The Role of the Carrier Mass in Semiconductor Quantum Dots

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Abstract

In the present work we undertake a re-examination of effective mass theory (EMT) for a semiconductor quantum dot. We take into account the fact that the effective mass \( m_i \) of the carrier inside the dot of radius \( R \) is distinct from the mass \( m_o \) in the dielectric coating surrounding the dot. The electronic structure of the quantum dot is determined in crucial ways by the mass discontinuity factor \( \beta \equiv m_i/m_o \). In this connection we propose a novel quantum scale, \( \sigma \), which is a dimensionless parameter proportional to \( \beta^2 V_0 R^2 \), where \( V_0 \) represents the barrier due to dielectric coating. The scale \( \sigma \) represents a mass modified “strength” of the potential. We show both by numerical calculations and asymptotic analysis that the charge density near the nanocrystallite surface, \( \rho(r=R) \), can be large and scales as \( 1/\sigma \). This fact suggests a significant role for the surface in an EMT based model. We also show that the upshift in the ground state energy is weaker than quadratic, unlike traditional EMT based calculations, and chart its dependence on the proposed scale \( \sigma \). Finally, we demonstrate that calculations based on our model compare favorably with valence band photoemission data and with more elaborate theoretical calculations.

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I. INTRODUCTION

Semiconductor nanocrystallites, more popularly known as quantum dots (QDs), have been extensively studied in the past decade and a half. The system is interesting from the point of view of basic physics, with the carriers being confined to an essentially “zero” dimensional structure. The efficient luminescence observed in some of these crystallites makes them promising candidates for opto-electronic devices. Further, the inexorable drive towards device miniaturization makes them technologically significant.

The physical dimensions of a typical QD are in the range 1-10 nm. It is coated by a dielectric which may be a polymer, glass, oxide, etc. depending on the method of preparation. In a simplified effective mass theory (EMT) approach, the QD is taken to be spherical with radius $R$ and the dielectric presents a finite barrier $V_0 \in [1 - 10 \text{ eV}]$ to the carriers (electrons/holes). This is shown in Fig. 1. The carrier confinement leads to an enhancement of the “band” gap which, in the simple quantum confinement model (QCM), scales inversely with the size ($1/R^2$). However, experimental observations and more elaborate theoretical calculations suggest that the gap dependence is infra-quadratic ($1/R^\gamma$, $1 < \gamma < 2$). Further, several workers have questioned QCM and suggested that it downplays the significance of surface-related effects.

In the present work we demonstrate that EMT can be reconciled with the observed infra-quadratic shift of the “band” edges. More importantly, an examination of the charge density in our EMT based model reveals the significant role of the surface in a direct fashion. To accomplish this, we re-examine the EMT taking into account the fact that the effective mass of the carrier inside the dot ($m_i$) is distinct from the mass outside ($m_o$). In other words, there is a mass discontinuity across the potential barrier depicted in Fig. 1. The ratio $\beta (\equiv m_i/m_o)$ can significantly affect the electronic properties of a QD. It is well known that the classical scale representing the surface to volume ratio ($S/V$) plays an important role in determining both classical and quantum properties. We propose a novel quantum scale $\sigma$ which is a dimensionless parameter proportional to $\beta^2 V_0 R^2$ (Eq. (15)). This scale...
represents a mass modified “strength” of the potential (MSP). The correction to the ground state energy $E_1$ and the charge density at the interface $\rho(r = R)$ scale in an appealingly simple way with the proposed scale $\sigma$.

In Sec. I we describe the basic model in brief. The carrier (electron/hole) is confined to a spherical QD of radius $R$ with a finite barrier of height $V_0$ (see Fig. 1). As suggested by Brus, the BenDaniel-Duke boundary conditions are appropriate for a system with a mass discontinuity across the barrier. This aspect has been ignored in a number of theoretical calculations in the past (see Sec. V). As will be shown subsequently, the physics of the problem is determined in crucial ways by the mass discontinuity factor $\beta(\equiv m_i/m_o)$. A pedagogical point, we highlight is that the BenDaniel-Duke boundary conditions must be applied to the full wavefunction and not to the partial wavefunction. The error involved in employing the partial wavefunction can be substantial and is presented in Table I.

