FINAL REPORT

"Scalable Methods for Electronic Excitations and Optical Responses of Nanostructures: Mathematics to Algorithms to Observables"

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I. SUMMARY OF WORK

Work in nanoscience has increased substantially in recent years owing to its potential technological applications and to fundamental scientific interest. A driving force for this activity is to capitalize on new phenomena that occurs at the nanoscale. For example, the physical confinement of electronic states, *i.e.*, quantum confinement, can dramatically alter the electronic and optical properties of matter. A prime example of this occurs for the optical properties of nanoscale crystals such as those composed of elemental silicon. Silicon in the bulk state is optically inactive due to the small size of the optical gap, which can only be accessed by "indirect" transitions. However, at the nanoscale, this material becomes optically active. The size of the optical gap is increased by confinement and the conservation of crystal momentum ceases to hold, resulting in the viability of indirect transitions.

Our work associated with this grant has focused on developing new scalable algorithms for describing the electronic and optical properties of matter at the nanoscale such as nano structures of silicon and related semiconductor properties. Our published work reflects this focus in that most of the papers are on nanoscale systems and the implementation of new algorithms.

From 2007 to 2009, we published 14 papers that were funded by this grant. This includes several papers published in high impact journals such as Nano Letters and Physical Review Letters.

Highlights

Short descriptions of our research activities during this funding period are provided below.

The Role of Quantum Confinement in p-Type Doped Indium Phosphide Nanowires, Nano Letters 7, 1878 (2007). In this work, we characterized impurity states responsible for current flow in zinc-doped indium phosphide nanowires using first-principles calculations based on a real-space implementation of density functional theory and pseudopotentials. We predicted the binding energy of the acceptor state to range from the value of the acceptor state in the bulk up to values of 0.2 eV in the thinner nanowires as a result of the two-dimensional quantum confinement. The location of the impurity atom within the nanomaterial is not found to play a prominent role in determining the characteristic properties of the state. Our results show that quantum confinement in thin nanowires can move the defect level deep into the energy gap.

Algorithms for the evolution of electronic properties in nanocrystals, Computer Physics Communications 177, 1 (2007). Here we illustrated recent progress in developing algorithms for solving the Kohn-Sham problem. Key ingredients of our new algorithms include pseudopotentials implemented on

a real space grid and the use of damped-Chebyshev polynomial filtered subspace iteration. This procedure allows one to predict electronic properties for many materials across the nano-regime, *i.e.*, from atoms to nanocrystals of sufficient size to replicate bulk properties. We will illustrated this method for large silicon quantum dots containing thousands of atoms.

Excited-state forces within time-dependent density-functional theory: A frequency-domain approach, Physical Review A 76, 054501 (2007). Excited state forces are difficult to compute as they cannot be extracted from ground state theories such as those based on the local density approximation. In this paper, we introduced a frequency-domain formalism for computing excited-state forces using linear response theory within the framework of *time-dependent* density-functional theory. We presented an implementation of the formalism within a real-space pseudopotential framework. We demonstrated the validity and usefulness of the approach by comparing its results to those obtained with a Green's function approach using the GW-Bethe-Salpeter-equation method, for the case of the CO molecule. We expect our method will be advantageous for computing excited-state dynamics in large systems.

Real-space pseudopotential calculations of spin-dependent electron transport in magnetic molecular junctions, Physical Review B 76, 235422 (2007). We developed a real-space pseudopotential approach to calculate the spin-dependent transport for nanoscale junctions. Our method is based on a self-consistent solution of the Kohn-Sham equation of density functional theory with asymptotic boundary conditions. We applied this method to a simple magnetic molecule, the Sc dimer, bridging nonmagnetic, planar jellium electrodes for a series of molecule-lead spacings. We found that the spin-dependent conductance within this formalism is rather robust over a wide range of electronic coupling parameters. The minority channel of parallel-aligned Sc_2 dimers produces a fairly stable conductance of roughly half of a quantum unit (e^2/h). Other systems show a sensitive dependence on the coupling strength. We discussed in some detail the origins of the spin dependence on conductance.

Real-space pseudopotential method for spin-orbit coupling within density functional theory, Physical Review B 76, 153407 (2007). The electronic structure of heavy elements such as Au or Pb requires a proper treatment of relativistic interactions, which can be large in such elements. We presented a formalism and implementation for real-space pseudopotential calculations that incorporate relativistic effects, including spin-orbit coupling. We demonstrate the validity of the method using the test cases of AuH and the Au_2 dimer. Our approach differs from nonrelativistic real-space calculations in the addition of nonlocal pseudopotential projectors, which are translated to small rank-1 matrix "stencils" operating on discretized wave functions. This formalism retains all the usual benefits of the real-space approach, especially with respect to massive parallelization and ease of implementation. We expect it to be readily applicable for computational studies of large systems that exhibit significant spin-orbit coupling.

