

Pseudopotential Study of Electronic and Optical Properties of InAs Semiconductor Nanostructures

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Abstract—We present an atomistic pseudopotential study of the electronic and optical properties of InAs quantum dots and nanorods as a function of increasing diameter and aspect ratio. As the aspect ratio increases, energy levels cross in both conduction and valence bands, reflecting their different dependence on confinement along a specific direction. Unlike in CdSe and InP quantum rods, however, the position of the crossover between highest occupied molecular orbitals with different symmetries is found to be size-dependent and the value of the aspect ratio at the crossing to increase with the rod diameter. The level crossings at the top of the valence band are crucial to explain the evolution with elongation of all optical properties in these systems. A common monotonic behaviour of band gap, Stokes shift, degree of linear polarization and radiative lifetime, is closely linked to the variation with aspect ratio of the electronic structure of the nanocrystal valence band edge.

I. INTRODUCTION

The evolution of the electronic structure of semiconductor nanocrystals (NCs) as a function of size and shape manifests itself as the transition from the molecular to the solid state regime. To date, a number of observations of atomic-like electronic states in semiconductor NCs have been reported [1]. In particular, InAs quantum dots and nanorods have been the subject of a large volume of experimental [2], [3] and theoretical [1], [4], [5], [6] work, as they provide a typical example of quantum confined systems in the technologically important group of narrow-gap materials, and exhibit a spectrum of interesting properties that can find a wide range of applications.

However, the effect of size and shape has only just started to be addressed because of the technological challenges presented by the controllable and reproducible variation of the NCs during growth which were overcome only recently. As a result, theoretical and experimental investigations of quantum dots and nanorods (NRs) are still in their early stages. There is therefore scope for the application of a more accurate theoretical treatment to try to improve our understanding of such nanostructures.

II. METHOD

There are three main steps in our calculation of the optical properties of semiconductor nanocrystals: (i) the construction of the atomistic structure of the NC; (ii) the solution of the single-particle Hamiltonian; (iii) the calculation of the many-body effects. Firstly, an As-centered InAs spherical quantum dot with the zincblende structure is constructed by adding

successive atomic layers up to a specific cutoff radius r_{cut} . Surface atoms with only one bond are systematically removed and the dangling bonds at the surface of the quantum dots are passivated by pseudo-hydrogen atoms [5].

The single-particle (SP) states of a quantum dot are then obtained by solving the Schrödinger equation :

$$\left[-\frac{1}{2}\nabla^2 + V(r) + V_{SO}\right]\psi_i(r) = \varepsilon_i\psi_i(r) \quad (1)$$

where V_{SO} is the spin-orbit coupling term and the local potential $V(r)$ is obtained as a superposition of screened atomic pseudopotentials for atom species α :

$$V(r) = \sum_{n,\alpha} V_\alpha(|r - R_{n,\alpha}|). \quad (2)$$

Equation (1) is then solved by expanding the pseudopotential wave functions in a plane-wave basis set, using the *folded spectrum method* [1], which provides selected near-edge eigensolutions without having to solve for deeper energy levels.

We then calculate electron-hole direct and exchange Coulomb integrals [7] using the SP wave functions solution of Eq. (1). To evaluate the Coulomb integrals, we employ a size- and position-dependent microscopic dielectric function $\epsilon(r_1, r_2)$ [7].

Finally, we perform configuration interaction (CI) calculations [7], where the exciton wave functions $\Psi^{(a)}$ are constructed as a linear combination of single substitution Slater determinants $\Phi_{v,c}$ composed of the antisymmetrized products of the SP wave functions $\psi_i(r)$ solutions of Eq. (1). Once the exciton wave functions have been obtained by diagonalizing the CI Hamiltonian, the dipole matrix elements for the optical interband absorption are calculated as:

$$M^{(a)} = \sum_{v,c} A_{v,c}^{(a)} \langle \psi_v | \mathbf{r} | \psi_c \rangle \quad (3)$$

where the coefficients $A_{v,c}^{(a)}$ are the eigenstates of the CI Hamiltonian. The optical absorption spectrum is then calculated by

$$I(E) = \frac{1}{V} \sum_a |M^{(a)}|^2 e^{-(E-E^{(a)})/\Gamma} \quad (4)$$

where $E^{(a)}$ is the exciton energy and Γ represents an experimental line broadening.

