Predicting the electronic properties of 3D, million-atom semiconductor nanostructure architectures

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Abstract: The past ~10 years have witnessed revolutionary breakthroughs both in synthesis of quantum dots (leading to nearly monodispersed, defect-free nanostructures) and in characterization of such systems, revealing ultra narrow spectroscopic lines of <1meV width, exposing new intriguing effects, such as multiple exciton generation, fine-structure splitting, quantum entanglement, multi-exciton recombination and more. These discoveries have led to new technological applications including quantum computing and ultra-high efficiency solar cells. Our work in this project is based on two realizations/observations: First, that the dots exhibiting clean and rich spectroscopic and transport characteristics are rather big. Indeed, the phenomenology indicated above is exhibited only by the well-passivated defect-free quantum dots containing at least a few thousand atoms (colloidal) and even a few hundred thousand atoms (self assembled). Understanding the behavior of nanotechnology devices requires the study of even larger, million-atom systems composed of multiple components such as wires+dots+films. Second, first-principles many-body computational techniques based on current approaches (Quantum Monte-Carlo, GW, Bethe-Salpeter) are unlikely to be adaptable to such large structures and, at the same time, the effective mass-based techniques are too crude to provide insights on the many-body/atomistic phenomenology revealed by experiment. Thus, we have developed a set of methods that use an atomistic approach (unlike effective-mass based techniques) and utilize single-particle + many body techniques that are readily scalable to ~10^3-10^6 atom nanostructures. New mathematical and computational techniques have also been developed to accelerate our calculations and go beyond simple conjugate gradient based methods allowing us to study larger systems. In this short paper based on a poster presented at the DOE SciDAC06 conference we will present the overall structure as well as highlights of our computational nanoscience project.

1. New algorithms for calculating electronic properties of large nanostructures

The infrastructure we have developed to perform atomistic pseudopotential calculations of large nanostructures is composed of a series of different steps as shown in Figure 1. The input geometry is determined from geometrical considerations and experimental data. The atomic positions are obtained by minimizing the strain field using the classical valence force field (VFF) method trained to reproduce LDA equilibrium geometries of prototype structures [1]. The potential of the system is then

calculated using a superposition of screened atomic potentials which are fitted to the experimental band structure and LDA wavefunctions. Once we have calculated the potential we need to define a basis set in which the single particle Schrödinger equation will be solved. We have developed two different methods, one that uses a simple planewave basis set up to a certain energy cut-off (ESCAN[2]) and the other which uses a linear combination of strained bulk bands (SLCBB[3]). The single-particle Schrödinger equation is then solved as an interior eigenvalue problem, i.e. only a few eigenstates near the band gap are computed using the folded spectrum method. Once the single-particle energies and wave functions have been obtained the next step is to calculate the electronic excitations of the quantum dot. This task is accomplished using the configuration interaction (CI) method after first calculating the Coulomb and exchange integrals. Finally we calculate different properties of the system such as absorption and emission spectrum (see Figure 1 for a full list) based on post processing of the outputs of the other codes. This pioneering methodology was developed by Zunger, Wang, Franceschetti and collaborators in the period 1995 to 2003.
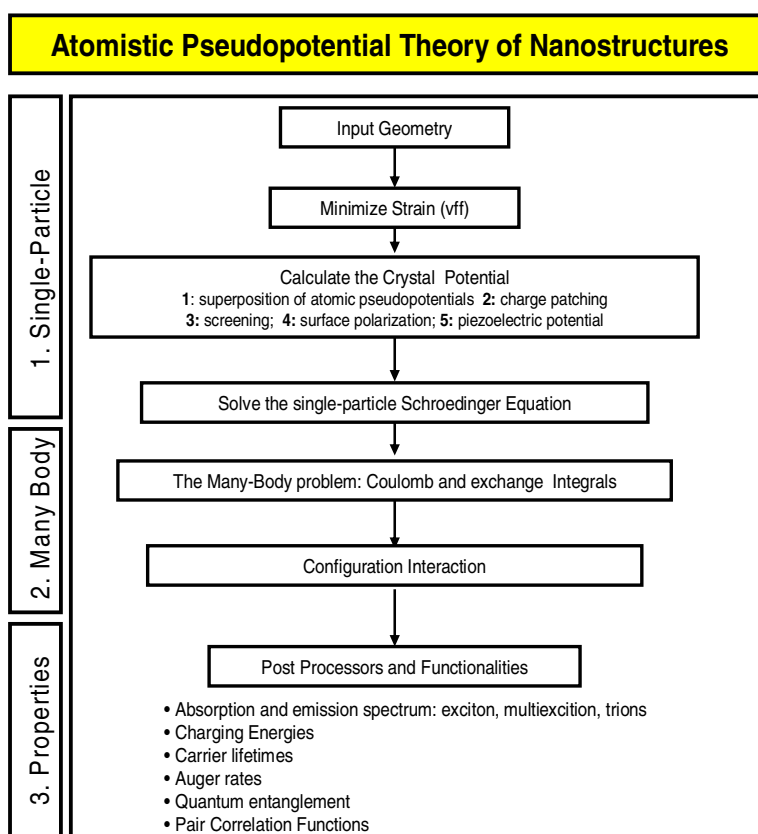