Size limits on doping phosphorus into silicon nanocrystals, Nano Letters 8, 596 (2008). Phosphorous doped silicon is a quintessential electronic material. Understanding its properties a small length scales is becoming important a electronic devices continue to be miniaturized. We studied the electronic properties of phosphorus-doped silicon nanocrystals using a real-space first-principles pseudopotential method. We simulated nanocrystals with a diameter of up to 6 nm and made a direct comparison with experimental measurements for the first time for these systems. Our calculated size dependence of hyperfine splitting is in excellent agreement with experimental data. We also found a critical nanocrystal size below which we expect the P dopant to be ejected to the surface of the silicon nanocrystal.

Ab initio methods for the optical properties of CdSe clusters, Physical Review B 77, 045404 (2008). We performed time-dependent density functional theory (TDDFT) and GW/Bethe-Salpeter calculations of the optical properties of a series of CdSe clusters ranging in size from 10 to 82 atoms. The clusters were passivated by fictitious atoms of half-integer charge to eliminate electronically active surface states. The two methods predict a different character of the optical excitations of the these clusters. TDDFT predicts the lowest-energy excitation is mainly due to a single-level to single-level transition. In GW/Bethe-Salpeter, there is a strong admixture of several different transitions, which is attributed to excitonic effects. Furthermore, GW/Bethe-Salpeter calculations predict the presence of dark transitions (optically forbidden) before the first bright transition for all but one of the clusters studied, whereas TDDFT predicts the presence of dark transitions for only the two largest clusters. In this paper, we plotted and analyzed the effective valence and empty state charge densities of these clusters. We determined that the admixture of transitions observed in the GW/Bethe-Salpeter calculations is mostly due to the Bethe-Salpeter kernel and not from the fact that quasiparticle wave functions are a linear combination of wave functions obtained from density functional theory. We calculated the radiative decay lifetime of the excitations, and we explained the selection rules that lead to the presence of dark transitions in two of the clusters: $Cd_{17}Se_{28}$ and $Cd_{32}Se_{50}$. We also compared time-dependent density functional theory and GW/Bethe-Salpeter absorption spectra to that of Mie theory, which has recently been shown to yield surprisingly accurate results for Si clusters.

Ab initio calculations for p-type doped bulk indium phosphide, Solid State Communications 146, 245 (2008). We characterized the impurity state responsible for current flow in zinc-doped indium phosphide using first-principles calculations based on a real-space implementation of density-functional theory and pseudopotentials. The identification of the acceptor state is performed via an hybridization process between states of the same symmetry introduced in the host system by the impurity, and involves a self-consistent computation of the electronic properties of crystals containing thousands of atoms. The character of the wave function of the acceptor state, the variation of the binding energy of the state with dopant concentration and the value of the binding energy in the bulk limit were reported in this work.

Real space method for the electronic structure of one-dimensional periodic systems, Journal of Chemical Physics 129, 144109 (2008). Prior to this work, we could not handle periodic systems in one dimension such as nano wires or nano tubes. Here we presented a real space pseudopotential method for calculating the electronic structure of such systems. As an application of this method, we examined H passivated Si nanowires. The band structure and heat of formation of the Si nanowires were presented and compared to plane wave methods. Our method is able to offer the same accuracy as the traditional plane wave methods, but offers a number of computational advantages such as faster convergence for heteropolar nanowires.

Role of Confinement on Diffusion Barriers in Semiconductor Nanocrystals, Physical Review Letters 102, 025901 (2009). The physical confinement of electronic states at the nanoscale results in strongly modified optical properties. In addition, other properties are also altered. In this work, we found that quantum size effects not only play an important role in the electronic properties of defects in semiconductor nanocrystals, but also strongly affect the incorporation of defect atoms into the nanocrystals. In particular, using ab initio methods based on density functional theory implemented in real space, we predicted that Mn defects will be energetically driven towards the surface of CdSe and ZnSe nanocrystals, and that the diffusion barrier of a Mn interstitial defect in a CdSe nanocrystal will be significantly lower than that in the bulk.

Role of dimensionality and quantum confinement in p-type semiconductor indium phosphide quantum dots, Physical Review B 78, 233101 (2008). We characterized the impurity state responsible for current flow in zinc-doped indium phosphide nanocrystals through first-principles calculations based on a real-space implementation of density-functional theory and pseudopotentials. We found that the activation energy of the acceptor state ranges from 0.03 eV in the bulk to up to a value of 2.5 eV in small nanocrystals as a result of the three-dimensional quantum confinement. This maximum value for the *nanocrystals* is an order of magnitude larger than the maximum value found for *nanowires* within the same theoretical approach. Our results demonstrate that the progressive reduced dimensionality in p-type indium phosphide materials strongly reduces the capability of the materials to generate free carriers.

