Impurities in a quantum dot: A comparative study

F. J. Ribeiro and A. Latgé*
Instituto de Física, Universidade Federal Fluminense, Outeiro de São João Batista s/n, 24020-004 Niterói, Rio de Janeiro, Brazil

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The donor binding energies and density of impurity states of a hydrogenic impurity in a quantum dot are presented within the effective-mass approximation following a variational procedure. The emphasis is placed on the dependence of the binding energy on the volume of the dot and on the impurity position. We show that the results for the donor binding energy in the quantum dot go to the exact limits of a square-cross-sectional quantum-well wire and a quantum well when appropriate limits are considered. Comparing the donor binding energies for cubic and spherical quantum dots, we found that the values are very close provided the dots have similar volumes.

Quantum dots (QD's) are considered nowadays to be the limit of electronic confinement and have been widely studied, since they provide ideal structures to be used in optical-electronic devices and as laser systems. Large changes in the optical absorption and refraction index are predicted for the optical properties of quantum dot structures.[1] Resonances in the characteristic curve (current × voltage) corresponding to the density of states of a zero-dimensional system were reported by Reed *et al.*[2] Hansen *et al.*[3] studied magnetic responses in QD systems and observed the magnetic-field induced bifurcation of quantum levels into surface and bulklike Landau states. Cibert *et al.*[4] presented evidence of quantum confinement by measuring low-temperature cathodoluminescence, which revealed new lines attributed to transitions from ground to excited levels of electrons within QD's. Discrete steps in the gate voltage dependence of the integrated absorption strength were observed by Meurer, Heitmann, and Ploog.[5]

The study of hydrogenic impurity-related properties in low dimensional semiconductor heterostructures has been extensively reported in the last decade.[6–14] Impurities in GaAs-(Ga,Al)As quantum-well wires (QWW's) were also theoretically studied and compared with recent laser-induced photoluminescence measurements on GaAs wire-shaped microcrystals.[6] The binding energies and density of states of shallow impurities in spherical GaAs-(Ga,Al)As QD's have been calculated as a function of the dot radius and the position of the impurity in the dot.[7] Zhu, Xiong, and Gu[8] have shown that the binding energy of a donor in a spherical QD and its maximum are strongly dependent on the barrier height potential. Theoretical and experimental work in semiconducting heterostructures shows that the position of the impurity plays an important role in the determination of optical properties of low-dimensional systems. Although from the mathematical point of view the spherical form is the easier geometry to be taken into account, it does not represent the more realistic realization of the quasi-zero-dimensional quantum system.

In the present work we are concerned with the calculation of the ground-state impurity binding energy and density of impurity states in a cubic GaAs QD. The emphasis here is placed on comparisons between results of the impurity binding energy of donors in cubic and spherical QD's and on recovering previous results obtained in retangular cross-sectional QWW's and quantum wells (QW's) by taking appropriate limits on the QD structure. We show that the impurity binding energies of on-center donors in spherical and cubic quantum dots are very similar provided the structures have the same volume. We have adopted a variational scheme within the effective mass approximation which has been considered an accurate method to determine impurity binding energies.[6,7,9,10]

We consider a quantum dot with lengths equal to L_x, L_y, and L_z. The origin is placed at the center of the dot cross section. The Hamiltonian of a single hydrogenic impurity in the QD within the effective mass approximation is

$$H = \frac{-\hbar^2\nabla^2}{2m^*} - \frac{e^2}{\mathcal{E}_o\sqrt{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2}} + V_b(x,y,z), \tag{1}$$

where m^* is the effective mass, $\mathcal{E}_o$ is the static dielectric constant, and (x_i, y_i, z_i) are the coordinates of the impurity along the quantum dot. The barrier potential $V_b(x,y,z)$ is taken as zero inside the QD and infinite otherwise. The energy levels of the unpertubed QD, i.e., in the absence of the impurity, are given by

$$E_{n,m,l} = (\hbar^2\pi^2/2m^*)[(n^2/L_x^2) + (m^2/L_y^2) + (l^2/L_z^2)], \tag{2}$$

where $n, m, l =$ 1,2,3,..., and the associated envelope function is

$$\Phi_{n,m,l}(x,y,z) = (2\sqrt{2}/\sqrt{L_xL_yL_z})\cos(\pi nx/L_x) \times \cos(\pi my/L_y)\cos(\pi lz/L_z). \tag{3}$$

