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Conduction-band anisotropy effects in spherical semiconductor nanocrystals: a theoretical study

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Abstract

The quantum confinement for a conduction-band electron within a spherical quantum dot is investigated in the framework of the effective-mass approximation. The conduction-band effective-mass anisotropy is fully taken into account. The exact solution for the electronic spectrum is provided, showing how the 'isotropic' mass levels map into the new spectrum which accounts for the anisotropy. The removal of degeneracies typical of the spherical dot, as well as its effects on the infrared transition energies, are discussed.

1. Introduction

The simplest model for studying the quantum confinement of electrons within quantum dots is based on the effective-mass approximation with hard-wall boundary conditions [1, 2]. The electron is treated as a free particle moving within an infinite potential well, with a renormalized mass which accounts for the conduction-band curvature (assumed to be parabolic around its minimum). In the case of a spherical quantum dot, this makes the solution of the Schrödinger equation straightforward, due to the spherical symmetry of the problem which allows one to find the exact quantum confined eigenvalues and eigenfunctions. It is also known that for many semiconductors of interest, like silicon, the bulk conduction band is anisotropic, giving rise to a transverse and a longitudinal effective mass. We want to show that it is possible to account for the band anisotropy and still give an exact solution of the problem. Taking into account the mass anisotropy immediately implies that the 'free'-particle Hamiltonian involved in the calculation becomes anisotropic, lowering the full spherical symmetry.

In previous work [3] it has been shown that quantum confinement within an ellipsoidal quantum dot can be exactly treated within a single-band, effective-mass model. That calculation relies on the separability of the Schrödinger equation for an electron confined within an infinite ellipsoidal well, assuming an isotropic mass. We are going to show that this result can easily be generalized to the case of an anisotropic effective mass, covering, in this case, most of the indirect band gap semiconductors.

It is worth pointing out that, even if the effective-mass Hamiltonian represents the simplest approximation for treating quantum-confined systems, meaningful information on the electronic spectrum of quantum dots can be obtained. It is known to fail for those systems which have dimensions comparable with the bulk material lattice constant, in which case a microscopic description is needed. For large dots the results obtained within such an approach can both qualitatively and quantitatively predict the main physical properties [4, 5].

In section 2 we show how the Schrödinger equation for an anisotropic-mass electron confined within a spherical quantum dot can be solved exactly. A discussion about the energy spectrum and symmetry-related degenerations of the quantum levels is provided. The energies relative to the ground and the first two excited states are calculated as a function of the longitudinal-to-transverse-mass ratio, indicating that they can significantly change with respect to the spherical mass model. Infrared transition energies are discussed as well.

In section 3 we extend the previous description to an ellipsoidal quantum dot, for which the exact solution can be provided if the longitudinal mass lies along the ellipsoid symmetry axis. We exhibit the constant volume ground-state energy, comparing the result with that obtained assuming a spherical mass, shown in [3].

2. The spherical quantum dot

The conduction-band mass anisotropy for semiconductors like silicon is related to the fact that they do not show a single band minimum at the centre of the Brillouin zone. The conduction band actually has six, symmetry-related, equivalent minima located along the $\langle 100 \rangle$ directions of the Brillouin zone. The constant-energy surfaces are ellipsoids of revolution with their major axes located along $\langle 100 \rangle$. Therefore, the parabolic expansion of the band energy around each minimum contains a longitudinal mass m_{l} related to the ellipsoid major axis and two, coincident transverse masses m_{t} corresponding to the ellipsoid minor axes.

The inclusion of the mass anisotropy breaks the spherical symmetry of the dot, making the solution more difficult even in the simplest, hard-wall model. Let us consider a conduction-band electron subject to a given potential $U(\vec{r})$. The single-band, effective-mass Hamiltonian can be written as

$$H = -\frac{\hbar^2}{2}\left[\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} + \frac{1}{m_3}\frac{\partial^2}{\partial x_3^2}\right] + U(\vec{r}) \tag{1}$$

where $x_1 \equiv x, x_2 \equiv y$ and $x_3 \equiv z$. Here, m_i indicates the effective-mass along the ith direction. If the mass tensor were isotropic ($m_1 = m_2 = m_3 = m^*$), this would give rise to a single, sixfold degenerate Schrödinger equation, with all three masses equal. Instead, three twofold degenerate equations are obtained, each one corresponding to the longitudinal mass along the x, y or z directions. The possibility of giving an analytical solution for these equations obviously depends on the boundary condition. The solution will lead to the effective-mass envelope wavefunction.

