A qualitative semi–classical treatment of an isolated semi–polar quantum dot

Toby D. Young
Instytut Podstawowych Problemów Techniki Polskiej Akademii Nauk
ul. Adolfa Pawińskiego 5b, 02-106 Warszawa, Polska
E-mail: toyoung@ippt.gov.pl

Abstract. To qualitatively determine the behaviour of micro–macro properties of a quantum dot grown in a non-polar direction, we propose a simple semi–classical model based on well established ideas. We take into account the following empirical phenomena: (i) The displacement and induced strain at heterojunctions; (ii) The electrostatic potential arising from piezoelectric and spontaneous polarisation; and (iii) The localisation of excitons (particle–hole pairs) arising from quantum confinement. After some algebraic manipulation used to cast the formalism into an arbitrarily rotated frame, a numerical model is developed for the case of a semi–polar wurtzite GaN quantum dot buried in a wurtzite AlN matrix. This scheme is found to provide a satisfying qualitative description of an isolated semi–polar quantum dot in a way that is accessible to further physical interpretation and quantification.

1. Introduction

Quantum dot structures are sometimes referred to as ‘designer atoms’ or ‘artificial atoms’ and have become an integral part of modern human life in the form of light detectors, chemical sensors, light emitters, and integrated circuits; with applications in medicine, engineering technology, and science. One outstanding property of the wurtzite crystal structure in particular is that it possesses a spontaneous piezoelectric field. The piezoelectric field has been shown to dominate the electronic properties of quantum dot structures; even given the presence of other mechanical fields (eg. elastic–electric displacements) [1]. Until now, nanostructures fabricated for scientific investigation and practical devices have been along the polar direction. These systems have typically been studied by theoretical modelling with a good degree of success (see for example references [2, 3]).

Recently, three–dimensional quantum dot nanostructures grown in the semi–polar (i.e. non-polar) directions and their related physical response have become an area of interest that is enigmatic to both the pure and applied sciences [4, 5]. For this reason in this contribution we investigate the elastic–electric and optical properties of an isolated semi–polar wurtzite GaN quantum dot embedded in a wurtzite AlN matrix that is chosen to be representative of experimental observation. Most such studies tend to make use of the $k \cdot p$ Hamiltonian within the effective mass and plane wave approximation [1, 2, 3]; so much so that this tends to be referred to as the ‘standard model’ of electronic structure theory [6]. While that Hamiltonian has its uses, in this contribution we provide the first few steps toward an alternative form for a semi–empirical model. In the next section the basics of the semi–empirical model and method are described. Following that, in section 3, the model is applied to a quantum dot grown for semi–polar angles $0 \leq \theta \leq \pi/2$. Finally, in section 4, we summarise this contribution and give a tentative outlook for future development.

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2. Model and method
The discussion that follows concerns heterostructures examined on the nanoscale that have a built–in spontaneous piezoelectric field, notably nanostructures with a wurtzite crystal phase (hexagonal space symmetry group $P6_3mc$) described by the geometrical parameters $a$ and $c$. Furthermore, given that we are interested in qualitatively describing the behaviour of micro–macro properties of three–dimensional quantum dot heterostructures, a model based on semi–classical mechanics is proposed that has a classical component and a quantum component.

To describe the elastic–electric properties and particle–hole states quantum confined to a semi–polar quantum dot encapsulated in a polyhedral volume $\Omega \in \mathbb{R}^3$, the following three models are taken to be adequate and sufficient:

(i) The traditional fully-coupled elastic–electric equation set [7, 8] for the elastic displacement $u$ and electric potential $V$ is written as a set of simultaneous equations for the stress state

$$\sigma_{ij} = C_{ijkl}(\partial_l u_k + \Delta_{kl}) - e_{mij}\partial_m V ,$$

(1)

and the electric displacement state

$$D_i = \epsilon_{ij}\partial_j V + e_{ijk}\partial_k u_j + P_i ,$$

(2)