Figure 1: Flowchart of the computational method developed for the electronic structure of large nanosystems (vff denotes the valence force field model).

   The new work in this project extends the scope of the previous work with more advanced methods that afford a degree of accuracy comparable to first principles methods, and more powerful algorithms that allow the study of much larger systems. In particular we have developed a charge patching method [4] to derive more accurate *ab initio* potentials without doing the direct *ab initio* calculation, We have also developed the capability to include piezo-electric fields in quantum dot calculations [5], and have developed new methods to solve the CI problem for large systems including millions of configurations. We have also tested out new solvers and preconditioners for solving the interior eigenvalue problem for the single particle Schrödinger equation. In the remainder of this paper we will present some highlights from this new work.

2. The charge patching method

The charge patching method (CPM) allows us to go beyond the empirical pseudopotential method (EPM) and generate *ab initio* quality potentials without doing an explicit direct *ab initio* calculation for the whole system. This is achieved by calculating charge motifs (the charge belonging to one atom) of atoms embedded in solids (or say, embedded in a local bonding environment). Then one patches these charge motifs together for a nanosystem to generate its total charge density [4]. The total charge density is then used via the density functional theory (e.g., LDA) to generate the total potential of the system. The motifs are calculated from self-consistent calculations of small prototype systems with the same local bonding environments as the large nanostructure. The resulting patched charge density is found to be very close (within 1%) of the fully self-consistent *ab initio* calculated charge density, and the electron eigenvalue difference is typically around 20 meV. We have further developed the charge patching method in the directions of surface passivation, surface motifs and polarized systems. Figure 2 shows some results for the charge response and screened potential, calculated using polarization motifs, for a GaAs slab with an external potential.
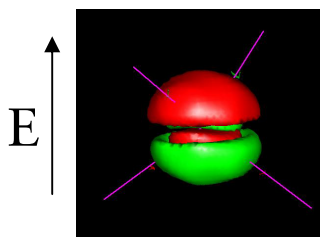

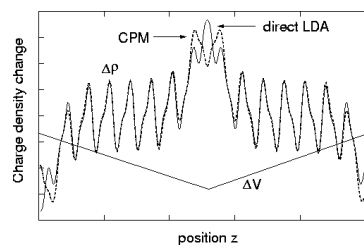**Figure 2 (a).** The polarization motif of Ga atom in GaAs.

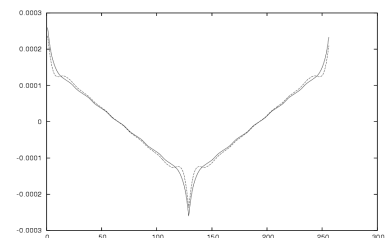**Figure 2 (b).** The charge response to a total additional potential ΔV in a GaAs slab.

Figure 2 (c). The screened potential of a V shaped external potential in a GaAs slab. Solid line: LDA; Dashed line: CPM.

