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How to Describe the Electronic Structure of Semiconductor Quantum Dots

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ABSTRACT

I describe a new strategy for predicting the electronic properties of zero-dimensional semiconductor quantum dots, including the excitonic spectrum. This methodology was applied recently to both "free standing" (e.g. colloidal) and t semiconductor-embedded (e.g. self-assembled) dots.

1. Experimental advances in growth and characterization of semiconductor quantum dots call for theoretical methods capable of predicting the measured electronic structure as a function of the shape and size of the dot. The objectives of such an endeavor are to predict (a) the single-particle energy levels and their confinement energies, (b) the electron-hole Coulomb and exchange energies, (c) the ensuing two-particle excitonic spectrum and transition probabilities, (d) the energies needed to charge quantum dots ("Coulomb blocade") and (e) the nature of the electronic states in the system (e.g. s,p,d..., heavy hole-like, light-hole-like, Γ-like or X-like, etc).

2. For quantum-wells and superlattices (that are confined in only one dimension), there is a highly successful "standard model" for addressing the above theoretical requirements. This is the well-known effective-mass-approximation (EMA) k•p method. In this approach the wavefunctions of the nanostructure are expanded in terms of N_B Bloch states of the underlying bulk -periodic solid. This expansion is limited, however, only to Brillouin-zone center ("gamma") Bloch states. If $N_B = 1$ we have the "single band EMA" or "particle in the box". If we use the top of the valence band Γ_{15V} state to expand the wavefunction of the nanostructure then $N_B = 6$ (due to 3-fold spatial degeneracy of this p-state, times the 2-fold spin degeneracy). This approximation is called "6x6 k•p". If we add to the basis the bulk conduction band minimum Γ_{1C}, then $N_B = 8$ and the approximation is called "8x8 k•p". For quantum wells and superlatteces, the "8x8 k•p" model has provided a very good account of the electronic structure, using input ("Luttinger") parameters drawn

from the band structure of the bulk-periodic solid.

3. Quantum-dots lack translational periodicity in all 3 spatial directions, so they are conceptually more removed from the 3D bulk-periodic crystal than are the 2D periodic quantum wells. Would a bulk-crystal-derived formalism such as the EMA suffice for describing quantum dots? Mathematically, this question means "how many gamma-like 3D periodic bulk Bloch states does it take to capture the essential features of the wavefunctions of nD periodic nanostructure?" (n=0 for dots, n=1 for wires).

4. Until recently, the answer to the above question was unknown, since there wasn't any method capable of using an arbitrary number N_B of bulk basis functions for expressing the nanostructure wavefunctions. In fact, the success of the EMA was examined primarily by contrasting its predictions directly with experiments. This is usually an eminently reasonable way to test the validity of any theory. However, this is not the case if one uses adjustable parameters to fit the theory to experiment. This was often done in application of the EMA to quantum dots. Indeed, often the EMA parameters were adjusted to fit the experiments they claim to explain theoretically. For example, consider k•p calculations on CdSe dots: Norris and Bawendi [1] say, "We use standard nonlinear least-squares method to globally fit the experimental data...our fitting routine adjusts three parameters: the Luttinger band parameters $\gamma 1$ and $\gamma 2$ and the potential barrier for electrons." In another work, Efros et al. [2] say, "The position of the quantum size levels are very sensitive to the valence band energy parameter; those used for calculation...give the best description of the CdSe microcrystal absorption spectra." Wind et al. [3] say, "Fig. 1 shows the experimental values...the lines in fig. 1 have been calculated following a model including the valence mixing...The best correspondence could be obtained [by] choosing a Luttinger parameter $\gamma = 0.38$..." Since in such cases the EMA theory is explicitly fit to experiment, it cannot examine the legitimacy of either its successes or its failures. In these cases, good agreement with experiment does not necessarily imply good theory.

5. So how many gamma-like 3D-periodic bulk states *are* needed to expand a wavefunction of a nanostructure? The answer was recently given by Wood et. al [4-5] for AlAs/GaAs (001) superlatteces and quantum wells, by Wang and Zunger [6] for X-like states in bulk solids, and by Fu, Wang and Zunger [7,8] for quantum dots. These authors "projected" the pseudopotential-calculated wavefunctions of superlatteces, quantum wells and dots onto the gamma-like states of bulk-periodic solid, finding how many of the latter are needed for expanding the former. The unpleasant answer is that a reasonable description of even the *band* structure away from the Brillouin zone center requires as many as $N_B = 30$ gamma bands, (see figures 3 and 4 in Ref.6), while small quantum dots require a *few hundred* bulk bands for a

quantitative description.