The numerical results are presented in Sec. II. Previous works in the field have devoted considerable attention to the upshift of the ground state energy $E_1$. We focus instead on the charge density $\rho(r)$. Brus had pointed out that the charge density near the nanocrystallite surface can be large if the carrier effective mass $m_i$ is small. We show that the charge density at the nanocrystallite boundary $\rho(r = R)$ is indeed large if $\beta (\equiv m_i/m_o)$ is small (Fig. 3). A more complete picture is provided by our proposed MSP scale $\sigma (\propto \beta^2 V_0 R^2)$. In Fig. 4 we demonstrate that $\rho(R)$ scales inversely with $\sigma$. For a quantum dot, $S/V$ ratio is large. Thus the fraction of unsaturated bonds on the surface increases and/or the formation of molecular complexes on the surface is favoured. The large charge density on the surface suggests a novel non-classical reason for the importance of the surface. We also show that the ground state energy $E_1$ exhibits a size dependence which is weaker than the quadratic ($1/R^2$) dependence one has come to expect from EMT (Fig. 5).

A detailed asymptotic analysis is presented in Sec. II to explain the numerical results of Sec. I and to present them in terms of the proposed quantum scale $\sigma$. We show that $\rho(R)$ scales as $\simeq 1/\sigma$. We introduce the notion of the penetration depth $\delta$ in this connection. We also explain the infra-quadratic dependence of the ground state energy on the size $R$. In
particular, we demonstrate that the correction to the quadratic term scales as $\sim -1/\sqrt{\sigma}$.

Section V constitutes the discussion. We show that our model compares favourably with the experimental valence-band photoemission data of Colvin et. al. on CdS (Fig. 3) and with more elaborate tight-binding calculations (Fig. 7). We summarize our work and suggest directions for future research.

II. BASIC THEORY

We consider a spherical semiconductor nanocrystallite of diameter $d = 2R$ (See Fig. 1). An additional electron in the “conduction band” of such a crystallite is described in effective mass theory by the Hamiltonian:

$$H = -\frac{\hbar^2}{2} \nabla \cdot \left( \frac{1}{m^*(r)} \cdot \nabla \right) + V(r)$$  \hspace{1cm} (1)

For a position dependent mass the appropriate hermitian kinetic energy operator is given by the first term on the right hand side of Eq. (1). The electron effective mass inside the nanocrystallite ($m_i$) is different from the effective mass in the dielectric coating ($m_o$). A useful parameter is the ratio ($\beta$) of the effective masses.

$$\beta = \frac{m_i}{m_o}$$  \hspace{1cm} (2)

For the experimentally relevant cases explored in the last two decades, $\beta$ is less than unity. For extreme cases, such as GaAs or InAs quantum dots, $\beta$ equals 0.067 and 0.02, respectively, where we have taken $m_o = m_e$, the free electron mass. An important aspect of the present study is to highlight the significance of this parameter $\beta$. The potential $V(r)$ in Eq. (1) is given by

$$V(r) = \begin{cases} 
0 & r \leq 0 \\
V_o & r > R 
\end{cases}$$  \hspace{1cm} (3)

Here $V_o$ is a large positive potential and represents the dielectric coating surrounding the nanocrystallite (See Fig. 1). Typically a nanocrystallite is surrounded by dielectrics such
as glasses, polymers, organic solvents or oxides and hydrides\(^5\). Thus, the electron is in a spherically symmetric well. The wavefunction for this spherically symmetric problem can be written in the form:

\[ \psi_{nlm}(r) = R_{nl}(r)Y_{lm}(\theta, \phi) \]  

(4)

where the symbols have their usual meanings. It is customary to write the radial wavefunction \( R_{nl} \) as:

\[ u_{nl}(r) = rR_{nl} \]  

(5)

The equation for the partial wavefunction \( u_{nl}(r) \) is:

\[ \frac{d^2u_{nl}}{dr^2} - \frac{l(l+1)}{r^2}u_{nl} + \frac{2m_iE_n}{\hbar^2}u_{nl} = 0 \]  

(6)

where \( m_i \) is the mass of the electron inside the potential well. The electron effective mass \( m^* \) assumes different values \( m_i \) inside and \( m_o \) outside the well.