Within the variational procedure, the trial wave function for the ground state when the impurity is included can be written as

$$\Psi(x,y,z;x_i,y_i,z_i) = N(\lambda;x_i,y_i,z_i)\Phi_{1,1,1}(x,y,z) \times\Gamma(\lambda;x,y,z;x_i,y_i,z_i), \tag{4}$$

for $|x| \le \frac{L_x}{2}$, $|y| \le \frac{L_y}{2}$, and $|z| \le \frac{L_z}{2}$, with λ being a variational parameter, $N(\lambda;x_i,y_i,z_i)$ the normalization factor, and

$$\Gamma(\lambda; x, y, z; x_i, y_i, z_i) = \exp[-\lambda\sqrt{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2}] \quad (5)$$

is the ground-state hydrogeniclike function. The impurity-binding energy $\mathcal{E}_b$ is calculated by means of a standard procedure whereas the energy of the system with the donor impurity, $\langle\Psi|H|\Psi\rangle$, minimized with respect to λ, is reduced from the ground-state energy $E_{1,1,1}$. The impurity-binding energy is given by

$$\mathcal{E}_b = -(\hbar^2\lambda^2/2m^*) + (e^2 I_1/\mathcal{E}_o I_2), \quad (6)$$

with

$$I_1 = \int_{-L_x/2}^{L_x/2} \cos^2\frac{\pi x}{L_x}\,dx \int_{-L_y/2}^{L_y/2} \cos^2\frac{\pi y}{L_y}\,dy \int_{-L_z/2}^{L_z/2} \times \cos^2\frac{\pi z}{L_z} \frac{\Gamma^2(\lambda, x, y, z; x_i, y_i, z_i)}{\sqrt{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2}}\,dz, \quad (7)$$

and

$$I_2 = \int_{-L_x/2}^{L_x/2} \cos^2\frac{\pi x}{L_x}\,dx \int_{-L_y/2}^{L_y/2} \cos^2\frac{\pi y}{L_y}\,dy \int_{-L_z/2}^{L_z/2} \times \cos^2(\pi z/L_z)\Gamma^2(\lambda, x, y, z; x_i, y_i, z_i)\,dz. \quad (8)$$

Both expressions were calculated numerically.

If the quantum dot volume is not too small, one may treat the impurity position as a continuous random variable and, provided that there is no intentional doping, define a density of impurity states[9] per unit energy, $g_{L_x,L_y,L_z}(E_i)$, as

$$g_{L_x,L_y,L_z}(E_i) = \frac{1}{L_x L_y L_z}\int_{S(E_i)} \frac{dS}{|\nabla(E_i)|}, \quad (9)$$

where $S(E_i)$ is the surface of constant energy $E = E_i$ and ∇ means the gradient with respect to the impurity position. In the case of a cubic GaAs, the density of impurity states was obtained via a histogram method[10] for a mesh of points uniformly distributed inside the irreducible part of the cubic QD. All the results are presented in reduced atomic units (a.u.*) which correspond to a length unit of an effective Bohr radius $a^* = \hbar^2\mathcal{E}_o/m^*e^2$, and an effective Rydberg, $R^* = m^*e^4/2\hbar^2\mathcal{E}_o^2$. For donor impurities in a GaAs QD these units correspond to $a^* \simeq 100$ Å and $R^* \simeq 5.72$ meV.

The binding energies of an on-center donor in a cubic GaAs QD ($L_x = L_y = L_z = L$) as a function of the length L are presented in Fig. 1(a). As expected, the values of the impurity binding energies are higher in the case of donors in quasi-zero-dimensional QD's than in the quasi-two and -one-dimension systems (QW's and QWW's). Moreover, if we compare our results for the donor binding energy of the cubic quantum box with those obtained for donors in a spherical GaAs quantum dot,[7] for the case of on-center donors, we conclude that both energy values are very close provided both structures have similar volumes [see Fig. 1(b)]. This is in agreement with previous results of impurities in QWW's of distinct geometries, which show that the binding energies of impurities in cylindrical and rectangular quantum-well wires are very similar when the respective cross-sectional areas are comparable.[11] We have also considered the case where the impurity is not at the center of the dot. Figure 1(c) shows the donor binding energy as a function of the impurity position for cubic (solid lines) and spherical (dashed lines) QD's, as a function of the donor position, for two volume values: $1.0a^{*3}$ and $125.0a^{*3}$. For cubic QD's, different impurity positions are considered along