where $C_{ijkl}$, $e_{ijk}$, $\epsilon_{ij}$, and $P_i$ are moduli of elastic, piezoelectric, permittivity, and spontaneous polarisation tensors respectively; and the symmetric gradient of the elastic displacements is defined as $\partial_l u_k := \frac{1}{2}(\partial_l u_k + \partial_k u_l)$. The strain arising from the lattice mismatch in equation (1) is defined by

$$\Delta_{kl} = \begin{cases} \frac{\alpha_{matrix}-\alpha_{dot}}{\alpha_{matrix}}\delta_{kl} & \text{if } k = l \in \{1, 2\} \\
\frac{\epsilon_{matrix}}{\alpha_{matrix}}\frac{\epsilon_{matrix}}{\alpha_{matrix}}\delta_{kl} & \text{if } k = l = 3 \\
0 & \text{if } k \neq l ,
\end{cases}$$

(3)

where the indices $\{i, j\}$ run over all degrees of freedom and $\delta_{kl}$ is the Kronecker delta function $\delta_{ij} = [i = j]$ for the Iverson bracket [·]. Zero boundary constraints are imposed by

$$u(x)|_{\partial \Omega} = V(x)|_{\partial \Omega} = 0 ,$$

(4)

and equations (1) and (2) are solved for $\partial_j \sigma_{ij} = \partial_l D_l = 0$.

(ii) The Hamiltonian operator for the wurtzite crystal structures is, in the first instance, written as two separable one–band Hamiltonian operators

$$H_{\text{eff}} = \partial_i \frac{1}{2m_i^*} \partial_i + q(V - E_{\text{gap}}) ,$$

(5)

where the indices $\{i, j\}$ run over all degrees of freedom, $m_i^*$ is the effective mass of a particle or hole, $q = \mp e$ for particles and holes respectively (where $e$ is the charge of a single electron), and $V$ is the electrostatic potential found from the elastic–electric problem. The operator is substituted into the Schrödinger equation:

$$H_{\text{eff}} \Psi = E \Psi , \quad \Psi = \sum_n c_n \psi_n ,$$

(6)

for normalisation constants $c_n$ and where $E \in \{E_p, E_h\}$ and $\Psi \in \{\psi_p, \psi_h\}$ are the particle and hole eigenenergies and eigenstates respectively. Zero boundary constraints are imposed by

$$\Psi(x)|_{\partial \Omega} = 0 ,$$

(7)

and equation (5) is then solved $\forall \psi \neq 0$. 2
The tensors of moduli of the above two models are written for a fixed-body Cartesian axis \( \{x, y, z\} \in \mathbb{R}^3 \) from which there exists a rotated-body Cartesian axis \( \{\tilde{x}, \tilde{y}, \tilde{z}\} \in \mathbb{R}^3 \), where the two spaces are connected by the well-known rotation tensor \( R_{ia} \). The rotation \( R_{ia} \) acts on all tensors of moduli \( T \) such that

\[
\tilde{T}_a = R_{ia} T_i , \quad \forall T_i \in \{ P_i, m_i^+ \} , \tag{8}
\]

\[
\tilde{T}_{ab} = R_{ia} R_{jb} T_{ij} , \quad \forall T_{ij} \in \{ \Delta_{ij}, \epsilon_{ij} \} , \tag{9}
\]

\[
\tilde{T}_{abc} = R_{ia} R_{jb} R_{kc} T_{ijk} , \quad \forall T_{ijk} \in \{ e_{ijk} \} , \tag{10}
\]

\[
\tilde{T}_{abcd} = R_{ia} R_{jb} R_{kc} R_{ld} T_{ijkl} , \quad \forall T_{ijkl} \in \{ C_{ijkl} \} , \tag{11}
\]

casting the moduli of the system in a semi-polar direction of growth \( \tilde{T} \) defined as the orientation vector \( g_i \) which lies parallel to the growth direction. At zero rotation, i.e. polar direction, the growth axis is \( g_i \parallel z \parallel c \). By tracing the rotational motion of the orientation vector \( \tilde{g}_a = R_{ia} g_a \) on \( \tilde{\Omega} \) the physical properties of “metastable” semi-polar states through a collective path can be found for any arbitrarily chosen orientation vector.

