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Influence of Aspect Ratio on the Lowest States of Quantum Rods

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ABSTRACT

The nature of the lowest states in a quantum rod is studied as a function of aspect ratio using a four-band Burt–Foreman model. Contrary to earlier work, the aspect ratio at crossing is found to be shape but not size dependent, and it is shown that the nonseparability and multiband nature of the problem leads to a complex ground-state envelope function and also to the phenomenon of level crossing. The intrinsic difference between the valence states of a quantum rod and those of a quantum wire is demonstrated.

Recently, there has been a resurgence of interest in quantum wires (QWRs) and quantum rods (QRs), due in part to new growth techniques for making free-standing and colloidal structures,[1] and also due to the observation of linearly-polarized photoluminescence in InP nanowires[1] and CdSe QRs[2,3] and the insensitivity of the interband transition energies on the length of the QRs.[2,4] An understanding of and control over these properties is necessary in order to make use of these nanostructures (e.g., as biological labeling and optoelectronic devices). Nevertheless, the theoretical study of these near-band-edge states is still at a primitive stage. Hu et al.,[2] using empirical pseudopotential theory, obtained a level crossing in the lowest two states in the valence band of a QR as the aspect ratio (diameter:length) is increased from 1:1 to 1:5 (the critical point being around 1:1.2−1:1.4 depending upon the diameter) and attributed this effect to be at the origin of the change in polarization from unpolarized for a spherical quantum dot (QD) to linearly polarized for a QR. Such a mechanism would lead to a sudden change in the polarization properties; unfortunately, the nature of the lowest two states was not extensively studied. Furthermore, their structural model of the QR is artificial, being a cylindrical shape embedded in a spherical dot. Katz et al.,[4] using a four-band Luttinger-Kohn $k\cdot p$ model within the axial approximation, found that an aspect ratio of about 1:2 was sufficient to lead to conduction- and valence-band energies that did not change much with the QR length. They also found that the lowest two states in the valence band are very close to each other, but they did not investigate possible crossing. We note that they assumed separability of the radial and longitudinal coordinates in their theory and the analysis appears to have been carried out for cubic CdSe. Li and Xia[5] modeled the QR as a spheroid and used a six-band wurtzite $k\cdot p$ model with an infinite barrier. Surprisingly, they found that the electron states were less dependent on the eccentricity than on the hole states, in contradiction to the results of Katz et al.[4] In addition, they also did not report any crossing of the lowest two states. Consequently, their mechanism for the polarization change with aspect ratio is a gradual one and differs from the results of Hu et al.[2] The most detailed study yet of the nature of the valence states appears to be due to Li and Wang;[6] however, they concentrated on the shape effect. Of relevance, though, is their conclusion that the ground state of the QR can be treated by a one-band model.

Here, we report a detailed investigation of the lowest few states in the valence band of InGaAs QRs as a function of the aspect ratio. The electron states can be treated within a one-band model and are not considered further in this paper. The goal is to understand the nature of these states without making the approximation of separability of Katz et al.[4] nor use the more artificial shapes of Hu et al.[2] and Li and Xia.[5] Indeed, we find that the nonseparability of the coordinates is crucial in getting the correct envelope functions, and the impact of the shape and size on the aspect ratio at the crossing point is clarified.

We modeled the free-standing and colloidal structures as a finite cylinder with an infinite potential barrier outside. This is the same model employed by Katz et al.[4] The calculations were done for two radii, $R = 25$ and 50 Å, and the length L was changed. We chose the material inside to

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be $In_{0.53}Ga_{0.47}As$. We decided on a cubic material rather than the hexagonal CdSe since the existence of a special *c*-axis in the latter presents additional complications.[7] The possibility of linearly-polarized emission from embedded cubic quantum wires had, in fact, been reported early on[8] and has been attributed to a band-mixing effect.[9]

The band structure of the nanostructures is calculated using a four-band $k\cdot p$ theory within the axial approximation, following the method of Sercel and Vahala.[10] It involves expressing the $k\cdot p$ Hamiltonian in terms of cylindrical polar coordinates ρ,ϕ, z and noting that a good quantum number is the projection of the total angular momentum (of the envelope function and Bloch state) along the rod axis (labeled z):

$$F_z = L_z + J_z \tag{1}$$

where the angular momentum L_z of the envelope function can only take integer values, and the J_z values belong to the $J = 3/2$ subspace of heavy-holes (HH) and light-holes (LH). The total wave function is then written as

$$\psi(\mathbf{r}) = \sum_{J_z} f_{J_z}(\rho, z) e^{i(F_z - J_z)\phi} \left| \frac{3}{2} J_z \right\rangle \tag{2}$$

where $f_{J_z}(\rho, z)$ are the envelope-function components. There is a double degeneracy with respect to the sign of F_z due to inversion symmetry. Two new features we have introduced into the Sercel−Vahala theory are the use of the Burt−Foreman Hamiltonian[11,12] (instead of the Luttinger−Kohn one) and the implementation of confinement along the rod axis. The latter is done exactly as a coupled ρ-z problem, rather than the decoupling assumed by Katz et al.[4] The calculations were performed using the finite element method (FEM). The FEM is a variational reformulation of the problem, so we do not need to treat the interfaces in any special way. It solves partial differential equations in weak form by integrating the equations. Thus slope discontinuities are captured, as calculations reveal, and one can get the correct result even with a fairly sparse grid.[13]