Role of quantum confinement and hyperfine splitting in lithium-doped ZnO nanocrystals, Physical Review B 78, 195324 (2008). The role of quantum confinement on the electronic properties of Li interstitial impurities in ZnO nanocrystals was examined using a real-space pseudopotential-density-functional method. The Li impurity was found to be partially ionized resulting in a significant charge transfer around the impurity site. To calculate the hyperfine interaction for this system using pseudopotentials, we modified Van de Walle and Blochl's method to include explicitly the off-site contribution

of the Li impurity wave function. Our modifications dramatically enhanced the agreement between the calculated and the measured isotropic hyperfine splitting constants. Our analysis with an effective-mass model demonstrates that the partial ionization of the impurity atom plays an important role both in the binding energy and in the shape of its wave function. Comparison between calculations using the local-density approximation (LDA) with LDA+U indicates that the local Coulomb correlation does not play a significant role in altering the impurity electronic states of interstitial Li-doped ZnO nanocrystals.

Efficient First-Principles Simulation of Noncontact Atomic Force Microscopy for Structural Analysis, Physical Review Letters 102, 176101 (2009). While atomic force microscopy (AFM) is one of the most widely used methods for probing atomistic structures, a theory basis for interpreting AFM images is lacking. In this work, we provide an efficient method for establishing the validity of a given model using AFM images. Specifically, we proposed an efficient scheme to simulate noncontact AFM images by using first-principles self-consistent potentials from the sample as input without requiring an explicit modeling of the atomic force microscopy tip. We applied our method applied to various types of semiconductor surfaces including Si(111)-(7 x 7), TiO_2 (110)-(1 x 1), Ag/Si(111)-($\sqrt{3}$ x $\sqrt{3}$) R30°, and Ge/Si(105)-(1 x 2) surfaces. We obtained good agreement with experimental results and previous theoretical studies, and our method can aid in identifying different structural models for surface reconstruction.

II. Publications from 2007 to 2009

1. M.M.G. Alemany, X. Huang, M.L. Tiago, and J.R. Chelikowsky: "p-type Doping in Indium Phosphide Nanowires: the Role of Dimensionality and Quantum Confinement in the Acceptor Impurity States," *Nano Lett.* **7**, 1878 (2007).

2. J.R. Chelikowsky, M.L. Tiago, Y. Saad, and Y. Zhou: "Algorithms for the Evolution of Electronic Properties in Nanocrystals," *Comp. Phys. Comm.* **177**, 1 (2007).

3. A. Sitt, L. Kronik, S. Ismail-Beigi and J.R. Chelikowsky: "Excited state forces within time-dependent density functional theory: A real-space, frequency domain approach," *Phys. Rev. A* **76**, 054501 (2007).

4. L. Kong, J.R. Chelikowsky, J.B. Neaton, and S.G. Louie: "Real-space pseudopotential calculations of spin-dependent electron transport in quantum point contacts," *Phys. Rev. B* **76**, 235422 (2007).

5. D. Naveh, L. Kronik, M.L. Tiago and J.R. Chelikowsky: "Real-Space Pseudopotential method for Spin-Orbit Coupling within Density Functional Theory," *Phys. Rev. B* **76**, 153407 (2007).

6. T.-L. Chan, M. L. Tiago, E. Kaxiras and J.R. Chelikowsky, "Size Limits on Doping Phosphorus into Silicon Nanocrystals," *Nano Letters* **8**, 596 (2008).

7. M. Lopez del Puerto, M.L. Tiago, and J.R. Chelikowsky: "Ab initio methods for the optical properties of CdSe clusters," *Phys. Rev. B* **77**, 045404 (2008).

8. M.M.G. Alemany, X. Huang, M. L. Tiago , L.J. Gallego, and J.R. Chelikowsky: "Ab initio calculations for p-type doped bulk indium phosphide," *Solid State Commun.* **146**, 245 (2008).

9. H. Kwak, M.L. Tiago, T.-L. Chan and J.R. Chelikowsky: "Hyperfine splitting of partially ionized Li donors in ZnO nanocrystals," *Chem. Phys. Lett.* **454**, 337 (2008).

10. J. Han, M. L. Tiago, T.-L. Chan, and J. R. Chelikowsky: "Real-Space First-Principles Method for the Electronic Structure of One Dimensional Periodic Systems," *J. Chem. Phys.* **129**, 144109 (2008).

11. T.-L. Chan, A. T. Zayak, G. M. Dalpian, and J. R. Chelikowsky: "Role of Confinement on Diffusion Barriers in Semiconductor Nanocrystals," *Phys. Rev. Lett.* **102**, 025901 (2009).