3. Semiconductor nano dumbbells

Single-particle (using the charge patching method) plus many-particle calculations of the electronic states of semiconductor nano dumbbells have been performed to demonstrate how geometrical features (e.g. the width of the dumbbell wire) determine, through quantum-confinement and electron-electron correlation effects, the localization of the wave functions. We have considered a nano dumbbell consisting of two CdTe quantum dots connected by a CdSe quantum wire of variable diameter. Remarkably, we find that for narrow CdSe wires many-particle effects can alter carrier localization and degree of entanglement, thus affecting the electronic properties of nano circuits that include quantum dots and quantum wires. In this work we use a new CI method that allows us to solve for a larger number of configurations and larger systems than previous approaches. More details of this work can be found in reference [6].
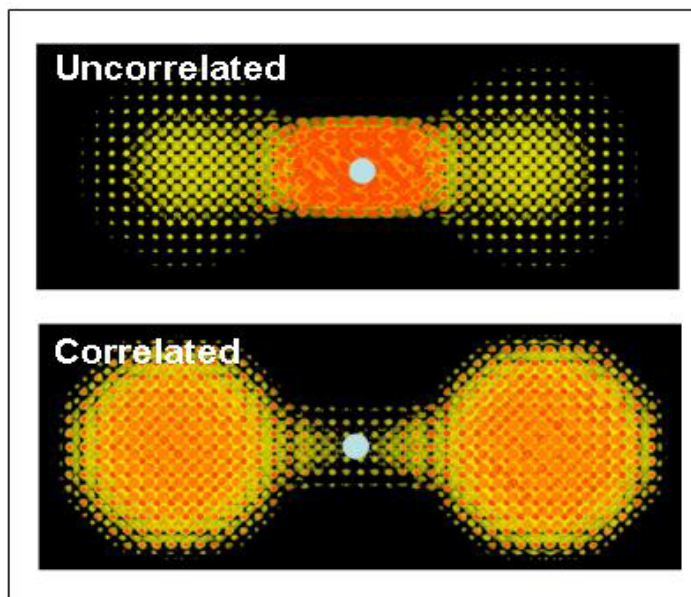
Figure 3: Correlation function for two electrons in a CdTe/CdSe nano dumbbell (~6,000 atoms). One electron is fixed at the center of the CdSe wire (white circle). The second electron is localized in the CdSe wire if electron-electron correlations are neglected and in the CdTe dots if correlation effects are included. This illustrates the importance of many-particle effects in describing the electronic properties of complex nanostructure architectures.
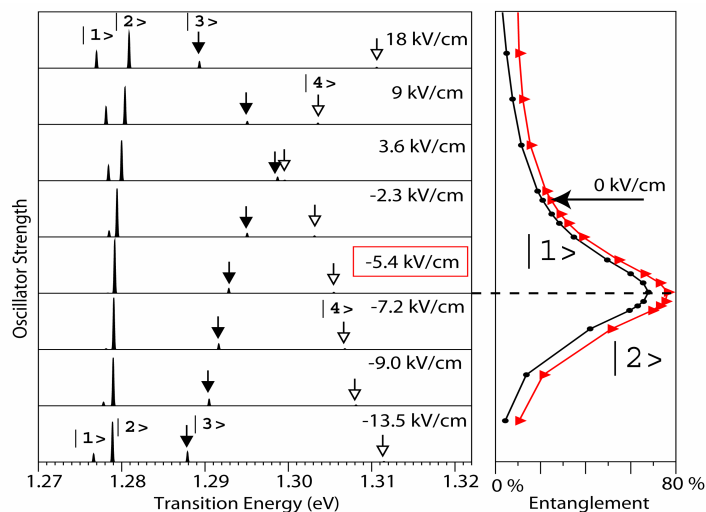

Figure 4: Calculated photoluminescence spectrum from a quantum dot molecule made of two vertically stacked InGaAs quantum dots as a function of the electric field. Degree of entanglement of the bright excitons as a function of electric field (left figure). At the field of -5.4 kV/cm the entanglement is maximized and reaches 80%. At this field, the state |1> anticrosses with states |2> and loses its oscillator strength. This gives a clear optical signature of entanglement. The dots contain about 50,000 atoms each and the complete system including the host barrier material contains about 1.6 million atoms.

