\hbar^2 k^2}{2m_b}$, with m_b denoting the effective mass in bulk. The boundary condition for the function $\phi_\ell(k, r)$, in the center of the structure is [9] $\lim_{r \rightarrow 0} (2\ell + 1)!! r^{-\ell-1} \phi_\ell(k, r) = 1$, i.e. $\phi_\ell(k, r \rightarrow 0) \rightarrow 0$. Far from the dot, where the potential is essentially constant (and taken to be zero), $\phi_\ell \sim e^{-kr}$ for bound and $\phi_\ell \sim$

$\sin(kr - \frac{\ell\pi}{2} + \delta_\ell(k))$ for free states. Accordingly, it is convenient to introduce a new function $F_\ell(k, r)$ related to $\phi_\ell(k, r)$ as $F_\ell(k, r) = \phi_\ell(k, r)e^{kr}$ for bound states, and $\phi_\ell(k, r) = \text{Im}[e^{-i(kr - \frac{\ell\pi}{2} + \delta_\ell(k))} F_\ell(k, r)]$ for free states, for which $F_\ell(k, r \rightarrow +\infty) = 1$ and $\frac{dF_\ell(k, r \rightarrow +\infty)}{dr} = 0$.

In the case of bound states the differential equation for $F_\ell(k, r)$ inside the dot (effective mass m_b), reads

$$\frac{d^2 F_{1\ell}}{dr^2} - 2k \frac{dF_{1\ell}}{dr} + \left[\left(1 - \frac{m_w}{m_b}\right) k^2 - \left(\frac{2m_w}{\hbar^2} U(r) + \frac{\ell(\ell+1)}{r^2}\right) \right] F_{1\ell} = 0 \quad (2)$$

and in the bulk ($r > R_0$) it has the form

$$\frac{d^2 F_{2\ell}}{dr^2} - 2k \frac{dF_{2\ell}}{dr} - \left(\frac{2m_b}{\hbar^2} U(r) + \frac{\ell(\ell+1)}{r^2}\right) F_{2\ell} = 0. \quad (3)$$

where the bound state energy is $E = -\frac{\hbar^2 k^2}{2m_b}$ with k real. Except for continuity at $r = R_0$, $F_\ell(k, r)$, has to satisfy

$$\frac{dF_{1\ell}(k, r = R_{0-})}{dr} = \frac{m_w}{m_b} \frac{dF_{2\ell}(k, r = R_{0+})}{dr} + \left(1 - \frac{m_w}{m_b}\right) \left(k + \frac{1}{R_0}\right) F_{2\ell}(k, r = R_{0+}). \quad (4)$$

and has to be zero at $r = 0$, which suffices for determination of bound state energies and wave functions. Finally, the normalization constant of $F_\ell(k, r)$ is to be found from the unity-norm condition.

For free state wave functions all the above expressions remain valid upon the substitution $k \rightarrow -ik$, the corresponding energy now being $E = \frac{\hbar^2 k^2}{2m_b}$. The phase shift $\delta_\ell(k)$ is determined from $\phi_\ell(k, r = 0) = 0$ and is given by

$$\tan(\delta_\ell(k)) = -\frac{\text{Im}\{F_{1\ell}(k, r = 0)\}}{\text{Re}\{F_{1\ell}(k, r = 0)\}}. \quad (5)$$

With bound states energies and wave functions of both bound and free states known, one may proceed to find the charge due to all occupied states and the corresponding electrostatic potential. The normalized bound state wave functions, upon taking their moduli squared, and multiplying by the Fermi-Dirac distribution function $f_{FD} = \left[e^{\frac{E_i - E_F}{k_B T}} + 1 \right]^{-1}$, are directly applicable for calculating the electron density on bound states, via

$$n_b(r) = \frac{1}{2\pi} \sum_{\ell=0}^{\ell_{\max}} (2\ell+1) \sum_{i=1}^{N_b(\ell)} |R_{i,\ell}(r)|^2 f_{FD}(E_i). \quad (6)$$

where $N_b(\ell)$ denotes the number of bound states for any particular value of ℓ , and the factor $2(2\ell+1)$,

accounts for spin and magnetic quantum number degeneracy. The functions are taken to be normalized as $\int_0^\infty R_{i,\ell}^2 r^2 dr = 1$.

The expression for free electron density, analogous to (6), depends on the type of free wave function normalization. Here we use the "box" normalization, i.e. take the structure to be embedded in a spherical box (infinite potential), its radius being very large. The continuous spectrum in such case becomes quasi-continuous, i.e., formally very dense discrete. Now, using the procedure described in Ref. [10] we find the electron density on free states

$$n_c(r) = \frac{1}{\pi^2} \sum_{\ell=0}^{\ell_{\max}} (2\ell+1) \int_0^\infty \frac{|\tilde{R}_\ell(k, r)|^2}{e^{\frac{\hbar^2 k^2 - 2m_b E_{Fb}}{2m_b k_B T}} + 1} dk \quad (7)$$

where the properly normalized function $\tilde{R}_\ell(k, r)$ asymptotically behaves as

$$\tilde{R}_\ell(k, r) \sim \frac{1}{r} \sin \left[kr - \frac{\ell\pi}{2} + \delta_\ell(k) \right]. \quad (8)$$

The bulk is taken to be uniformly doped with donors, and degree of their ionization being

$$n_d(r) = \frac{N_d}{1 + 2e^{\frac{(E_{Fb} - E_{Db} - U(r))}{k_B T}}} \quad (9)$$

where N_d , E_{Fb} and E_{Db} denote the donors density, bulk Fermi level and donor ionization energy. Eq. (9) accounts for the influence of the local potential $U(r)$ on the degree of ionization.