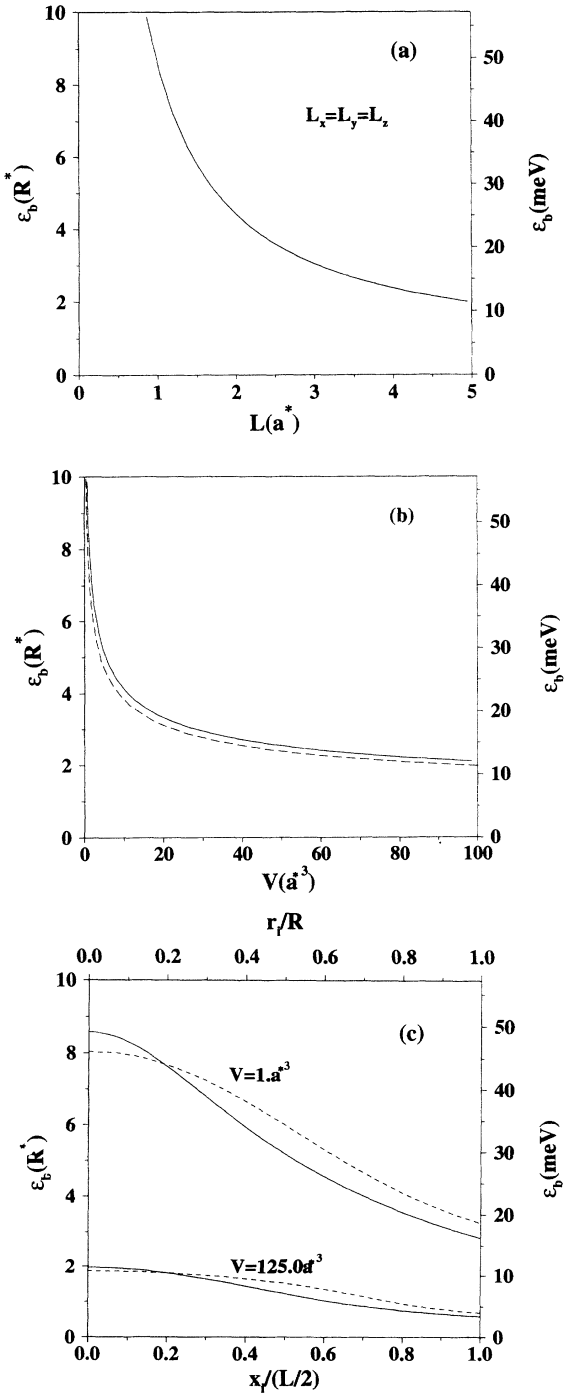

FIG. 1. (a) Binding energies of an on-center donor impurity in a cubic GaAs QD as a function of the QD size. (b) Binding energies of a donor in a cubic GaAs (solid line) and a spherical GaAs (dashed line) QD as a function of the volume (in units of a^{*3}). In both cases the donor is placed at the center of the QD. (c) Binding energies for cubic (solid lines) and spherical (dashed lines) QD's with the same volume V, as a function of the impurity position.

the diagonal of the square cross sectional at $z_i = 0$; this is the suitable direction to compare with the impurity positions r_i inside the spherical dot of radius R. These results show that the impurity-binding energies are not remarkably different for cubic and spherical dots with the same volume even when the impurity is not at the center of the structure. It is also clear that the differences between the energies in the two cases, spherical and cubic dots, reduce as the volume of the system increases, as is expected.

In Fig. 2(a) we present the binding energies of donors in a cubic GaAs quantum box with $L = 100$ Å as a function of the impurity position inside the GaAs structure considering different symmetry lines within the system: along the cube diagonal (curve A), along the diagonal of the square cross section at $z_i = 0$ (curve B), along the diagonal of the cube face ($z_i = L/2$) with $x_i = y_i$ (curve C) and along the cube face ($z_i = L/2$) taking $x_i = 0$ and varying y_i from 0 to $L/2$ (curve D). The dependence of the binding energy on the length L of the cubic GaAs QD for different donor positions is shown in Fig. 2(b) (see inset in the figure for details). When the size of the box is comparable to the extension of the wave function of the bound states ($a^* \simeq 100$ Å), the spread on the binding energy values is very high and, of course, it reduces as the size of the box increases. These results [Figs. 2(a) and 2(b)] are clear evidence of the dependence of the donor binding energy on the impurity position. This effect would be very important in a detailed study of impurity-related optical properties in QD's as has been pointed out in the case of impurities in QW's and QWW's.[6]