The solution scalars/vectors \( \{ u_i, V, \Psi \} \) are determined in the fixed–body axis and are therefore directly comparable among themselves independently of the growth direction.

2.1. Computational details

The computational procedure involves solving first the elastic–electric problem cf. equations (1) and (2); and second the Schrödinger equation cf. equation (5). This is repeated for any choice of rotation vector. The system is duly assembled in variational form according to the above prescription and subsequently solved with an application program using a set of standard computational tool kits: In particular, (i) Differential Equations Analysis Library (deal.II) \cite{9, 10}, which conveniently provides the abstract base for finite element methods; and (ii) Portable, Extensible Toolkit for Scientific Computation (PETSc) \cite{11, 12} and Scalable Library for Eigenvalue Problem Computations (SLEPc) \cite{13} for linear algebra computations and eigensystem computations respectively.

3. A representative half hyper-spheroidal quantum dot

![Figure 1. An illustration of photon emission in the particle–hole picture for the two–times–one band Hamiltonian in which a particle collapses to a hole state and emits a photon. Open circles denote particle (unoccupied) states and filled circles denote hole (occupied) states.](image)

It is instructive in the discussion below to consider the two–times–one band Hamiltonian of equation (5) as a particle–hole pair moving in an effective potential generated by the respective energy gap \( E_{\text{gap}} \) and electrostatic potential \( V \), which is in turn generated by the combined elastic–electric state
Table 1. Table of empirical constants used in this contribution. All data was taken directly from [3].

| Parameter | GaN (nm) | AlN (nm) | Parameter | GaN (eV) | AlN (eV) |
|-----------|----------|----------|-----------|----------|----------|
| $a$       | 3.189    | 3.112    | $E_g$     | 3.475    | 6.230    |
| $c$       | 5.185    | 4.982    | $m^*_z$   | 0.20     | 0.28     |
| $C_{11}$  | 390      | 396      | $m^*_i \in \{x,y\}$ | 0.20     | 0.32     |
| $C_{12}$  | 145      | 137      | VBO eV    | 0        | -0.8     |
| $C_{13}$  | 106      | 108      |           |          |          |
| $C_{33}$  | 398      | 373      |           |          |          |
| $C_{44}$  | 105      | 116      |           |          |          |
| $e_{13}$  | -0.49    | -0.60    |           |          |          |
| $e_{13}$  | -0.49    | -0.60    |           |          |          |
| $e_{13}$  | 0.73     | 1.46     |           |          |          |
| $P_{sp}$  | -0.029   | -0.081   |           |          |          |
| $\epsilon_z$ | 10.01 | 8.57     |           |          |          |
| $\epsilon_i \in \{x,t\}$ | 9.28   | 8.67     |           |          |          |

of the materials. This picture, illustrated in Figure 1 is reminiscent of the quantum oscillator model and the central potential model in atomic physics [14] as well as the Bardeen–Cooper–Schrieffer theory of superconductivity [15]. This picture asserts that we discard many–body effects that normally arise from the underlying atomic structure of the system at hand. Furthermore, in this contribution, many–body effects arising from the interactions of particles–particles, particles–holes, and holes–holes are discarded for simplicity.

Figure 2. High resolution transmission electron microscopy image along the [$\bar{1}100$] zone axis showing self-assembled GaN quantum dots grown by molecular beam epitaxy in an AlN matrix. The heterostructure was deposited on (0001) AlGaN template. The average quantum dot height is 2 nm and their projected radius is 5–8 nm. The projected quantum dot morphology is half–ellipsoidal. Credits: Thanasis Kehagias and George P. Dimitrakopoulos, Department of Physics, Aristotle University of Thessaloniki, Greece. (Used with permission).