In solving the Poisson equation we account for the radial dependence of dielectric permittivity $\epsilon(r)$, which depends on material composition just as does the effective mass. Thus, taking the potential and the field to be zero in the center of the structure, integrating the Poisson equation twice yields the expression for the potential

$$\varphi(r) = \frac{1}{r} \int_0^r \frac{v(v-r)\rho(v)}{\epsilon(v)} dv. \quad (10)$$

where the charge density is $\rho(r) = -e[n_b(r) + n_c(r) - n_d(r)]$.

Within the self-consistent procedure the Schrödinger and Poisson equations are solved iteratively. Somewhat different from the conventional self-consistent procedure we here employed parametrization of the electrostatic (Hartree) potential [11] within each iterative step, which enforces the charge neutrality and contributes to the stability of the procedure. We have taken the three-parameter Morse function (potential)

$$\phi(r - R_0) = \frac{\phi_0}{1 - \beta} \left[e^{-\lambda(r - R_0)} - \beta e^{-2\lambda(r - R_0)} \right],$$

$$r \geq R_0 \quad (11) \quad 3. \text{ NUMERICAL RESULTS AND DISCUSSION}$$

where ϕ_0 represents the potential at the heterointerface ($r = R_0$), while λ and β are related through the conservation of dielectric displacement at the interface:

$$\beta = \frac{\varepsilon_h \lambda V_0 + \varepsilon_w \left. \frac{d\phi_0}{dr} \right|_{r=R_0-}}{2\lambda \varepsilon_h \phi_0 + \varepsilon_w \left. \frac{d\phi_0}{dr} \right|_{r=R_0-}} \quad (12)$$

with $\varepsilon_h(\varepsilon_w)$ denoting the dielectric permittivity of the bulk(dot) material. Therefore, a single free parameter (λ) remains to fit the Morse potential in order to get the global charge neutrality of the structure $\int_0^\infty (n_b(r) + n_c(r) - n_d(r))r^2 dr = 0$, which, in terms of quantities defined above, may be written as

$$\begin{aligned} & \frac{1}{\pi^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \\ & \times \left[\frac{\hbar^2}{4m_b k_B T} \int_0^\infty \frac{\delta_\ell(k) k dk}{\cosh^2\left(\frac{\hbar^2 k^2 - 2m_b E_{Fb}}{2m_b k_B T}\right)} - \frac{\delta_\ell(0)}{1 + e^{-\frac{E_{Fb}}{k_B T}}} \right] + \\ & \frac{1}{2\pi} \sum_{\ell=0}^{\ell_{\max}} (2\ell + 1) \sum_{i=1}^{N_b(\ell)} f_{FD}(E_i) - \int_0^{R-\infty} (n_{cb} - n_d(r))r^2 dr \\ & = 0 \end{aligned} \quad (13)$$

where n_{cb} in the last integral denotes the electron density in the bulk. In case of a quantum well the convenience of the Morse potential stems from the fact that it is a sum of two exponential functions, which enables a rather fast solving of the Schrödinger equation via series expansions [11]. In a quantum dot, however, the presence of the centrifugal potential ($\sim \ell(\ell + 1)/r^2$) does not allow the same method to be employed. Instead, the Morse potential is here used in a different manner. If some i -th iteration has been estimated to have not yet converged, the potential in the bulk region ($r > R_0$) is substituted by the Morse potential with the parameter λ chosen so to satisfy the global neutrality condition (while the potential inside the dot is kept as calculated). The new potential constructed this way is then used, through a weighted average with the potential used in i -th iteration, as the input potential for $(i + 1)$ -th iteration. The iterative procedure (1)-(13) starts with $\varphi(r) \equiv 0$, i.e. the non-self-consistent solution, and is terminated when the self-consistent potential becomes essentially reproduced in subsequent iterations.

Numerical calculations were performed for a *GaAs* dot with the radius $R_0 = 5\text{nm}$ embedded in *Al_{0.3}Ga_{0.7}As* bulk. Based on data in Ref. [12] the following parameters were used in calculation: the effective masses in the dot and bulk materials $m_w = 0.067$ and $m_b = 0.092$ (in free electron mass units), and the dielectric permittivities $\varepsilon_w = 13.18$ and $\varepsilon_b = 12.24$ respectively, the donor binding energy $E_{Dh} = 8.21\text{meV}$ and conduction band offset $\Delta E_c = 227.9\text{meV}$. The Fermi level for a given donor doping level was calculated from Eqn. (9). All the calculations were done for the temperature $T = 300\text{K}$.