4. Coupling and Entanglement of Dot Molecules

Two self-assembled quantum dots can be placed on top of each other forming a so-called quantum dot molecule. We addressed the question as to whether such a system can store an entangled exciton state and if the entanglement in such a geometry is tunable by electric fields. This is a relevant question for the field of quantum computation where quantum bits (qubits) must be coherently superposed into states with high entanglement. Figure 4 (left figure) shows the photoluminescence (PL) of such a double-dot for different electric fields and the right figure, the corresponding degree of entanglement. We find that entanglement can be tuned by electric fields (in our case 5.4 kV/cm gives a degree of entanglement of 80%) and that highly-entangled states give a clear optical signature in PL: the two bright excitons lines |1> and |2> coalesce. A more detailed description of this work can be found in reference [7]

5. Material optimization using the "Hydra" representation of an alloy unit cell

One would like to automatically design materials with specified properties. For example, what arrangement of atoms in a semiconductor alloy results in minimum internal strain? To that end, we have adapted an approach from reference [8], specifically, to constrain the atoms to a fixed underlying crystal lattice, within our existing alloy optimization infrastructure. In this approach, the defining "unit cell" of a crystal is represented by a "hydra," a snake-like chain with (in this case) three heads. The heads define the periodic repetitions of the unit cell, while the rest of the body defines the locations and identities of the atoms in the unit cell. Our hierarchically parallel implementation [9] has solved a strain-minimization problem for a 48-atom InGaN alloy unit cell with fewer objective function evaluations than other methods. More details of this work will be published elsewhere.
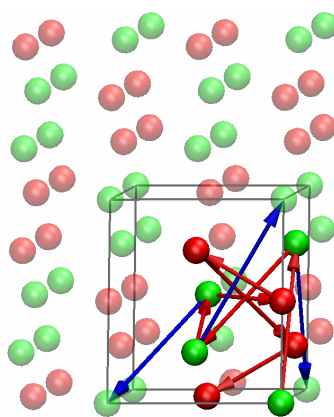

Figure 5: Eight cation hydra configuration, the resulting unit cell and the chalcopyrite structure it defines

6. The interior eigenstate problem for large nanosystems

The primary mathematics and computational science challenge within the atomistic quantum-mechanical approach is the development of an efficient solution methodology for finding interior eigenstates of very large systems. The initial method implemented in the PESCAN (Parallel Energy SCAN) package is based on a conjugate gradient (CG) type algorithm applied with the "Folded Spectrum Method (FSM)" [2]. This method is fairly efficient and extremely robust when compared to other classical algorithms but its convergence may become unacceptably slow for systems of increasing size. We have investigated other strategies using state-of-the-art algorithms for the eigenvalue problems at hand, in particular variations of the CG, the locally optimal block preconditioned CG (LOBPCG), and Jacobi-Davidson methods. Figure 6 shows a comparison of several eigensolvers in terms of number of matrix-vector products and in terms of time to solution for

finding 10 eigenstates corresponding to the highest VBM states for four CdSe quantum dots of increasing size from 39 to 1061 atoms. More details of this work can be found in references [10,11].
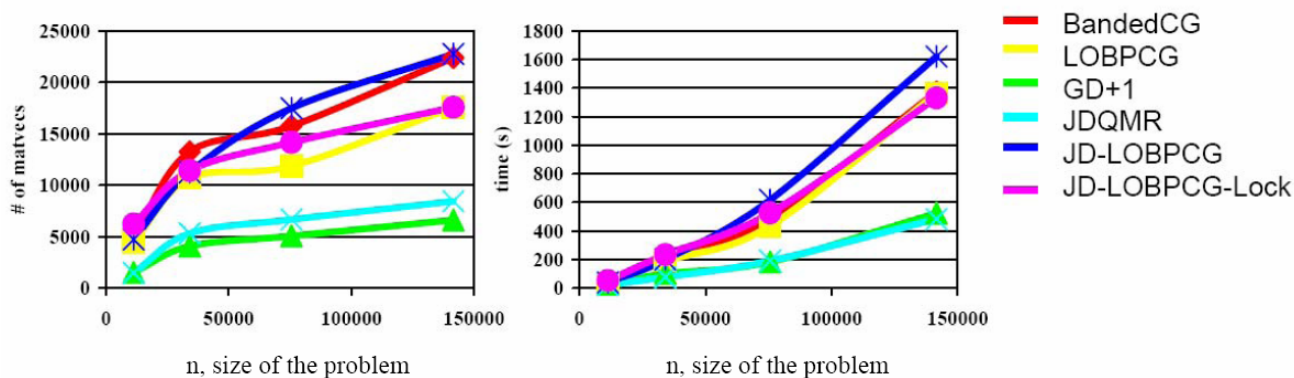

