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Tight-binding theory of the excitonic states in colloidal InSb nanostructures

Worasak Sukkabot*

Department of Physics, Faculty of Science, Ubon Ratchathani University, 85 Sathollmark Rd. Warinchamrab, Ubon Ratchathani 34190, Thailand

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ABSTRACT

This study achieves atomistic calculations of both InSb nanocrystals (NCs) and nanorods (NRs) which are important members of the III−V semiconductor family. A more accurate model of tight-binding theory together with an applicable configuration interaction is utilized for such purposes. The discovered comparisons demonstrate that the excitonic energies calculated using tight-binding theory are more consistent with experimental results rather than others computed by the eight-band Pidgeon and Brown model within zinc-blende and wurtzite structure. In addition, detailed predictions of single-particle gaps and excitonic gaps for InSb nanorods as a function of length-to-diameter ratios are theoretically observed. When aspect ratios are increased, a reduction of single-particle gaps and excitonic gaps is duly presented because of the resulting quantum confinement. The electron and its associated hole are more confined within zinc-blende than containment in wurtzite nanostructures owing to coulomb interaction. Finally, an analysis of InSb nanostructures can provide useful guidelines for the designs required for electronic and optical properties pertaining to near-infrared active III-V semiconductor nanostructures.

1. Introduction

III-V semiconductors exhibit outstanding physical properties which are broadly implemented for possible applications which include: solar cells [1], luminescence labeling [2], light emitting diodes [3], and quantum computations [4]. In the family of indium binary compounds, until now only InP and InAs nanocrystals have been widely synthesized. Their optical properties and device applications have been extensively investigated [5–8]. However, a significant progress pertaining to InSb nanocrystals remains unexplored. Owing to small direct band gaps and very high carrier mobility properties, InSb is an excellent candidate for infrared devices and ultrafast electronic devices [9]. Of late, there are few theoretical and experimental results studying the electronic structures and optical properties of InSb nanocrystals. Maksym Yarema et al. [10] reported a new synthetic pathway for growing monodispersed colloidal InSb nanocrystals. Their results revealed that zinc-blende/wurtzite polymorphism and polytypism of InSb nanocrystals were conveniently controlled by In/Sb molar ratios with precursors. Size-dependent optical spectra of wurtzite-types of InSb nanocrystals were clearly observed. Wenyong Liu et al. [9] presented a colloidal synthesis of monodispersed nanocrystals of InSb in which the cubic zinc-blende crystal structure of InSb nanocrystals was identified using X-ray Diffraction analysis. InSb nanocrystals displayed size-dependent excitonic transitions in the near-infrared spectral range. In terms of theoretical investigations, Efros and Rosen [11] studied the size dependence of electrons and associated hole levels in spherical semiconductor nanocrystals embedded into an infinite potential

* Tel.: +66 84535 3401 4; fax: +66 845 288 381.
E-mail address: w.sukkabot@gmail.com

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barrier by using analytical theories of quantum size levels within a spherical eight-band Pidgeon and Brown model. The optical properties were determined from the inter-band transitions reduced by the energy of electron–hole coulomb interaction. The excitonic spectra agreed less well with optical gaps measured using photoluminescence excitation, especially in the smaller nanocrystals [9,10]. According to the literature above, there is only one analytical model which certifies the optical properties of zinc-blende and wurtzite InSb nanocrystals. Therefore, it is a significant challenge to implement a more realistic and accurate model which investigates the excitonic states of InSb nanocrystals. An atomistic tight-binding theory is mainly determined for this purpose. Size-dependent comparisons amongst the tight-binding method, an eight-band Pidgeon and Brown model, as well as experimental data are obviously comprehended in both crystal structures.

Apart from the spherical nanocrystals, detailed calculations of colloidal InSb nanorods are still unidentified. Semiconductor nanorods have already demonstrated substantial advantages over spherical nanocrystals in several possible applications. CdSe nanorods exhibit better performance in photovoltaic cells due to better charge transport properties [12,13]. It was found that the implementation of elongated nanocrystals could reduce the non-radiative carrier losses from Auger recombination when compared with spherical nanocrystals emitting light within a similar wavelength [14,15]. An atomistic pseudo-potential method was used to study the evolution of the electronic structure and optical properties of 4.00 nm diameter InAs nanocrystals as a function of aspect ratios by Puangmali et al. [16] Hence, it is major curiosity for providing detailed predictions of the single-particle and excitonic gaps for InSb nanorods as a function of increasing length-to-diameter ratios using the tight-binding method. These forecasts can be useful to engineer the physical properties of InSb nanorods for further applications.