For the \( l = 0 \) case, the standard form for the radial wavefunction is obtained on solving Eq. (6). This is:

\[ R_{n0}(r) = A \sin(k_{n}^{in}r) \]  

(7)

for \( 0 < r < R \) and

\[ R_{n0}(r) = Be^{-k_{n}^{out}r} \]  

(8)

for \( r > R \), where

\[ k_{n}^{in} = \sqrt{\frac{2m_iE_n}{\hbar^2}} \]  

(9)

and,

\[ k_{n}^{out} = \sqrt{\frac{2m_o(V_o - E_n)}{\hbar^2}} \]  

(10)

and \( A \) and \( B \) are normalization constants.
Standard text books on quantum mechanics state the condition of continuity of the derivative of the wavefunction inside and outside the well as:

\[ \frac{dR_{nl}}{dr} \bigg|_{r \to R^-} = \frac{dR_{nl}}{dr} \bigg|_{r \to R^+} \]  

(11)

However, as has been discussed in the semiconductor literature, this condition must be replaced by the BenDaniel-Duke condition in case the effective masses are different across the interface. The condition now reads

\[ \frac{1}{m_i} \frac{dR_{nl}}{dr} \bigg|_{r \to R^-} = \frac{1}{m_o} \frac{dR_{nl}}{dr} \bigg|_{r \to R^+} \]  

(12)

A further point needs to be made at this stage. Many textbooks, in the process of the solution of the Schrödinger equation, define the partial wavefunction \( u_{nl} \) (Eq. (5)) and then further state that the continuity conditions at the interface may be imposed on \( R_{nl}(r) \). They claim that this would yield the same eigenvalue conditions as imposing these conditions on \( u_{nl}(r) \). Quoting Schiff, “The energy levels are obtained by ...(this is equivalent to making \( 1/R \) \( dR/dr \) continuous there)”. It is shown that this is manifestly incorrect when we use the modified boundary condition. It is further shown that in the limit the effective masses become equal across the interface, the two treatments indeed become equivalent for this special case. Imposition of the modified boundary condition on the full wave function leads, after some algebraic manipulations, to

\[ k_n^{in} \cot(k_n^{in} R) = -\beta k_n^{out} + \frac{1 - \beta}{R} \]  

(13)

whereas, the use of the same condition on the partial wavefunction \( u_{nl}(r) \) leads to

\[ k_n^{in} \cot(k_n^{in} R) = -\beta k_n^{out} \]  

(14)

The two conditions are evidently *quite* different. However, they agree when \( \beta \) is unity, recovering thereby the elementary case. There are three parameters, \( \beta \), \( V_0 \) and \( R \), in the above transcendental equation. As can be readily seen from the two equations, the eigenvalues calculated using Eq. (13) would deviate more and more from those calculated using Eq. (14)
for smaller β and smaller R. The energy eigenvalues obtained for a particular set of parameters is presented in Table I. For β=0.1, V₀=1.0 and R=20.0 Å, the disagreement is even worse, being as large as 57%. In the sections that follow, we shall employ Eq. (13).

III. RESULTS

In this section, we present the results of our numerical calculations. Further, this section and the next contains the interpretation of our results. In what follows, we focus our attention on the spherically symmetric (l = 0) case.

A quantity of central interest to us is the radial charge density ρ(r)

$$\rho(r) = r^2 R_{n0}^2(r)$$

Where the multiplicative constant, e, the carrier charge, has been ignored. We examine the dependence of the equilibrium charge density on the ratio of the effective masses β (≡ m_i/m_o), the barrier height V₀ and the radius of the nanocrystallite R. In Fig. 2, we have plotted the charge density for different values of β and V₀ = 1.5 eV. The radius of the crystallite is R = 50 Å. As can be readily seen, the value of the equilibrium charge density at the crystallite boundary, ρ(r = R), falls rapidly with increasing β. The peak in the charge density occurs at r ∈ [R/2, R]; in other words, close to the surface of the crystallite. For small values of β, the peak is at r ≃ R. Examples of small β are InP, InAs, GaAs, etc. Even if the carrier is photogenerated in the interior of the crystallite, it rapidly redistributes itself such that the equilibrium charge density is large near the boundary. In nanocrystallites with large β(≈ 1) the peak in the charge density shifts towards R/2. In other words r = R/2 is a “fixed point” for the charge density. Figure 3 shows this more systematically. We have plotted the charge density at the boundary as a function of β, and taking V₀ = 5 eV. There is a clear decrease in the charge density as the value of β increases. In the next section, we shall show this more rigorously in the limit of large V₀. An appropriate perspective on ρ(r = R) is obtained by defining a mass modified “strength” of the potential (MSP), σ.
\[ \sigma = (\beta \kappa_0 R)^2 \]  
\[ \kappa_0 = \sqrt{\frac{2m_o V_0}{h^2}} \]  

Conventional textbooks define the strength of potential as \( V_0 R^2 \). As will become apparent in the next section, a more appropriate definition for the case under study is \( \sigma = (\beta \kappa_0 R)^2 \).