Let us consider a given choice of the m_i's. The coordinate transformation $x_i' = \sqrt{m_i}x_i$, $i = 1, 2, 3$ reduces the Schrödinger equation associated with the Hamiltonian (1) to an isotropic-mass equation. The boundary conditions as well as the potential $U(\vec{r})$ will transform accordingly.

The hard-wall boundary conditions (namely, $U(\vec{r}) = 0$ inside the dot, $+\infty$ outside) for a spherical quantum dot with radius R correspond to the requirement that the envelope wavefunction is null on the surface with equation

$$x^2 + y^2 + z^2 = R^2. \tag{2}$$

According to the transformation outlined above, this surface is transformed into an ellipsoid, with equation

$$\frac{x'^2}{m_1R^2}+\frac{y'^2}{m_2R^2}+\frac{z'^2}{m_3R^2}=1. \tag{3}$$

Because we are dealing with semiconductors whose constant-energy surfaces around each minimum are ellipsoids of revolution, two of the three masses are the same. This implies that the surface represented by equation (3) is that of an ellipsoid of revolution with semi-axes $a'=b'=R\sqrt{m_t}$ and $c'=R\sqrt{m_l}$. Being $m_l > m_t$, c' represents the ellipsoid major axis. Therefore, the symmetry axis of the surface (3) lies along the direction which the longitudinal effective mass has been associated with. Moreover, its aspect ratio is given by $\chi'=c'/a'=t$, where $t=\sqrt{m_l/m_t}$. The original problem of finding the solutions of the anisotropic equations associated with the Hamiltonian (1) with the isotropic hard-wall boundary condition is therefore transformed into the solution of the isotropic Schrödinger equation with a unit mass

$$-\frac{\hbar^2}{2}\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{\partial^2}{\partial z'^2}\right)\Psi=E\Psi \tag{4}$$

with the condition that the wavefunction is null on the ellipsoidal surface (3). The exact solution of this last problem has been addressed in [3]. Without going through all the mathematics, it is enough to recall here that the dot energy levels can be written as

$$E_{nlm}=\frac{\hbar^2}{2c'^2}\epsilon_{nlm}(\chi')=\frac{\hbar^2}{2m_1R^2}\epsilon_{nlm}(t) \tag{5}$$

where n is a positive integer, $l=0,1,\ldots$ and $m=-l,\ldots,0,\ldots,l$. The important point is that the energy levels can be expressed in terms of the universal function $\epsilon_{nlm}(u)$ which, for the spherical dot, depends only on the longitudinal-to-transverse-mass ratio and on the labels (n,l,m) related to the energy, parity and the angular momentum components along the symmetry axis, respectively. This universal function can be calculated numerically and analytical fits for the ground state $(1,0,0)$ and the excited states $(1,1,0)$ and $(1,1,1)$ are available [6]. It is worth stressing that this picture gives an exact solution for the quantum confinement of a conduction-band electron within a spherical quantum dot, using an effective-mass approach which takes into account a single, anisotropic band. For completeness, we report the analytical fits for the function $\epsilon_{nlm}(t)$, which hold for $1\leqslant t\leqslant 5$ (numerical results are reproduced within 0.4%):

$$\begin{aligned}
\epsilon_{100}(t)&=2.970\,35+6.595\,69(t+0.023\,61)^{1.953\,95}\\
\epsilon_{110}(t)&=11.0548+8.206\,60(t+0.058\,27)^{1.883\,90}\\
\epsilon_{111}(t)&=3.169\,83+15.716\,08(t+0.0416)^{1.975\,43}.
\end{aligned} \tag{6}$$