When implementing nanocrystals or nanorods for feasible applications, detailed knowledge of the structural and optical properties across these nanostructures is considered indispensable. Currently, there are various theoretical approaches ranging from first-principle calculations to empirical models. Owing to the high computational demand of first-principle calculations, empirical models are widely implemented to study nanostructures. There are two main empirical models: the pseudo-potential [17,18] and tight-binding model [19–23] which describe wave functions by atomistic description. The distinction between these two atomistic models is the degree of atomic detail included in the model. Within a tight-binding model, atomistic detail is limited to a small basis set, whilst in a pseudo-potential model the atomistic description is described with a large basis set. Thus, the tight-binding model is computationally less expensive than the pseudo-potential model. The atomistic tight-binding model is an excellent candidate to study such relatively immense and complicated systems.

The paper is organized as follows. Section 2 gives a brief description of the sp^3s^* empirical tight-binding method, and the electron–hole interaction in such nanostructures. In Section 3, the paper discusses the comparisons of single-particle-gaps and excitonic gaps for InSb nanostructures. Fine concordance is found with recently available experimental data. In addition, calculations of InSb nanorods with various aspect ratios are presented. Finally, Section 4 summarizes the results.

2. Theory

2.1. The empirical tight-binding description of nanostructures

The computational process starts with a definition of atomic positions. The crystal lattice of an InSb nanostructure is taken to be in zinc-blende or wurtzite structures depending upon the experimental data. The wave function is written as a linear combination of atomistic orbitals localized on each atom. The single-particle wave functions are defined as

$$\psi = \sum_{R=1}^{N_{at}} \sum_{\alpha=1}^{10} C_{R,\alpha}\varphi_{\alpha}(\vec{r}-\vec{R}) \tag{1}$$

where α stands for the localized atomic orbitals on atom R with N_{at} being the total number of atoms in the system. In this work, I have implemented the sp^3s^* empirical tight-binding model for this purpose. The coefficients $C_{R,\alpha}$ determining the ith single-particle state and the corresponding single-particle energies are found by diagonalizing the empirical tight-binding Hamiltonian [24]:

$$H_{TB} = \sum_{R=1}^{N_{at}} \sum_{\alpha=1}^{10} \varepsilon_{R\alpha} c_{R\alpha}^{\dagger} c_{R\alpha} + \sum_{R=1}^{N_{at}} \sum_{\alpha=1}^{10} \sum_{\alpha'=1}^{10} \lambda_{R\alpha\alpha'} c_{R\alpha}^{\dagger} c_{R\alpha'} + \sum_{R=1}^{N_{at}} \sum_{R'=1}^{N_{at}} \sum_{\alpha=1}^{10} \sum_{\alpha'=1}^{10} t_{R\alpha,R'\alpha'} c_{R\alpha}^{\dagger} c_{R'\alpha'} \tag{2}$$

in which the operator $c_{R\alpha}^{\dagger}(c_{R\alpha})$ creates (annihilates) the particle on the orbital α of atom R. The Hamiltonian is parameterized by the on-site orbital energies $\varepsilon_{R\alpha}$, the spin-orbit coupling constant $\lambda_{R\alpha\alpha'}$ and the hopping matrix elements $t_{R\alpha,R'\alpha'}$ connecting different orbitals situated at neighboring atoms. In this model, a nearest-neighboring approximation is used and the parameterization is also used in this work [25].

2.2. Description of electron–hole interaction confined in the nanostructures

Once the single-particle spectra are numerically found, the Hamiltonian of interacting N_e electrons and N_h holes distributed on the single-particle states is defined as [26]

$$H = \sum_i E_i c_i^{\dagger} c_i + \sum_{\alpha} E_{\alpha} h_{\alpha}^{\dagger} h_{\alpha} + \frac{1}{2}\sum_{ijkl} V_{ijkl}^{ee} c_i^{\dagger} c_j^{\dagger} c_k c_{ll} + \frac{1}{2}\sum_{ijkl} V_{ijkl}^{hh} h_i^{\dagger} h_j^{\dagger} h_k h_l - \sum_{ijkl} V_{ijkl}^{eh} h_i^{\dagger} e_j^{\dagger} e_k h_l \tag{3}$$

The first two terms account for the single-particle energies, the third and fourth terms describe the electron–electron and hole–hole coulomb interactions, respectively, and the last term introduces the electron–hole coulomb interactions. Small contributions from electron–hole exchange terms have been omitted. The negative sign in the last term stems from the fact that electrons and