6. So what happens if we disregard the above noted "mathematical warning" and go ahead using the EMA with a small number N_B of bands? Can we adjust the many parameters and still get away with this? The answer is that one can not do this with impunity. For example, the EMA with small N_B can even misrepresent the correct *physical symmetry* of the nanostructure, leading to qualitatively incorrect predictions. Here are a few examples:

- A film made of p monolayers of zincblende material can either have or lack reflection symmetry, depending on whether p is odd or even. Consequently, the energy levels of thin films oscillate [9] with the film thickness. The continuum-like EMA does not recognize reflection symmetry *and produces a monotonic dependence of the film energy levels on the film thickness.* Pseudopotential calculations [9] produce the expected odd-even oscillations.

- A spherical dot made of zincblende material (e.g., InP, AlAs) does not have spherical symmetry. Its physical T_d (tetrahedral) symmetry permits, in fact, mixing of s-like with p-like character in the wavefunctions. [10] The simple EMA, on the other hand views such dots as spherical with "s-like" or "p-like" states. This led to the expectation [11,12] that single-photon absorption experiments ("s→s" or "p→p") and two-photon ("s→p") experiments will reveal radically different spectra, reflecting "different level symmetries". In fact, the measured single-photon and two-photon spectra are virtually identical. This is the case for CuCl [11], CdSe [12] and InP dots. Analysis [10] of the real wavefunctions reveal indeed heavy mixing of s and p character, consistent with experiment.

- A square-based pyramidal dot made of zinc blend material (e.s, InAs) does not have C_{4V} symmetry [13]. Consequently, the two in-plane directions [110] and [$\bar{1}$10] are not equivalent. In contrast, the EMA k•p views the square-based pyramid as a classic pyramid, with 4-fold rotation symmetry. Consequently, the polarization ratio P[110] / P[$\bar{1}$10] for the lowest electron-hole transition in SK dots of InAs is ~ 1 in k•p. A realistic Pseudopotential calculation [14] gives a ratio of 1.3. The same problem exists in (001) superlatteces that lack a common atom, e.g. [15] InP/GaAs or InAs/GaSb: k•p leads to a polarization ratio of 1, while experiment and pseudo potential calculation give a "giant polarization".

7. Other difficulties when using the EMA:

- Sometimes quantum dots have X-derived or L-derived low-energy states that are missed by the Γ based EMA. Examples include: (a) Sufficiently small GaAs dots,

wires and films have an X_{1C}-like conduction band minimum [16,17,18] (b) The second bound electron state of InP dots is L_{1C}-derived [10] (c) Under hydrostatic pressure, InP dots [19] and GaAs-embedded-InAs dots[20] have X_{1C}-derived conduction band minium. (d) The Γ-X coupling matrix element in superlatteces and quantum dots[19,20] can be as large as the level spacings.

● Real surfaces (e.g. chemically-passivated, or reconstructed, or defects at surfaces) and real interfaces (e.g. coherently strained and/or inter diffused) can not be modeled by the EMA that is inherently "surfaceless".

● In strained quantum dots (e.g. InAs embedded in GaAs) the electronic levels shift and split due to strain, but EMA-based methods describe this coupling only via *linear* deformation potentials. Recent calculations [14] have shown that the linear approximation can lead to errors of a few hundred meV for strongly strained dots (e.g. InAs/GaAs, with its 7% strain).

8. Is there an easy way out?

One could add more basis functions to the conventional k•p, but this comes with an unpleasant rapid increase in mathematical complexity and in the number of fictitious adjustable parameters that are not "physical observables" which could be measured. It is likely that the inertia of the EMA for quantum dots, propelled by its many successes in higher-dimensional nanostructures (e.g. quantum wells) and its inherent simplicity and adjustability, will continue to promote its widespread use, especially among experimentalists, as proclaimed in this meeting by Ray Tsu. However, there is a possibility of moving forward, using a completely different approach, which we have recently developed [21-27]. It is not always an *easy* way out, but it overcomes *all* of the objections we have raised above, it provides all physical quantities listed in paragraph 1, and can be applied to dots, wires and films of almost any semiconductor, with any shape or strain profile.

9. So what is the basic idea?

Molecules, quantum dots and solids are made of atoms that can be characterized by approximately transferable atomic pseudopotentials $v_\alpha(r)$. The EMA does not recognize atoms or potentials. Instead, it describes the electronic structure via matrix elements over Bloch functions, retaining the "coarse", or "long-wavelength" characteristics of the molecule or dot, thus smoothing over its "fine", or "atomistic" structure. Not only does this remove sometimes the true physical symmetry of the molecule or dot, but it also results in a large number of parameters (=matrix elements) whose magnitude and coupling to strain are difficult to determine

as $N_B \rightarrow \infty$. Instead, we will treat a molecule, dot or solid as a linear combination of atomic pseudopotentials placed spatially where atoms are located. This immediately gives you the right symmetry of the object at hand, including the opportunity to model its surface or interface with atomic detail. Also, since such molecular potentials depend on the atomic positions within the molecule, and since "strain" is merely a collection of (displaced) atomic positions, this approach gives you in a natural way the full coupling of strain to the electronic structure. What we need to know is the screened atomic potential for each atomic type. The theory of construction of screened atomic psudopotentials that correctly reproduce a given set of measured bulk or molecular properties and *ab-initio* calculated wavefunction is described in refs [21,28] and will not be discussed here. The full informational content of the chemistry of our problem is encoded in the functions $V\alpha(r)$ for each atom type α.