It is easy to see that the symmetry group for the problem of the spherical dot with anisotropic mass is $D_{\infty h}$, which is the group of homonuclear diatomic molecules [7]. We can therefore label the states using the $D_{\infty h}$ irreducible representations ($\Sigma_g^{\pm}$, Π_g, $\Delta_g\ldots$) instead of (n,l,m) quantum numbers used in our previous works [3, 6]. In this way, for example, the (100), (110) and (111) electronic states correspond, respectively, to $1\Sigma_g^+$, $1\Sigma_u^-$ and $1\Pi_u$. Since the $D_{\infty h}$ irreducible representations are only single or double degenerate and there are six valleys, we expect sixfold (for Σ states) or 12-fold (for Π, $\Delta\ldots$ states) degenerations (being the boundary condition with spherical symmetry, the six Schrödinger equations only differ by a change of the name of two coordinates, leading to the same eigenvalues but with different eigenfunctions).

In figure 1 we show the quantum-confined energies relative to the ground and the first two excited states as a function of t. ϵ_{nlm} is the adimensional function defined in equations (5)

Table 1. The longitudinal-to-transverse-mass ratio for several materials (see footnote 1) with anisotropic conduction bands. The data are taken from [8].

Semiconductor	$t^2 = m_l/m_t$
Si	4.81
GaP	5.50
AlSb	7.13
AlAs	8.21
Ge	19.48

and (6). The arrows point to t values relative to specific materials, for which the longitudinal-to-transverse-mass ratio is shown in table 1[1]. It is seen that the energies can significantly change with respect to the spherical-mass model which corresponds to $t = 1$. In particular, the symmetry lowering due to the anisotropic mass leads to the splitting of the degenerate Σ_u^- and Π_u states.

Finally, it is expected that the transition energies (differences between the curves in figure 1) will change with respect to the spherical-mass model. In particular, the $1\Sigma_g^+ \leftrightarrow 1\Sigma_u^-$ transition energy is always overestimated in this last case.

3. The ellipsoidal quantum dot

Let us consider an ellipsoidal quantum dot with rotational symmetry around the z axis. The dot surface is given by the equation

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{c^2} = 1, \tag{7}$$

where a and c are the semi-axes in the x–y plane and along the z direction respectively. The structure aspect ratio can be defined as $\chi = c/a$.

The simple considerations outlined in the previous section can be extended to quantum confinement within such a dot, providing an exact solution for the case in which the longitudinal mass is associated with the z direction (namely, the constant-energy ellipsoid and the 'physical' ellipsoid major axes are the same). The solution for the same problem with a spherical mass can be found in [3].

The coordinate transformation discussed in the previous section still leads to the isotropic Schrödinger equation with a unit mass (4) (which does not depend on the problem boundary). The main difference is that now the boundary condition requires the wavefunction to be null on the surface of the ellipsoid with semi-axes $a' = a\sqrt{m_1}$, $b' = a\sqrt{m_2}$ and $c' = c\sqrt{m_3}$.

The two coincident effective-mass equations related to the valleys $k_z, -k_z$ correspond to the choice $m_1 = m_2 = m_t$, $m_3 = m_l$. The boundary is transformed into an ellipsoid of revolution, with semi-axes $a' = b' = a\sqrt{m_t}$, $c' = c\sqrt{m_l}$ and aspect ratio $\chi' = c'/a' = \chi t$. The associated symmetry group is $D_{\infty h}$, leading to two- or fourfold degenerate energy levels. The eigenvalues are again in the form (5), but in this case they depend on both the longitudinal-to-transverse-mass ratio and the ellipsoid aspect ratio χ. Let us note that the ellipsoidal surface of

[1] It should be noted that for germanium there are eight conduction band minima located at the end points L of the $\langle 111 \rangle$ axes of the Brillouin zone. This does not prevent us from exactly solving the Schrödinger equation with the anisotropic mass. Rather, in this case the x_3 axis does not lie along the z direction of the Brillouin zone, but it is chosen to be parallel to the equivalent $\langle 111 \rangle$ directions (therefore, a different axis is chosen for each minimum). This only implies that the eigenfunctions will be calculated in this new reference frame, and their expression in terms of x, y and z will be obtained by a suitable coordinate rotation. Moreover, since there are eight equivalent minima, 8- and 16-fold degenerate levels are obtained.