Figure 6: Comparison of eigensolvers in terms of number of matrix-vector products and in terms of time to solution for finding 10 eigenstates corresponding to the highest VBM states for four CdSe quantum dots of increasing size from 39 to 1061 atoms. The x axis is the number of plane waves. The runs were performed on 16 processors of an IBM SP. The results show best performance for the JDQMR method, a classical Jacobi-Davidson method that uses a QMR iterative solver to obtain corrections for the eigenvectors of interest, and the GD+1 method (Generalized Davidson+1).
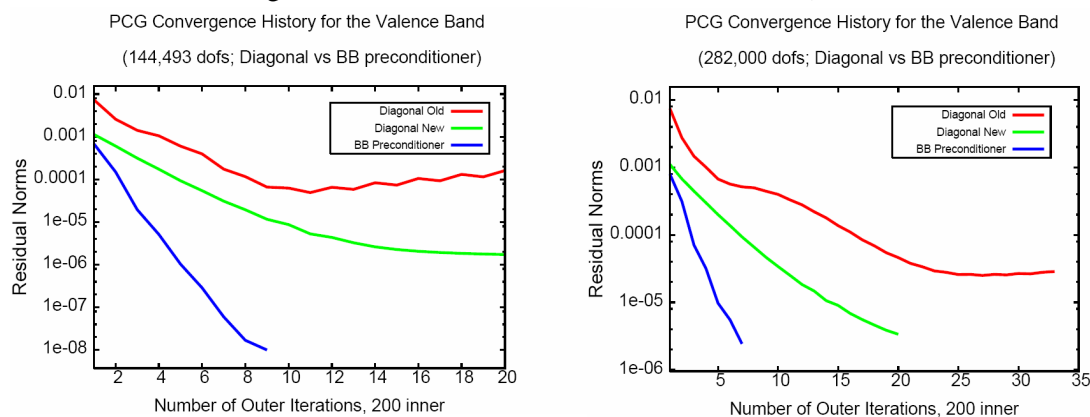

Figure 7: A comparison of diagonal *vs.* BB preconditioning with the folded spectrum for a 1,523 (left) and 3169 atom (right) CdSe quantum dot. Dofs is the number of degrees of freedom for the system which corresponds to the number of plane waves. There is stagnation in the convergence using a diagonal preconditioner (in red) because of clustered eigenvalues. The convergence is improved with a properly chosen BB based starting vector (green), and finally using both the BB based starting vector and the BB preconditioner (blue) gives the best convergence. Results are similar for a larger quantum dot (right).

7. Bulk-Band based preconditioner for large scale nanostructures

A new preconditioner, called bulk band (BB), has been developed for the acceleration of large scale nanoscience calculations using the PESCAN electronic structure code. The acceleration is based on using a modified form of the solution of the bulk system corresponding to the nanostructure we wish to study as a preconditioner in the eigensolvers developed. The theoretical basis for the success of this method is that in the interior of the nanostructure the properties of the system are bulk-like and

therefore the bulk solutions are good approximations to the true solutions in that region. The bulk solutions are easily derived in a negligible amount of time and from them the new preconditioner is calculated. Figure 7 demonstrates the acceleration achieved on two quantum dots of increasing size. A more detailed description of this work can be found in reference [12].

8. Acknowledgments

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