12. M. M. G. Alemany, L. Tortajada, X. Huang, M.L. Tiago,L. J. Gallego, and J.R. Chelikowsky: "The role of dimensionality and quantum confinement in p-type semiconductor indium phosphide nanomaterials," *Phys. Rev. B* **78**, 233101 (2008).

13. H. Kwak, M.L. Tiago, T.-L. Chan, and J.R. Chelikowsky: "The Role of Quantum Confinement and Hyperfine Splitting in Li Doped ZnO Nanocrystals," *Phys. Rev. B* **78**, 195324 (2008).

14. T.-L. Chan, C. Z. Wang, K. M. Ho, and J.R. Chelikowsky: "Efficient first-principles simulation of non-contact atomic force microscopy for structural analysis," *Phys. Rev. Lett.* **102**, 176101(2009).

III. Invited talks from 2007 to 2009

1. J.R. Chelikowsky: "Doping of Nanocrystals and the Role of Self-Purification," TMS 2007 Annual Meeting, Orlando, FL, February, 2007.

2. J.R. Chelikowsky: "Doping Nanocrystals and the Role of Quantum Confinement," Frontiers of Characterization and Metrology for Nanoelectronics, NIST, Gaithersburg, MD, March, 2007.

3. J.R. Chelikowsky: "The Emergence of Magnetism in Iron Nanocrystals," 5^{th} International Symposium on the Theory of Atomic and Molecular Clusters, Richmond, VA, May, 2007.

4. J.R. Chelikowsky; "The End of Crystallinity," Symposium on Electronics and Photonics, MIT, Cambridge, MA, May, 2007.

5. J.R. Chelikowsky: " New Algorithms for the Electronic Structure Problem," Roberto Car Symposium, Trieste, Italy, June 2007.

6. J.R. Chelikowsky: "Numerical Methods for Time Dependent Density Functional Theory," Gordon Research Conference, Colby College, ME, July, 2007.

7. J.R. Chelikowsky: "Algorithms for Predicting Defect Properties in Nanostructures," 24th International Conference on Defects in Semiconductors, Albuquerque, NM, July, 2007.

8. J.R. Chelikowsky: "Algorithms for Spanning the Nano-Regime," Classical and Quantum Approaches in Molecular Modeling Workshop, Institute for Mathematics and Its Applications, Minneapolis, MN, July, 2007.

9. J.R. Chelikowsky: 'The Structural, Electronic and Optical Properties of Silica Using the Standard Model: Pseudopotentials and Density Functional Theory," Workshop on Modelling the structures and reactivity of silica and water: from molecule to macroscale, CECAM, Lyon, France, September, 2007.

10. J.R. Chelikowsky: "Temperature effects in the optical response of clusters using time dependent density functional theory," Nanoquanta Workshop, Aussois, France, September, 2007.

11. J.R. Chelikowsky: "Algorithms for Nanostructures," 2007 Condensed Phase and Interfacial Molecular Science Meeting, DOE, Warrenton, VA, October, 2007.

12. J.R. Chelikowsky: "Algorithms for Doping Nanostructures," Symposium to honor Carmen Varea, Mexico City, Mexico, November, 2007.

13. J.R. Chelikowsky: "Doping of Semiconducting Nanocrystals and the Role of Quantum Confinement," 35^{th} Conference on the Physics and Chemistry of Surfaces and Interfaces, Sante Fe, NM, January 2008.

14. J.R. Chelikowsky: "Physical Properties at Small Length Scales: The Role of Quantum Confinement in the Nanoworld," International Conference on Quantum Simulators and Design 2008, Tokyo, Japan, May, 2008.

15. J.R. Chelikowsky: "Quantum Modeling of Nano-structured Materials," 1st Portuguese Workshop on Functionally Graded Materials:an integrated approach, Guimaraes, Portugal, October, 2008 [Plenary Talk].

16. J.R. Chelikowsky: "Quantum Theory of Nanostructures," Molecular Foundry Workshop, Lawrence Berkeley Laboratory, Berkeley, CA, November, 2008.

17. J.R. Chelikowsky: "High Performance Algorithms for Quantum Confined Systems," Fourth International Workshop on High Performance Computing for Nano-science and Technology, Austin, TX, November, 2008.

18. J.R. Chelikowsky: "High Performance Algorithms for Nanoscale Systems," SIAM Conference on Computational Science and Engineering, Miami, FL, March, 2009.

IV. Recognitions received

We received several national recognitions for our DOE sponsored work as listed below:

- Fellow of the American Association for the Advancement of Science, 2007.
  Citation: *For contributions to the basic understanding of properties of materials through theoretical calculations, and for excellence in teaching, lecturing and writing.*

- Fellow of the Materials Research Society, 2011.
  Citation: *For outstanding contributions to the theory of electronic materials.*

- Aneesur Rahman Prize, American Physical Society, 2013.
  Citation: *For computational applications of quantum theories to understand and predict material properties.*