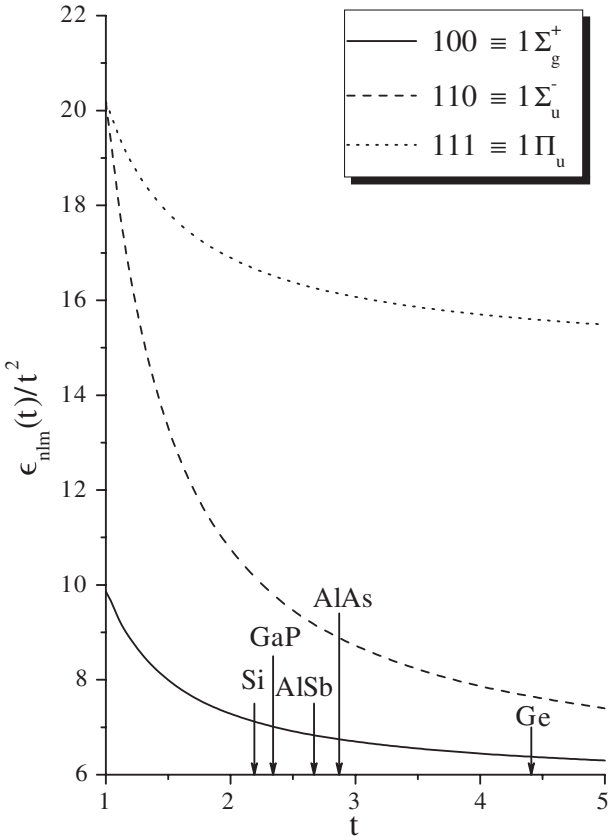

Figure 1. The eigenvalues relative to the ground and the first two excited states for a confined electron within a spherical quantum dot are plotted as a function of $t = \sqrt{m_l/m_t}$. ϵ_{nlm} is defined in equation (5). The arrows point to specific materials.

equation (7) is transformed into a spherical surface (according to the coordinate transformation we are using) when $\chi' = 1$, namely $\chi = 1/t$. This raises the problem symmetry from $D_{\infty h}$ to $O^+(3)$ (group of proper rotations [7], which has s, p, d, ... or, equivalently, $l = 0, 1, 2, \ldots$ representations with dimension $2l + 1$).

The effective-mass equations related to the four valleys along k_x, $-k_x$ and k_y, $-k_y$ are obtained from the Hamiltonian (1) setting either $m_1 = m_l$ or $m_2 = m_l$. Unfortunately, the change of variables leads in this case to imposing the boundary conditions on an ellipsoidal surface with three different axes for which we do not have effective-mass results. The quantum states can be labelled according to the irreducible representations of the D_{2h} Abelian group, which has eight one-dimensional representations ($A_{1_u^g}$, $B_{1_u^g}$, $B_{2_u^g}$, $B_{3_u^g}$). The four valleys give rise to equations which differ just for the change $x \leftrightarrow y$ and have different eigenfunctions but the same eigenvalues. Therefore, we expect all quantum levels to be fourfold degenerate.

Let us note that if $\chi = t$ the coordinate transformation for the four equations derived from the $k_x, -k_x, k_y, -k_y$ valleys map the 'physical' ellipsoid of revolution (7) into an ellipsoid which has two coincident axes. This raises, for this special point, the symmetry from D_{2h} to $D_{\infty h}$, so the eigenvalues are expected to be fourfold and eightfold degenerate.