In this contribution we consider a half oblate quantum dot of radius $A = 7.5$ nm and height $C = 4$ nm cf equation (12); which approximates the observations in high resolution transmission spectroscopy for
Table 2. Table of eigenenergies of particle \((E_p)\) and hole \((E_h)\) states and photon emission energies \((E_\gamma = E_p - E_h)\) for three selected rotation angles \(\theta \in \{0, \pi/6, \pi/3\}\) radians. All units are in eV.

| State | \(\theta\) | \(\psi_{00}\) | \(\psi_{10}\) | \(\psi_{01}\) | \(\psi_{11}\) | \(\psi_{20}\) | \(\psi_{02}\) |
|-------|---------|-------------|-------------|-------------|-------------|-------------|-------------|
| \(E_p\) | 0       | 4.00        | 4.43        | 4.43        | 4.94        | 5.00        | 5.00        |
|       | \(\pi/6\) | 3.94        | 4.40        | 4.42        | 4.92        | 4.95        | 4.99        |
|       | \(\pi/3\) | 3.66        | 4.18        | 4.33        | 4.78        | 4.82        | 4.90        |
| \(E_h\) | 0       | -0.23       | -0.51       | -0.51       | -0.68       | -0.77       | -0.77       |
|       | \(\pi/6\) | -0.17       | -0.46       | -0.50       | -0.67       | -0.75       | -0.76       |
|       | \(\pi/3\) | -0.11       | -0.23       | -0.40       | -0.56       | -0.61       | -0.65       |
| \(E_\gamma\) | 0 | 4.23        | 4.94        | 4.94        | 5.62        | 5.77        | 5.77        |
|       | \(\pi/6\) | 4.11        | 4.86        | 4.92        | 5.59        | 5.70        | 5.75        |
|       | \(\pi/3\) | 3.77        | 4.41        | 4.73        | 5.34        | 5.43        | 5.55        |

quantum dots grown in the polar \((z)\) direction (Figure 2). The GaN material occupied by the quantum dot is then a (partial) spheroid described by the simple equation

\[
\frac{x^2}{A^2} + \frac{y^2}{B^2} + \frac{z^2}{C^2} \leq 1, \quad \text{where } A = B > C, \quad z \geq 0 \quad (12)
\]

with the origin at the centre. To emulate semi–polar growth at an angle \(\theta\) measured from the \(z\) axis, we make use of a rotation tensor that operates around the \(y\)–axis. The grid on which all computations were performed was a hyper–ball of radius 75 nm containing \(O \sim 10^5\) degrees of freedom. Values for the moduli were taken directly from Reference [3] and are given in Table 1 for completeness.

3.1. Results

The eigenenergies of the quantum dot system for three angles of rotation are given in Table 2. The results we obtain for the low–lying eigenenergies of the polar quantum dot \(\theta = 0\) are comparable to alternative schemes described in the literature (Reference [3, 2]); to the author’s knowledge there is no currently available data for a semi–polar GaN/AlN quantum dot system. However, we note that our model overestimates the energy gap between particle–hole states. This is most probably due to the lack of coupling between particles and holes. In other words, we have computed the particle–hole states as a vector–valued problem with the Hamiltonian operator

\[
H_{ij} = \begin{pmatrix} H_p & H_{ph} \\ H_{hp} & H_h \end{pmatrix}, \quad \forall H_{ph} = H_{hp} = 0, \quad (13)
\]

which ignores interactions between particle–hole states (ie. no mixing terms). This can be corrected in a straightforward manner by choosing a correct form of the terms \(H_{ph}\) and \(H_{hp}\).

One point of interest to note from the energies in Table (2) is that as the rotation angle increases (that is, as the growth direction diverges from the polar direction of growth) a splitting of energy levels is observed, from the standard degeneracies known from the quantum oscillator problem, to independent energetic states. This symmetry breaking is reflected in the region of increasing angle of rotation in which the particle and hole energies become closer to the vacuum state. The consequence of this is that the energy of photon emission, taken to be the energetic difference between a particle and a hole state \((E_\gamma = E_p - E_h)\) tends to decrease as the rotation angle increases.