Figure depicts that \( \rho(r) \) falls with \( \sigma \). This decrease is observed to be nearly linear. We shall have occasion to examine this universal parameter parameter \( \sigma \) in the next section.

In Fig. we study the dependence of the ground state energy \( E_1 \) \( (n = 1, l = 0) \) of the carrier on the crystallite size \( R \). We have taken \( V_0 = 5 \text{ eV} \) for this figure. We observe that this dependence is infraquadratic, i.e. weaker than \( 1/R^2 \). We note that this infraquadratic behaviour has been reported both experimentally and on the basis of tight-binding (TB) calculations. In the present case infraquadratic behaviour can be traced to the finite nature of the barrier and the change of the effective mass across the barrier. Inspection of Fig. reveals that with decreasing value of \( \beta \), the behaviour increasingly departs from the quadratic case. This is demonstrated rigorously in the next section on asymptotic analysis (Eq. (23)), where we see that

\[ E_1 = \frac{c_1}{R^2} - \frac{c_2}{R^3} \]  

\( c_1 \) and \( c_2 \) being constants. An attempt to coerce the above expression into the form

\[ E_1 \simeq \frac{C}{R^\gamma} \]  

will yield \( 1 < \gamma < 2 \). We have presented the salient results of our model in this section. Additional results related to experiments and earlier theoretical calculation on specific semiconductor nanocrystallites will be presented in the last section (Sec. V). The following section on asymptotic analysis will attempt to explain the numerical results obtained in this section.
IV. ASYMPTOTIC ANALYSIS

We now present an asymptotic analysis of Eq. (13) in an attempt to explain the results of our calculations in the previous section. For an infinite potential well, the eigenvalue condition reduces to:

\[ k_{n}^{in} R = n\pi \]  \hspace{1cm} (18)

where \( k_{n}^{in} \) is defined in Eq. (9). We consider the case of the ground state i.e. \( n = 1 \). For a well which is “sufficiently” deep but finite, we approximate the above expression by:

\[ k_{1}^{in} R = \pi - \epsilon \]  \hspace{1cm} (19)

where \( \epsilon \) is a small number. Using Eq. (19) in Eq. (13), we obtain:

\[ \frac{\epsilon}{\pi} \simeq \frac{1}{\beta(1 + \kappa_{o}R)} \]  \hspace{1cm} (20)

where \( \kappa_{o} = \sqrt{\frac{2m_{o}V_{o}}{\hbar^{2}}} \)  \hspace{1cm} (21)

where we have assumed that \( V_{o} \gg E_{1} \), the ground state energy. The condition on the smallness of \( \epsilon \) is now apparent. If either of these parameters \( \beta, R, V_{o} \) is large then \( \epsilon \) would be small. It is clear that \( \epsilon \) is inversely dependent on the mass modified “strength” of the potential defined earlier in Eq. (13)

\[ \epsilon \simeq \frac{\pi}{\sqrt{\sigma}} \]  \hspace{1cm} (22)

when \( \sqrt{\sigma} \gg \beta \). We are now in a position to obtain an approximate expression for the ground state energy \( E_{1} \). Using Eqs. (19) and (20) and the definition of \( k_{1}^{in} \) from Eq. (9), one obtains,

\[ E_{1} = \frac{\pi^{2}h^{2}}{2m_{i}R^{2}} \left[ 1 - \frac{2}{\beta\kappa_{o}R} + \ldots \right] \]  \hspace{1cm} (23)

\[ = \frac{\pi^{2}h^{2}}{2m_{i}R^{2}} \left[ 1 - \frac{2}{\sqrt{\sigma}} + \ldots \right] \]  \hspace{1cm} (24)
Thus one can see that the ground state energy has the size dependence depicted in Fig. 5, namely,