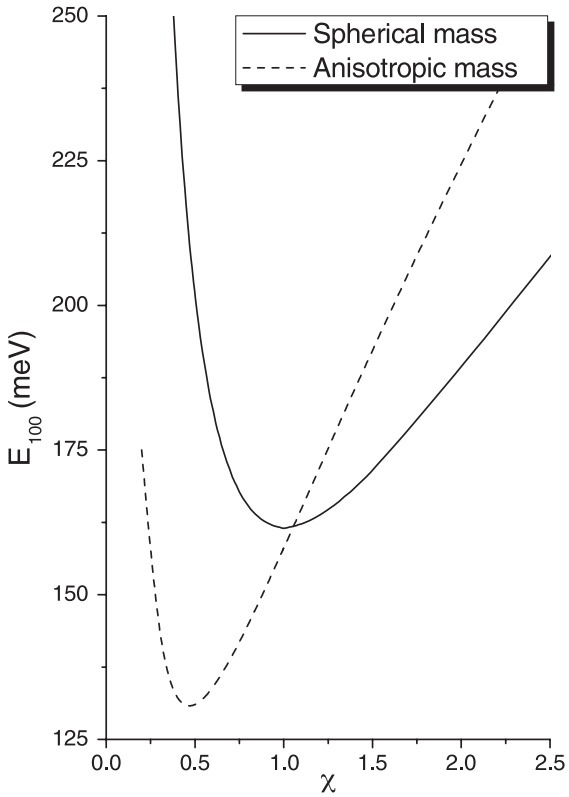

Figure 2. The constant volume ground-state energy for silicon ellipsoidal quantum dots as a function of the aspect ratio χ. Both the spherical- (solid curve) and anisotropic-mass (dashed curve) results are shown. The volume is the same as that of a sphere with a 3 nm radius.

Table 2. The symmetry groups of the effective-mass Hamiltonian for an electron confined within an ellipsoidal ($\chi \neq 1$) or spherical ($\chi = 1$) quantum dot. The effective-mass equations derived from each valley are considered (assuming six valleys along the ⟨100⟩ directions, which does not applies to germanium). Note the special points $\chi = 1/t$ and t (t^2 is defined as the longitudinal-to-transverse-mass ratio).

	$\pm k_x$	$\pm k_y$	$\pm k_z$
$\chi = 1/t$	D_{2h}	D_{2h}	$O^+(3)$
$\chi = 1$	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$
$\chi = t$	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$
$\chi \neq 1/t, 1, t$	D_{2h}	D_{2h}	$D_{\infty h}$

The symmetries of the six effective-mass equations related to the six conduction-band valleys are summarized in table 2. Let us note that for $\chi = t$ both the quantum levels derived from the $k_x, -k_x, k_y, -k_y$ valleys and those derived from the $k_z, -k_z$ valleys are related to $D_{\infty h}$ symmetry, but the two families of eigenvalues are not degenerate with each other.

The effect of the mass anisotropy is, in this case, even more evident than for the spherical dot. In figure 2 we show the result for the ground state energy derived from the $k_z, -k_z$ valleys (this case can be treated exactly as stated above) as a function of the 'physical' ellipsoid aspect ratio χ (dashed curve). The energy is plotted keeping the volume constant, which means that

a and c are changed in such a way that the volume is the same as a that of a sphere with a 3 nm radius. We use the silicon conduction-band masses ($t = 2.193$). In the same plot we show (solid curve) the same result obtained using a spherical average of the two masses [3]. In this last case the minimum energy is obtained for a spherical dot, as simple geometrical considerations would suggest. The anisotropic-mass result shows instead this minimum moved from $\chi = 1$ (sphere) to $\chi = 1/t$. This is easily understood by considering that, as previously discussed, the coordinate transformation maps the ellipsoidal dot into a spherical dot ($a' = b' = c'$) for that value of χ.

4. Conclusions

In this paper we have shown that it is possible to provide an exact solution for the effective-mass Schrödinger equation for an electron confined within a spherical quantum dot, if the anisotropic conduction-band effective mass is fully taken into account. It is shown how the break of the spherical symmetry of the problem, due to the mass, modifies the quantum-confined spectrum, as a function of the longitudinal-to-transverse-mass ratio. The infrared transitions can be significantly affected, being overestimated in the simpler, spherical mass model.

Moreover, it has been shown how the exact solution can also be provided for quantum confinement within an ellipsoidal quantum dot. The constant-volume ground-state energy has been compared with that calculated within the spherical-mass approach, showing how the minimum confinement energy is obtained for an ellipsoid with aspect ratio $\chi \simeq 0.5$ (for a silicon dot), while a simple geometrical argument would suggest the occurrence of that minimum for a sphere.

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