This feature is emphasised in Figure 3 for hole states which exhibit a more dramatic change in energy than their particle counterparts. The reason for the splitting of eigenenergies can be explained by
Figure 3. Polar plot of the six lowest hole states. Grid lines mark polar coordinates and the $x$–axis denotes the modulus of the energy of the holes states. Rotations are performed in an anti–clockwise direction and the eigenenergy is read from the $x$–axis. The results at specific rotation angles $(0, \pi/6, \pi/3, \pi/2)$ given in Table 2 correspond to radial axis lines.

observing the symmetry of the system. In general terms, the eigenfunctions ‘see’ material symmetries with respect to the rotation vector $g_i$. As the system is rotated, eigenfunctions become localised within the corners of the quantum dot and the effect of curvature of the quantum dot surfaces on the localisation of the eigenfunctions becomes more pronounced. In Figure 3, in the limit of an angle of rotation $\pi/2$ radians the eigenenergies are seen to collapse toward the vacuum as particle–hole states are ‘squeezed’ into a decreased volume at the bottom of the quantum dot. Nevertheless, this effect is possibly not wholly representative of real behaviour in semi–polar quantum dots but rather is a manifestation of the supposition that there are no inter–particle interactions given in our simplified model. If we were to take into account these interactions, we may expect that the energy splitting and divergence would be softened by the Coulomb potential.

Given the discussion above we now focus on the form of the eigenfunctions for two rotation angles $\theta \in \{0, \pi/6\}$ that are given in Figure 4. It is clear for the polar growth direction that the eigenfunction symmetries approximately follow those of the quantum oscillator; namely, we find states with degenerate symmetries, and in the order $\psi_{00}, \psi_{01} \sim \psi_{01}$ (and $\psi_{11} \sim \psi_{20} \sim \psi_{02}$). We find for polar quantum dots (upper panel of Figure 4) that particles are located at the top of the quantum dot and holes are located at the bottom of the quantum dot. These results are similar to those of Reference [3]. The picture changes,
Figure 4. Contour plots of the lowest three eigenfunctions of the model (colour online). Upper panel \( \theta = 0 \) and lower panel \( \theta = \pi/3 \). Gold shaded regions denotes particle eigenfunctions and blue shaded areas show hole eigenfunctions. The gray shaded region gives a shadow image of the quantum dot region. All eigenfunctions are \( l_2 \)-normalised.

as is to be expected, when the rotation vector \( g_i \) is aligned at \( \pi/6 \) radians (lower panel of Figure 4. In those cases the particle–hole separation align themselves along the vector \( g_i \) which immediately tends to the conclusion that the spontaneous polarisation vector \( P_i \parallel g_i \) is the dominating physical quantity in semi–polar quantum dots as it is in polar quantum dots. This compliments the observations found in Reference [1]

4. Summary
In summary we first note that in all of the above we have surreptitiously invoked the supposition that the morphology of an isolated quantum dot is unaffected by the given orientation (growth) vector \( g_i \), and vice–versa. In other words, in this paper we have assumed that a half–spheroidal geometry correctly describes the morphology of a quantum dot in any given growth direction. It is known from high resolution electron microscopy [5] that this supposition is not necessarily a good one! Nevertheless, to obtain a general scope of understanding about the effects of growth orientation, such as strain, the induced electrostatic potential, quantum confinement, and band–gap profile, it is useful to somewhat simplify the geometrical approach as has been done in this investigation.

The semi–classical model introduced in this paper was constructed by solving the elastic–electric equations followed by the two–times–one band Schrödinger equation for stationary bound states in a potential. In essence this is a revival and extension of the atomic theoretical approach to nanoscale structures. It was found that eigenenergies and eigenfunctions of the system followed those of the quantum oscillator for polar grown quantum dots. For semi–polar quantum dots, band splitting was observed due to the fact that the eigenfunctions see a distorted confinement symmetry. This scheme has been found to provide a satisfying qualitative description of an isolated two–level semi–polar quantum dot in a way that is accessible to further physical interpretation and quantification. For example, the inclusion of strain effects in the two–times–one band Hamiltonian operator [16] should improve the quantitative description of semi–polar quantum dots.

Moreover this qualitative scheme is extensible for further elaboration. For instance, one could consider taking into account inter–particle interactions using a Hartree–Fock like method, or to consider the electrostatic potential and particle–hole states within a Schrödinger–Poisson picture. These (and other considerations) are to be the concern of future investigations which, given this promising start,
indicate that this is feasible and should be rewarding. That is a good thought on which to end this paper.

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