\[ E_1 = \frac{C_1}{R^2} - \frac{C_2}{R^3} \]
\[ \simeq \frac{C}{R^\gamma} \]

with effective exponent \( \gamma < 2 \), as mentioned earlier. The EMT literature on nanocrystallite semiconductors commonly quote \( \gamma = 2 \). However, absorption and luminescence experiments as well as the tight-binding calculations\(^{10,11}\) yield \( \gamma < 2 \). We have thus formally demonstrated how even within the EMT approach, an infraquadratic exponent (\( \gamma < 2 \)) is obtained. The calculation depicted in Fig. 5 attests to this.

Garrett\(^{12}\) has proposed a penetration depth for the one dimensional finite well problem with \( \beta = 1 \). We define an analogous penetration depth (\( \delta \)) for the carrier in the three dimensional potential well and for the general case \( \beta \neq 1 \).

\[ \delta = \frac{1}{\beta \kappa_o} = \frac{R}{\frac{\sqrt{\sigma}}{R}} \]

Next we shall examine the charge density at the surface. An appealing, intuitive way to understand the nature of \( \rho(r = R) \) is to use the concept of the penetration depth. It is easy to see from Eq. (27) that the penetration depth will be large in case \( \beta \) is small. This is already a confirmation of the result that the charge density is large at the boundary for small \( \beta \) (Figs. 2 and 3). Thus one would expect that when the carrier mass in the semiconductor is small (InSb, GaAs, CdS) then the charge density at the interface will be large. The penetration depth \( \delta \) indicates the extent of the wavefunction penetration into the forbidden region.

We can present a more rigorous analysis of \( \rho(r = R) \) by examining the wavefunction. The normalized wavefunction inside the potential well is:

\[ R_{10}(r) = A \frac{\sin(k_{1n}^r r)}{k_{1n}^r r} \]

\[ k_{1n}^r = \frac{\sqrt{2m^* \sigma}}{\hbar} \]

\[ \hbar = \sqrt{\frac{\pi}{\sigma}} \]

\[ k_{1n}^r = \frac{\sqrt{2m^* \sigma}}{\hbar} \]

\[ A \frac{\sin(k_{1n}^r r)}{k_{1n}^r r} \]

(28)
where
\[ A = \frac{k_1^{\text{in}}}{\sqrt{4\pi}} \left[ \frac{R}{2} \left( 1 - \frac{\sin(2k_1^{\text{in}}R)}{2k_1^{\text{in}}R} \right) + \frac{1 - \cos(2k_1^{\text{in}}R)}{4k_1^{\text{out}}} \right]^{-\frac{1}{2}} \]  
(29)

Using Eq. (19) in Eq. (28), we obtain after some algebraic manipulations:
\[ R_{10}(r) \approx A \left( 1 + \frac{\epsilon}{\pi} \right) \left[ \sin \left( \frac{\pi r}{R} \right) - \frac{\epsilon}{\pi} \cos \left( \frac{\pi r}{R} \right) \right] \]  
(30)

whence we get for the charge density \( \rho \),
\[ \rho(\epsilon, r) \equiv r^2 R_{10}^2(r) = A^2 \left( 1 + \frac{\epsilon}{\pi} \right) \left[ \left( \frac{R}{\pi} \right)^2 \sin^2 \left( \frac{\pi r}{R} \right) + \left( \frac{r \epsilon}{\pi} \right)^2 \cos^2 \left( \frac{\pi r}{R} \right) - \left( \frac{r \epsilon}{\pi} \right)^2 \sin \left( \frac{2\pi r}{R} \right) \right] \]  
(31)

The charge density at the interface is:
\[ \rho(R) = r^2 R_{10}^2(r) \bigg|_{r=R} = A^2 \left( 1 + \frac{\epsilon}{\pi} \right) \left( \frac{\epsilon}{\pi} \right)^2 R^2 \]  
(32)

Recall that \( \epsilon^2 \sim 1/\sigma \) (\( \equiv 1/(\beta \kappa_o R)^2 \)). It is therefore clear that \( \rho(r = R) \) would fall with increasing \( \beta \). This prediction is in agreement with Fig. 3 where \( \rho(R) \) is \( 1/\beta^{1.85} \).