III. RESULTS AND DISCUSSION

A. Electronic structure

We investigate the evolution of the electronic structure in InAs nanocrystals with a diameter of 4.0 nm and different aspect ratios (ρ), covering the length regime at the transition from spherical to wire-like structures.

Figure 1 shows the evolution of the carrier density distribution in both conduction and valence bands, where the single particle energy levels are labelled as e_i and h_i , respectively. It is evident that, unlike in spherical structures, in NRs there are two types of envelope functions (π -like and σ -like), depending on the symmetry of the wave functions in the xy -plane.

However, as in the case of spherical NCs, the character of the VB states in elongated structures displays some degree of mixing (especially evident when compared to the purer nature of the states in the CB), due to the close proximity in energy of the different levels and the large spin-orbit coupling. States with the same symmetry are further characterized according to the number of nodes along a given direction. As the aspect ratio increases, crossings of π and σ states occur in both the valence and conduction bands. In particular, the VBM symmetry changes from π to σ at a ratio $1.5 < \rho < 2.3$. It is also important to notice that the VBM is σ -type with 1 node for $\rho = 2.3$, and σ -type with 0 nodes at a ratio of 3.1. These features will have important consequences for the optical properties of NRs discussed below.

B. Optical properties

Our results, summarized in Fig. 2, clearly show a common behaviour for the shape-dependence of all optical properties considered in this work (band gap, Stokes shift, degree of linear polarization and radiative lifetimes) which can be traced back to the variation with aspect ratio of the electronic structure of the NC valence band: a fast initial variation with increasing ρ , reflecting the crossover between π - and σ -like states at the top of the VB, is followed by a slower change accompanying a further smoother crossover between σ -like

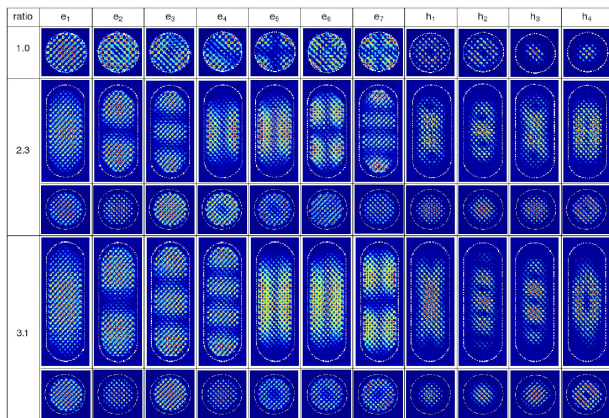


Fig. 1. Envelope functions for the four uppermost (seven lowermost) states in the valence (conduction) band in InAs NCs with aspect ratios $L/D=1, 2.3$ and 3.1, and a diameter $D = 4.0$ nm.

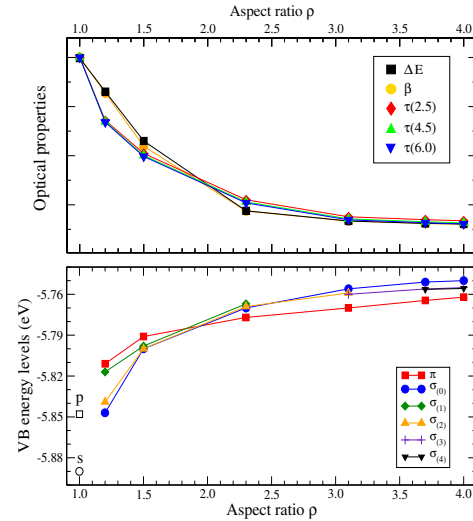


Fig. 2. The evolution with elongation of all optical properties (optical gap (ΔE), linear polarization (β), radiative lifetime (τ)) considered in this work can be traced back to the variation with aspect ratio of the electronic structure of the NC valence band. There are no labels or units on the y -axis in the upper panel as all data sets have different units and are plotted on different scales.

states with different (1, 2 and 0) numbers of nodes along the z direction. All curves then reach a plateau once the VBM becomes a $\sigma_{(0)}$ state, with the same symmetry as the CBM.

IV. CONCLUSION

The semiempirical pseudopotential method was used to investigate the evolution with elongation of the electronic structure and optical properties of 4-nm-diameter InAs NCs with aspect ratios ranging between 1 and 4, corresponding to lateral size dimensions of up to 16 nm and containing up to ~ 7000 atoms. Based on our analysis we conclude that, in contrast with the case of CdSe rods, the optical properties are not expected to show any non-monotonicity even once the excitonic Bohr radius is exceeded.

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