In order to compare our results with those obtained for donors in GaAs QW's and rectangular QWW's, we have calculated the binding energy as a function of the impurity position in two limiting situations: (a) when one of the sides of the quantum box is taken to be much larger than the other two, and (b) when two sides are much larger than the third one. This would transform the quasi-zero-dimensional system in a rectangular quantum-well wire and in a single quantum well, respectively. As the length of one of the cube's sides is increased,

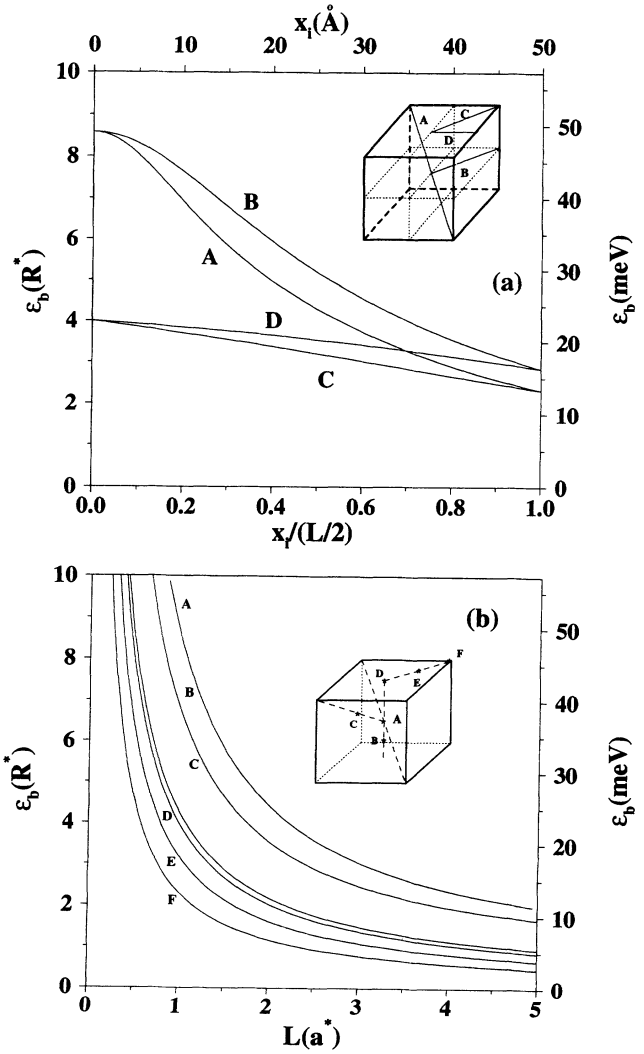

FIG. 2. Binding energies of a donor in cubic GaAs QD (a) as a function of the impurity position and for $L = 100$ Å, along distinct symmetry lines: the cube diagonal (curve A), the diagonal of the square cross section at $z_i = 0$ (curve B), the diagonal of the cube face where $x_i = y_i$ and $z_i = L/2$ (curve C), and the cube face taking $x_i = 0$ and $z_i = L/2$ and varying y_i from 0 to $L/2$ (curve D), and (b) as a function of the size L for distinct impurity positions in the cubic GaAs system.