Within the range of validity of approximation in Eq. (19), \( \epsilon \) is much less than unity. Therefore, Eq. (32) may be written as
\[ \rho(R) \approx A^2 \frac{R^2}{\sigma} \]  
(33)

One can thus understand the inverse dependence of \( \rho(R) \) on \( \sigma \) in Fig. 4. It is interesting to note that the charge density can be related to the penetration depth defined in Eq. (27),
\[ \rho(R) \approx A^2 \delta^2 \]

One may also obtain the peak position, \( r_{\text{peak}} \), in the charge density by a simple differentiation of \( r R_{10}(r) \), where \( R_{10}(r) \) is given by Eq. (30). This yields
\[ \left( \frac{\pi r_{\text{peak}}}{R} \right) \tan \left( \frac{\pi r_{\text{peak}}}{R} \right) = -\frac{1 - \epsilon/\pi}{\epsilon/\pi} \]  
(34)

It can be seen easily, either by plotting Eq. (31) or by solving Eq. (34) numerically, that the peak in the charge density \( \rho \) is located at values of \( R/2 \leq r \leq R \) and shifts to \( r = R/2 \) as
the value of $\epsilon$ is decreased. Decrease in $\epsilon$ is brought about by an increase in $\sigma$. Equation (34) indicates that $r_{\text{peak}} \in [R/2, R]$. When $\beta$ is small, $r_{\text{peak}} > R/2$ and this is also graphically borne out by Fig. 4. Since the peak is shifted towards the crystallite boundary, the charge density at the boundary becomes substantial. When the MSP scale $\sigma$ is large, Eq. (34) implies that $r_{\text{peak}} \rightarrow R/2$. In other words there is a fixed-point or “attractor” at $r = R/2$. The peak in the wavefunction does not shift to a value below $R/2$, no matter how large $\sigma$ is.

V. DISCUSSION

The objective of the present work is to explore EMT in the context of the variation of the carrier effective mass across semiconductor - dielectric interface in a QD. We consider a simple Hamiltonian described by Eq. (1) in order to illustrate the essential physics. It would be worthwhile to compare our results with other theoretical calculations and experiments. Below we present two such comparisons.

We compare our results with the valence band photoemission experiment carried out by Colvin et. al. on CdS quantum dots. Their work represents the first non-optical observation of the electronic structure of semiconductor nanostructures. The experiment measures the energy shift of the valence band maximum as the cluster size decreases, taking the largest cluster of $R = 35$ Å as a reference. For this case, $\beta = 0.53$ and Fig. 6 depicts the dependence of the valence band shift on the cluster size as calculated by us. We fit our data to $C/R^\alpha$. We get an exponent $\alpha = 1.26$, which is in good agreement with the experimental observation. Colvin et. al. attribute this shift to two factors: (i) the kinetic energy enhancement due to the quantum confinement of the hole; (ii) the polarization of the crystallite and the loss of dielectric solvation energy. As is clear from Fig. 6 a finite barrier quantum confinement model with appropriate effective masses provides a reasonable explanation for the experimental behaviour. We also note in passing that Takagahara has argued that the polarization term can in general be neglected.
Lippens and Lannoo\cite{Lippens} have theoretically studied the same system. Our model can be compared with their results for the valence band shift. Fig. 7 depicts such a comparison. We have taken the barrier height $V_0 = 2$ eV. A majority of the literature claim that TB calculations are in better agreement with experiments. The EMT with quadratic dependence on size ($\sim 1/R^2$) represents an extreme case. As can be seen from Fig. 7 our EMT based model is in close agreement with the experimental observations. On the other hand, the standard EMT calculation of Lippens and Lannoo is at variance with their TB calculation.

The majority of the theoretical work for the absorption and luminescence in quantum dots takes excitonic effects into account. In other words, the Hamiltonian involves both a hole and an electron. We propose to extend our simple EMT model to the excitonic case as well as to study excited states in the future. We also plan to study the capacitance of QDs by analyzing multi-electron effects in our model.

We emphasize that the EMT calculation should be carried out with the correct boundary condition as presented in Eq. (12). This fact has been pointed out by Brus\cite{Brus}. The use of this boundary condition leads to an eigenvalue condition (Eq. (13)) which is different from the one normally encountered in textbooks\cite{Textbook1, Textbook2, Textbook3} (Eq. (14) with $\beta = 1$). A further point to note is that the boundary condition must be imposed on full wavefunction $R_{nl}(r)$. Imposing it on the partial wavefunction $u_{nl}(r)$ would lead to incorrect results.