Once we have constructed the molecular potential, we place each molecule/dot in a fictitious large unit cell and periodically repeat the cell so as to create (artificial) 3D periodicity. When studying 'free-standing" (e.g. colloidal) dots we surround each dot in a unit cell by a chemical passivation layer, followed by a thicker layer of vacuum, intended to separate the quantum dots. When studying matrix-embedded (e.g. InAs-in-GaAs "self assembled") dots, we surround each dot in a unit cell by its (usually strained) matrix material.

Now that we have a mathematically translationally periodic Hamiltionian, we can find its eigen solutions by employing much the same methods used in ordinary "band theory". We can expand the wavefunction of the dot as a linear combination of plane waves[22-27], or as a Linear Combination of Bloch bands (LCBB)[29]. The problem is that a dot has many more atoms per supercell (10^3-10^6) than an ordinary periodic solid ($\sim$10 atoms). Thus, the size of the Hamiltionian matrix for a dot is too large. Fortunately, however, the problem can be drastically simplified by realizing that the physics of quantum dots is often restricted to the energy levels in the vicinity of the band gap. For example, a dot made of 1000 Si atoms has 2000 occupied valence levels (assuming s+3p states for each atom), but all we care about is the 10-100 highest energy valence levels (plus a similar number of empty conduction states). We have invented a "Folded Spectrum Method" [22, 26] that permits us to find eigen solutions in a desired "energy window", without wasting computational effort on obtaining the remaining, less interesting states. Thus, the total computational effort rises only slowly (in fact, linearly) with the number of atoms N in the dot, rather than the N^3 scaling in common band structure methods.

Once we have found the energy levels and wavefunctions in the vicinity of the HOMO and LUMO, we can set-up a "configuration interaction" treatment [30,31] for describing the excitonic spectra beyond "mean field" theory. An excitonic state

is formed form a linear combination of products of a valence orbital times a conduction orbital. The expansion coefficients in this linear combination are found by seeking a variational solution. The hamiltonian matrix of this problem corresponds to both Coulomb and exchange electron-hole interactions that are computed explicitly from the orbitals. Solving the variational problem gives the two-particle excitonic levels and wavefunctions, thus the excitonic absorption spectrum.

10. Summary and references of what has been calculated so far with this method for free-standing (colloidal) dots:

- Band gap vs size for Si [26,32,33], InP [34], CdSe [35,36] and InAs [37] dots. The size scaling R^{-m} has $m \approx 1\text{-}1.5$ not $m=2$ as in EMA.

- Wavefunction analysis of InP dots, showing that the HOMO is s-like, not p-like as predicted by the EMA [8].

- The electron-hole Coulomb energies [38] of Si, InP and GaAs, showing that the EMA overestimates them by up to 40%. The size scaling R^{-n} has $n<1$.

- The electron-hole exchange energies [30] of Si, InP and CdSe showing that an hitherto neglected, long-range component exists, reflecting monopole-interactions. The size scaling R^{-p} has $p\sim 2$, not $p=3$ as previously assumed.

- The full excitonic spectrum of CdSe [36], InP [10] and InAs [37] dots.

- The effect of imperfect surface passivation (leading to cation and anion "dangling bonds") on the electronic structure, including the appearance of localized gap states capable of trapping carriers [34].

- Effects of pressure on direct-to-indirect transitions in InP dots [19].

- Effects of size on direct-to-indirect transitions in GaAs dots [16,17].

11. Summary and references of what has been calculated with this method so far for embedded ("self assembled") quantum dots:

- The prediction that while free-standing InP dots have a direct band gap, a GaP-embedded InP dot has an interface-localized "indirect" conduction band [39].

- The prediction that under pressure, the GaAs-embedded InAs dot will also have an interface-localized conduction band [20].

- The prediction [40] that a set of nested spheres ("Russian Doll") of GaAs/AlAs/GaAs/AlAs... can be made so that the hole wavefunction is localized on the central GaAs sphere, while the electron wavefunction is localized on an external shell, thus affecting charge-separation *on the same material.*

- The electronic structure of square-base InAs pyramid embedded in a GaAs matrix, showing [14,41,25] (a) splitting of the electron p state (b) strong in-plane anisotropy of the lowest excitonic transition (c) that as many as 5 confined electron levels exist and (d) that the hole states are so heavily intermixed that no (s, p, d...) nodal structure remains. All of these predictions are surprising in light of previous EMA calculations.

ACKNOWLEDGMENT

I would like to thank my collaborators in this project A. Franceschetti, H. Fu, J. Kim, L.W. Wang and A. Williamson. This work was supported by US DOE through OER-BES-DMS.

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