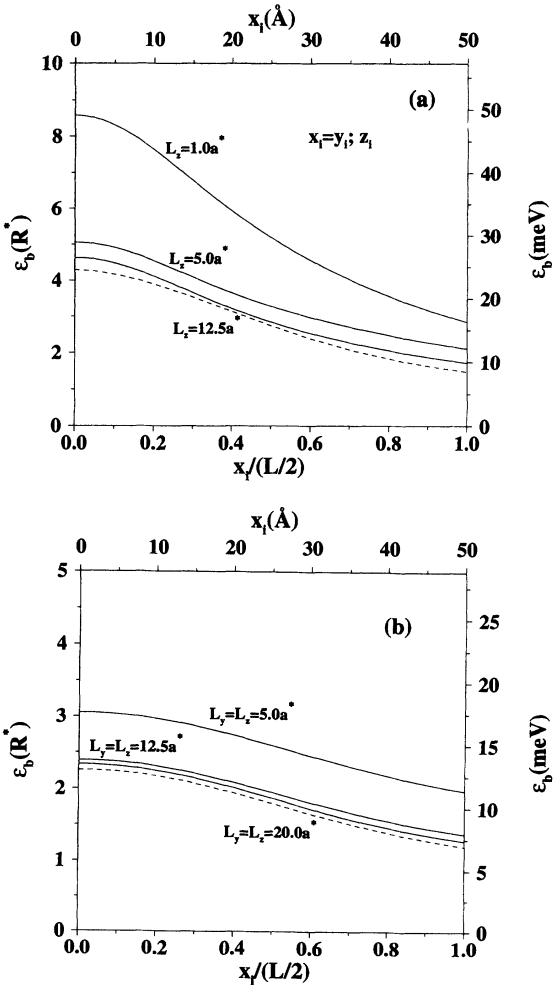

FIG. 3. Binding energies of a donor impurity in a GaAs QD with (a) $L_x = L_y = 1.0a^*$, and $L_z = 1.0a^*$, $5.0a^*$, and $12.5a^*$ (solid curves), as a function of the impurity position; (b) $L_x = 1.0a^*$ and $L_y = L_z = 5.0a^*$, $12.5a^*$, and $20.0a^*$ as a function of the impurity position.

the donor binding energy is reduced until it reaches the QWW value, as can be seen in Fig. 3(a). The three curves correspond to the situation where $L_x = 1.0a^*$, $L_y = 1.0a^*$, and $L_z = 1.0a^*$, $5.0a^*$, and $12.5a^*$. When $L_z = 12.5a^*$, the donor binding energies in the GaAs QD are very close to those obtained for donors in a square cross-sectional quantum-well wire[12] (dashed curve). In Fig. 3(b) we present the donor binding energies for a donor in a GaAs QD with $L_x = 1.0a^*$ and L_y and L_z both equal to $5.0a^*$, $12.5a^*$, and $20.0a^*$ (solid curves). The last one is clearly very close to the results for the binding energy of a donor in a single quantum well (dashed curve).[13]

As the impurity binding energy is a quantity that clearly depends on the impurity position, a knowledge of the detailed shape of the density of impurity states may be relevant for understanding future experimental results on shallow impurities in QD's. As was shown previously,[7] the donor impurity density of states for a spherical GaAs QD with small radius ($R = 0.5a^*$) exhibits an important feature at low energies. The results of the impurity density of states for a cubic GaAs with $L = 1.0a^*$ (solid line) and for a spherical GaAs QD with radius equal to $\simeq 0.62a^*$ (dashed line) are shown in Fig. 4. This corresponds to the situation where both structures have the same volume. It is apparent from the results that the two impurity density of states have the same important feature: a peak at lower energies coming from the contribution of impurities near the edge of the small systems, which seems to be a signature of the quasi-zero-dimensional system. For the case of donors in GaAs QW's,[13] the impurity density of states exhibits a double-peaked feature, which shows the importance of both on-center and on-edge impurity positions in the density of states and on the impurity-related optical absorption and photoluminescence spectra.

As the box size is increased we would expect a density of states converging to the bulk value which presents a peak at the energy of an effective Rydberg. However, as a consequence of the high electronic confinement of the quasi-zero-dimensional structure we are concerned with, this limit is reached for a larger value size of the cubic dot ($L > 15.0a^*$), in contrast to the cases of donors in QWW's (Ref. 14) and in QW's.[13]

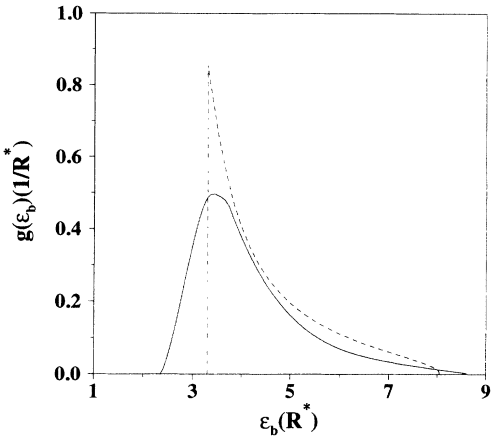

FIG. 4. Density of donor states (in arbitrary units) as a function of the binding energy in a cubic GaAs QD with $L = 1.0a^*$ (solid curve) and in a spherical GaAs QD of radius $0.62a^*$ (dashed curve).

Summing up, we presented a comparison between impurity binding energies and density of states for donors in cubic and spherical QD's. Provided the QD's have similar volumes we have shown that the results for the impurity-binding energies and the shapes of the density of states do not depend on the geometric details of the quantum systems. This is an interesting result, since experimentally the cubic form is more realistic. We have gone beyond the spherical form that has been treated previously.[7] We have also shown that the impurity-binding energy is a physical quantity which is very dependent upon the impurity position in the system. This fact is very important for a correct description of impurity-related absorption and photoluminescence experiments.

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* Electronic address: GFILATG@BRUFF.BITNET

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