EMT based calculations have normally been carried out using an infinite barrier\cite{InfiniteBarrier}. In this case, the charge density at the nanocrystallite boundary is zero. It is therefore not surprising that the significance of the surface is downplayed. Further, workers who recognize the finite nature of the barrier have ignored the mass discontinuity across the barrier\cite{MassDiscontinuity1, MassDiscontinuity2} and the reason sometimes stated is that most of the population density of the carrier is still confined well within QD\cite{PopulationDensity}. The LDA based calculations on dot capacitance and shell filling effects also ignore the mass discontinuity\cite{LDA}. Porous silicon, which is a disordered agglomeration of silicon nanocrystallites, presents a case-study for the debate between the quantum confinement and the surface state schools of thought. This debate has been reviewed by a number of workers\cite{Review1, Review2, Review3}. In this work we have shown that the charge density can be large at the surface.
even in an EMT based framework. This is more so for semiconducting materials with small carrier effective masses and dielectric coatings representing a small potential barrier. Hence, the contention that surface related effects are significant appears valid.

Another demerit of the infinite barrier model is its prediction of an inverse quadratic \((1/R^2)\) shift of the band gap. We have already stated that this does not agree with experiments and with more elaborate theoretical calculations\(^{10, 11, 25, 26}\). We have shown through our work that a calculation for finite barrier model leads to a good agreement with the experimental infraquadratic dependence.

The highlights of the work are:

1. Ground state energy within EMT scales infraquadratically with the crystallite size (Eq. (23) – (26)).

2. The parameter of relevance is our proposed mass modified “strength” of the potential, the MSP scale \(\sigma = (\beta \kappa R)^2\). Our proposed parameter \(\sigma\) presents a more complete picture of the physical situation than \(\beta\) alone does\(^{1}\).

3. The charge density at the boundary \(\rho(R)\) can be large (Figs (2) – (4)) and scales inversely with \(\sigma\). This is unlike what one normally expects from EMT. In the literature of semiconductor nanocrystallites there has been a longstanding debate between theories for quantum confinement versus surface states\(^{21, 24}\). The present work provides a fresh perspective on the importance of surface related phenomena.

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REFERENCES

1 L. E. Brus, J. Chem. Phys. 79, 5566 (1983).

2 D. J. BenDaniel and C. B. Duke, Phys. Rev. 152, 683 (1966).

3 V. L. Colvin, A. P. Alivastos, and J. G. Tobin, Phys. Rev. Lett. 66, 2786 (1991).

4 P. E. Lippens and M. Lannoo, Phys. Rev. B 39, 10935 (1989).

5 Y. Wang and N. Herron, J. Chem. Phys. 95, 525 (1991).

6 L. Schiff, Quantum Mechanics, pp. 82-84 (McGraw-Hill Book Co., Singapore, 1968).

7 J. Powell and B. Crasemann, Quantum Mechanics (Addison-Wesley Publishing Co. Inc., New York, 1971).

8 F. Schwabl, Quantum Mechanics, pp 307 (Springer-Verlag, Berlin, 1992).

9 P. M. Mathews and K. Venkatesan, A Textbook of Quantum Mechanics, pp. 54 (Tata McGraw-Hill Publishing Company Limited, New Delhi, 1990).

10 C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B 48, 11024 (1993).

11 V. Ranjan and V. A. Singh, in Proc. of the Ninth International Workshop on the Physics of Semiconductor Devices, Delhi, INDIA (Narosa, London, 1998), pp. 98 – 101.

12 S. Garrett, Amer. J. Phys. 47, 195 (1979).

13 L. E. Brus, J. Chem. Phys. 80, 4403 (1984).

14 T. Takagahara, Phys. Rev. B 47, 4569 (1993).

15 U. Woggon, Optical Properties of Semiconductor Quantum Dots (Springer Verlag, Berlin, 1997), Vol. 136.

16 Y. Kayanuma and H. Momiji, Phys. Rev. B 41, 10261 (1990).

17 S. Nomura and T. Kobayashi, Sol. State Commun. 78, 677 (1991).
18 T. Shimura and M. Matsuura, Phys. Rev. B 56, 2109 (1997).