To find the energy spectrum Eqs. (2-3) for bound and the corresponding ones for free states were numerically integrated (from the origin to $r = 30\text{nm}$). The employed numerical procedure was very stable and of high accuracy [13]. The charge density was calculated according to (6) and (7). Within the continuous spectrum the energy range included in calculation extended to $E_{\max} = 130\text{meV}$ above the bulk c.b. edge. This was sufficient to cover all significantly populated states while keeping the nonparabolicity low (the largest k -vector amounted to $< 1/20$ of the distance to the Brillouin zone boundaries). Furthermore, only the lowest three orbital terms (with $\ell = 0, 1, 2$) had to be taken into account when evaluating the continuous states charge in the dot region. This is because higher ℓ states experience a strong repulsive core potential, and the corresponding wave functions amplitudes therein are negligible. Actually, the $\ell = 0$ state of the continuum gives by far the largest contribution to free states charge in the dot region. For $\ell > 0$, the significantly populated, low-energy states hardly penetrate into the dot, and those with higher energies are almost empty. They may thus be safely ignored when calculating the charge in the dot region, their only role is to make up the constant charge density deep inside the bulk.

The bound state is well localized in the dot, its population increasing as the doping, i.e., the Fermi level, increases. The contribution of free states to the charge density in the dot region is given in Fig. 1 (actually displayed is the "excess" charge, measured from the normal density deep inside the bulk). There is obviously a depression of this part of the total charge in the dot, for reasons that are clear from the above discussion of the corresponding wave functions properties. As the bulk doping increases this depression becomes more prominent, due to an increased repulsion of these states by the enlarged bound state charge in the dot. As intuitively expected, the free charge depression is strongest in the region close to the dot-bulk

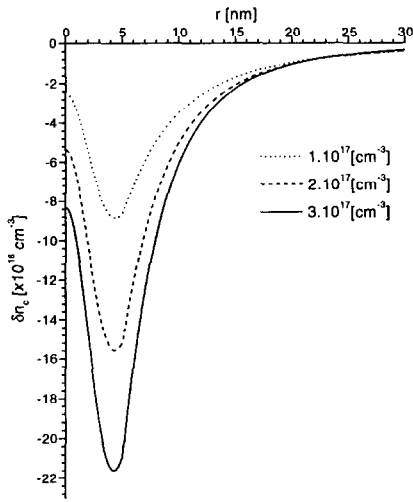


Fig. 1. The self-consistent free electron "excess" density (referenced to the bulk value) in the $R_0 = 5$ nm $GaAs/Al_{0.3}Ga_{0.7}As$ quantum dot structure for different doping levels, at $T = 300$ K.

interface, where the total (electronic + ionized donors) accumulated charge acquires a maximum.

The calculated self-consistent Hartree potential for three values of doping is given in Fig. 2, indicating the increasing importance of the self-consistent calculation as the doping increases. The space charge of free states gives a reasonably large contribution to the Hartree potential, increasing it by approx. 5 meV from what was calculated with free states neglected, and significantly extends its range (Fig. 2). The energy of single bound state (with $\ell = 0$) of this dot is -89.7 meV, -89.5 meV and -90.7 meV at bulk doping levels of $1 \times 10^{17} \text{ cm}^{-3}$, $2 \times 10^{17} \text{ cm}^{-3}$ and $3 \times 10^{17} \text{ cm}^{-3}$ respectively, when measured from the c.b. edge deep in the bulk, while the non-self-consistent value is -116.4 meV. The contribution of free states space charge to this shift of energy is rather small, however, never exceeding 1 meV.

4. CONCLUSION

In conclusion the self-consistent procedure for calculating the electronic structure and charge density in semiconductor quantum dots, taking account of both

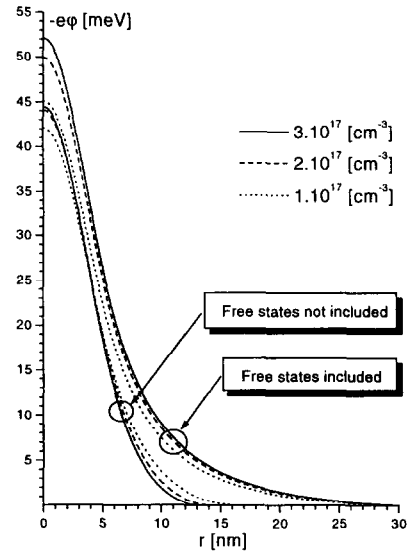


Fig. 2. The self-consistent Hartree potential, with free states charge included or neglected in the quantum dot structure, with parameters as in Fig. 1.

the discrete and continuous parts of energy spectrum is presented. Numerical calculations performed for a $GaAs - Al_{0.3}Ga_{0.7}As$ based quantum dot show that bound state(s) predominantly contribute to the charge in the dot region, while including the free states is necessary only in case of high levels of bulk doping, to get the structure of the depleted region outside the dot, and the free states wave functions therein.

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