The first question we addressed was that of the aspect ratio necessary for the lowest states in the valence band to have converged to within 1 meV. We found that the lowest two levels converge after an aspect ratio of approximately 1:6. Of course, higher excited states will take longer to converge. But, if one is only interested in the lowest state, it can be said that, beyond an aspect ratio of 1:6, the QR is already behaving like an infinite QWR. This aspect ratio is larger than the one given by Katz et al.[4] because they did not require the same degree of convergence. Indeed, the resolution of their experimental data is of the order of tens of meV. To compare more directly to the results of Katz et al.,[4] we plot in Figure 1 the lowest states as a function of the length L near an aspect ratio of 1:1. Note that the lowest states have larger energies due to the inverted nature of the valence band and the bulk valence-band top is set at zero energy. The variation in the lowest state is seen to be about 20 meV in the range plotted. Furthermore, the energy difference between

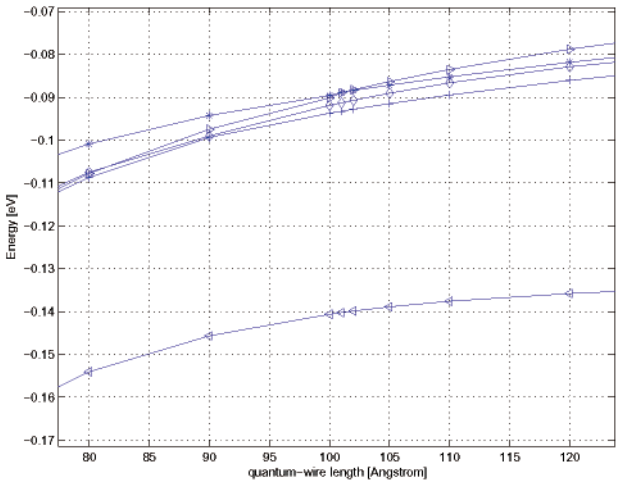

Figure 1. Lowest states as a function of length for $R = 50$ Å.

the result at an aspect ratio of 1:2 and the converged value is approximately 15 meV. Hence, the variation is outside the resolution of the experiment of Katz et al.[4]

The nature of the ground state is found to change significantly with the length L of the structure. We discuss the case of $R = 50$ Å in detail. The variation of the energies of the lowest few states is given in Figure 1. The first two curves (with asterisk and triangular markers) are for $F_z = 1/2$; the other two are for $F_z = 3/2$. We see that, at an aspect ratio slightly greater than 1:1, there is a crossing of the lowest two states. The aspect ratio did not change when we reduced the radius to 25 Å. This can, in fact, be understood in terms of the scaling of the problem. It can be shown that the eigenvalues of the Schrödinger equation (subject to appropriate boundary conditions that are applicable here) for the same quantum-dot shape but at two different length scales can be related to each other. The simpler problem of the Helmholtz equation was recently discussed.[14] Here, the use of an infinite barrier leads to a constant rescaling of all the energies; thus, the level crossing will occur at the same aspect ratio. The calculations of Hu et al.,[2] on the other hand, reveal a significant change in the critical aspect ratio. While some fraction of the change should be due to the noninfinite but large potential barrier, we believe most of it is due rather to the artificial shape chosen and which is not shape invariant as the aspect ratio is changed (in their case). Note, furthermore, that they did point out some disagreement with their experiments.

The nature of the states can be inferred from the envelope functions. We first plot the sum squared of the envelope-function components; we will call this the envelope function for short. For $L = 80$ Å, the ground state is found to have a bell-like shape (Figure 2). This is what one would expect intuitively but a proof for a multiband problem in three dimensions does not exist. Indeed, when $L = 120$ Å it can be seen that the profile in the z-direction depends on the radial position (Figure 2); furthermore, there is a node near the center of the rod. This behavior is, of course, very different from an infinite QWR for which there is separability of the coordinates and, therefore, the only dependence on z would be via the plane-wave factor $e^{ik_z z}$. Since Katz et al.[4]

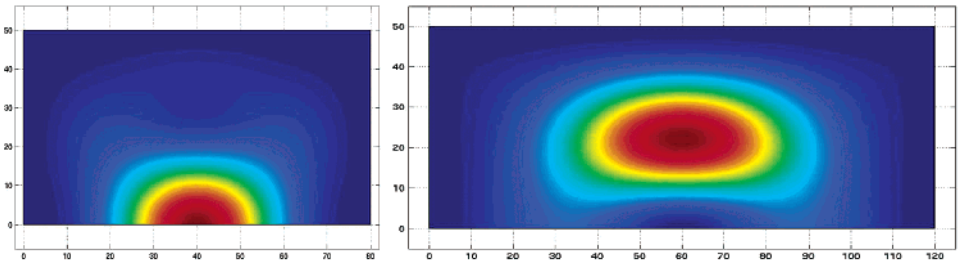

Figure 2. Sum squared of envelope-function components for lowest state for $L = 80$ Å (left) and $L = 120$ Å (right). Dark blue region has zero amplitude. Horizontal direction is z, vertical is ρ starting from center of rod.