19 U. Laheld and G. Einevoll, Phys. Rev. B 55, 5184 (1997).

20 M. Macucci, K. Hess, and G. J. Iafarate, Phys. Rev. B 55, R4879 (1997).

21 Y. Kanemitsu, Phys. Reports 263, 1 (1995).

22 S. M. Prokes, J. Mater. Res. 11, 305 (1996).

23 A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. 82, 909 (1997).

24 G. C. John and V. A. Singh, Comments Cond. Matt. Phys. 18, 163 (1997).

25 H. Fu and A. Zunger, Phys. Rev. B 56, 1496 (1997).

26 S. Ogut, J. Chelikowsky, and S. Louie, Phys. Rev. Lett. 79, 1770 (1997).
TABLE I. Comparison of eigenvalues obtained by applying the correct boundary condition on the full wavefunction (Eq. (13)) and on the partial wavefunction (Eq. (14)). The values of the parameters employed are $\beta = 0.1$, $V_0 = 2.5 \text{ eV}$ and $R = 40 \text{ A}^\circ$.

|                  | Eigenvalues with full wavefunction | Eigenvalues with partial wavefunction | Percentage difference |
|------------------|----------------------------------|--------------------------------------|-----------------------|
|                  | 0.13                             | 0.15                                 | 12.04                 |
|                  | 0.61                             | 0.65                                 | 3.21                  |
|                  | 1.52                             | 1.56                                 | 2.53                  |
FIGURES

FIG. 1. The left side of the figure depicts an idealized spherical quantum dot (QD) surrounded by a dielectric coating. This is modeled by a potential well of height $V_0$. The carrier effective mass is $m_i$ inside the well and $m_o$ in the dielectric coating outside.

FIG. 2. A typical normalized charge density $\rho(r)$ inside a crystallite of size $R = 50 \, \text{Å}$. Note that for small $\beta = (m_i/m_o)$, $\rho(r)$ is large at the crystallite surface ($r = R$). As $\beta$ increases, the position of the peak $r_{\text{peak}}$ in $\rho$ shifts to $R/2$.

FIG. 3. The charge density at the crystallite boundary, $\rho(r = R)$. The charge density $\rho(R)$ falls with increasing $\beta$. We fit our data for $\rho(R)$ to $C_1/\beta^\alpha$, with $\alpha = 1.85$. This is in good agreement with the prediction of Eq. (32). $C_1$ is a constant.

FIG. 4. The dependence of the charge density $\rho(R)$ at the crystallite boundary on the proposed quantum scale $\sigma \equiv (\beta\kappa_0 R^2)$. The scale $\sigma$ represents a mass modified “strength” of the potential (see text). The data for $\rho(R)$ fit well to $C_2/\sigma^\alpha$ with $\alpha = 0.98$, and in agreement with the prediction of Eq. (33). $C_2$ is a constant. The dotted line is a fit to the calculated data (diamonds).

FIG. 5. The ground state energy $E_1$ versus the crystallite size $R$. The calculated data are for four different values of $\beta$ and are fitted to $C/R^\gamma$, where $C$ is a constant. The values of $\gamma$ for the different values of $\beta = 2.0, 0.4, 0.1$ and $0.01$ are respectively $1.95, 1.76, 1.39$ and $1.03$. We can see that the energy shift is increasingly infraquadratic for smaller values of $\beta$.

FIG. 6. The data taken from the valence band photoemission spectra for CdS crystallite due to Colvin et. al. (Ref. 3) is indicated by diamond symbols. Our calculation is indicated by the dotted line. A fit to $C/R^\alpha$ leads to $\alpha = 1.26$ for both cases. Our calculation gives a much improved result as compared to traditional EMT with $\alpha = 2$. See Sec. V for further discussion.
FIG. 7. Valence band shift with size of the CdS crystallite. Our results (solid line) are very close to the tight-binding (TB) calculations (diamonds) of Lippens and Lannoo (Ref. 4). In contrast, there is less agreement between the EMT (dashed line) and TB (diamond symbols) calculations of Ref. 4.
Our model

Colvin et. al. [Ref. 3]

R (Angstroms)

\( E_{VB} \) (eV)
Ref. 4. (TB)  
Ref. 4. (EMT)  
Our Model