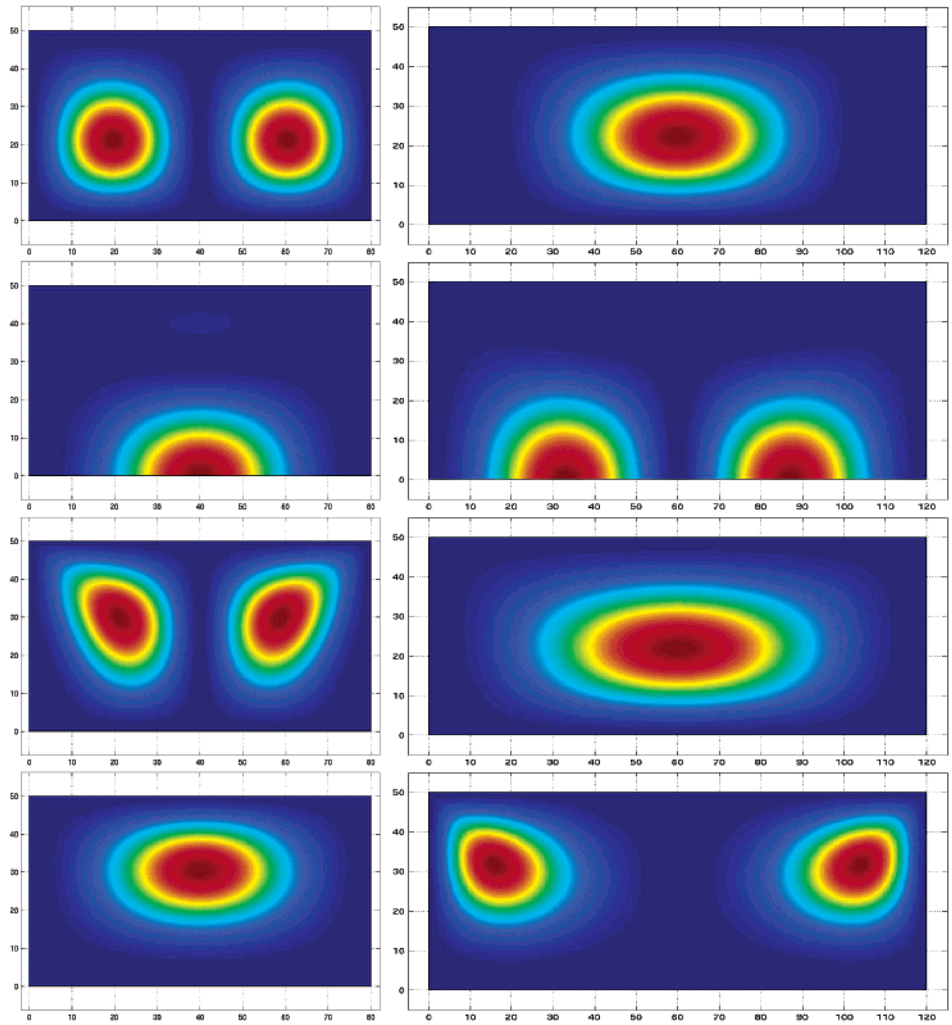

Figure 3. Envelope-function components squared (from top to bottom, $J_z = 3/2, 1/2, -1/2, -3/2$) for lowest state for $L = 80$ Å (left) and $L = 120$ Å (right).

assumed such a separability, they would not have been able to obtain this behavior. Quantitatively, this can also be expected to lead to a weaker length dependence of their valence energies.

To get more information about the nature of the states, we also plot the individual envelope-function component (modulus squared) in Figure 3. Each envelope-function component is seen to be either nodeless (even) or with one node (odd). Integrating over the structure, we find that, for $L = 80$ Å, the two most significant contributions are from $J_z = 1/2$ (81%) and $J_z = 3/2$ (13%). For $L = 120$ Å, there are three significant contributions: $J_z = -1/2$ (54%), $J_z = 3/2$ (30%), and $J_z = 1/2$ (15%). In both cases, the wave function is predominantly $|J_z| = 1/2$, but there is HH−LH mixing as for a QWR;[10] hence, we do not believe a one-band description, as suggested by Li and Wang,[6] would be appropriate. Since both states have the same F_z value, the envelopes have the same orbital angular momentum. Therefore, these two envelope functions essentially differ only in the ρ-z plane, and this is further proof that the complex behavior results from the nonseparability of the problem.

In summary, have obtained an aspect ratio of 1:6 for the

convergence of the lowest two states of a QR to within 1 meV. Crossing of the lowest two states is confirmed for our cylindrical QR based upon cubic materials. It is found that the aspect ratio at the level crossing is shape but not size dependent. The ground state is shown to be nodeless only for short QRs. Deviation from that shape for larger length is due to the nonseparability and multiband nature of the problem. The impact of this on the optical properties is currently under study.

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