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

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Synopsis

The work reported here took place at the University of Minnesota from September 15, 2003 to November 14, 2005. This funding resulted in 10 invited articles or book chapters, 37 articles in refereed journals and 13 invited talks. The funding helped train 5 PhD students.

The research supported by this grant focused on developing theoretical methods for predicting and understanding the properties of matter at the nanoscale. Within this regime, new phenomena occur that are characteristic of neither the atomic limit, nor the crystalline limit. Moreover, this regime is crucial for understanding the *emergence* of macroscopic properties such as ferromagnetism. For example, elemental Fe clusters possess magnetic moments that reside between the atomic and crystalline limits, but the transition from the atomic to the crystalline limit is not a simple interpolation between the two size regimes. To capitalize properly on predicting such phenomena in this transition regime, a deeper understanding of the electronic, magnetic and structural properties of matter is required, *e.g.*, electron correlation effects are enhanced within this size regime and the surface of a confined system must be explicitly included.

A key element of our research involved the construction of *new* algorithms to address problems peculiar to the nanoscale. Typically, one would like to consider systems with thousands of atoms or more, *e.g.*, a silicon nanocrystal that is 7 nm in diameter would contain over 10,000 atoms. Previous *ab initio* methods could address systems with hundreds of atoms whereas empirical methods can routinely handle hundreds of thousands of atoms (or more). However, these empirical methods often rely on *ad hoc* assumptions and lack incorporation of structural *and* electronic degrees of freedom.

The key *theoretical* ingredients in our work involved the use of *ab initio* pseudopotentials and density functional approaches. The key *numerical* ingredients involved the implementation of algorithms for solving the Kohn-Sham equation without the use of an explicit basis, *i.e.*, a real space grid. We invented algorithms for a solution of the Kohn-Sham equation based on Chebyshev “subspace filtering.” Our filtering algorithms dramatically enhanced our ability to explore systems with thousands of atoms, *i.e.*, we examined silicon quantum dots with approximately 11,000 atoms (or 40,000 electrons). We applied this algorithm to a number of nanoscale systems to examine the role of quantum confinement on electronic and magnetic properties:

- Doping of nanocrystals and nanowires, including both magnetic and non-magnetic dopants and the role of self-purification
- Optical excitations and electronic properties of nanocrystals
- Intrinsic defects in nanostructures
- The emergence of ferromagnetism from atoms to crystals.

Publications (2003-2006) supported in full or partially through this DOE award

Book Chapters and Invited Articles

1. J.R. Chelikowsky: "Simulation of Quantum Confinement in Silicon Nanocrystals," *Encyclopedia of Nanoscience and Nanotechnology*, Editor: J.A. Schwarz, Marcel Dekker, Inc., p. 3563 - 3574, 2004.
2. J.R. Chelikowsky, L. Kronik and I. Vasiliev: "Time dependent density functional calculations for the optical spectra of molecules, clusters and nanocrystals," *J. Phys. Cond. Matt.* **15**, R1517 (2003).
3. J.R. Chelikowsky: "Real-space methods for ab initio electronic structure calculations," in the *Handbook of Materials Modeling*, Editor: Sidney Yip, Kluwer, (2005), Section 1.7, p. 121.
4. J.R. Chelikowsky and Y. Saad: "Electronic Structure of Clusters and Nanocrystals," *Handbook of Theoretical and Computational Nanotechnology*, Editors: Michael Rieth and Wolfram Schommers. (American Scientific) **8**, 797 (2006).
5. J.R. Chelikowsky: "Electronic Structure: Electronic structure of nanostructures," *Encyclopedia of Condensed Matter Physics*, Editors: F. Bassini, J. Liedl, and P. Wyder, (Elsevier, 2005), Vol. 4, p 51.
6. J.R. Chelikowsky: "Structure and Electronic Properties of Complex Materials: Clusters, Liquids and Nanocrystals," in *Contemporary Concepts of Condensed Matter Science*, Series editors: E. Burstein, M.L. Cohen, D.L. Mills and P.J. Stiles; *Conceptual Foundations of Materials: A standard model for ground- and excited-state properties*, Editors: M.L. Cohen and S.G. Louie, (Elsevier, 2006), Chapter 4, p. 97.
7. J.R. Chelikowsky, Y. Saad, and I. Vasiliev: "Atoms and Clusters," in *Time Dependent Density Functional Theory*, edited by M. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke and E.K.U. Gross, "Lecture Notes in Physics" series. (Springer-Verlag, Heidelberg), Chapter 17, **706**, 259 (2006).
8. J.R. Chelikowsky: "Using Silicon to Understand Silicon: Doping of Nanostructures," *The Electrochemical Society Interface* (special issue on "Silicon-Based Nanoelectronics: Evolving Directions") **14**, 24 (2005).
9. J.R. Chelikowsky: "Shining Light on Semiconductors," book review of *The Semiconductor Story* by John Orton, *Science* **307**, 1724 (2005).
10. J.R. Chelikowsky and A. Demkov, editors. *physica status solidi (b)* **243**, (9) (2006). [Proceedings of the workshop on Computational Materials and Electronics held in Austin, TX in October, 2005.]

Articles in Scientific Journals

1. W. R. Burdick, Y. Saad, L. Kronik, M. Jain, I. Vasiliev and J.R. Chelikowsky: "Parallel Implementation of Time-Dependent Density Functional Theory," *Comp. Phys. Comm.* **156**, 22 (2003).
2. D.V. Melnikov and J.R. Chelikowsky: "Ab Initio Absorption Spectra of Germanium Nanocrystals," *Solid State Comm.* **127**, 361 (2003).
3. M. C. Tropicovsky, L. Kronik, and J.R. Chelikowsky: "Optical Excitations in CdSe Quantum Dots," *J. Chem. Phys.* **119**, 2284 (2003).
4. S. Ögüt, R. Burdick, Y. Saad, and J.R. Chelikowsky: "Ab Initio Calculations for the Large Dielectric Matrices of Confined Systems," *Phys. Rev. Lett.* **90**, 127401 (2003).
5. L. Kronik, R. Fromherz, E. Ko, G. Ganteför, and J.R. Chelikowsky: "Photoemission spectra of deuterated silicon clusters: experiment and theory," *Euro. Phys. J. D* **24**, 33 (2003).
6. M.M.G. Alemany and James R. Chelikowsky: "Edge-sharing tetrahedra: Precursors of the E'_{γ} defects in amorphous silica," *Phys. Rev. B* **68**, 054206 (2003).
7. D.V. Melnikov and J.R. Chelikowsky: "Electron affinities and ionization energies of semiconductor nanocrystals," *Phys. Rev. B* **69**, 113305 (2004).
8. D.V. Melnikov and J.R. Chelikowsky: "Quantum confinement in phosphorus-doped silicon nanocrystals," *Phys. Rev. Lett.* **92**, 046802 (2004).

9. M.M.G. Alemany, M. Jain, J.R. Chelikowsky and L. Kronik: "A real space pseudopotential method for computing the electronic properties of periodic systems," *Phys. Rev. B* **69**, 075101 (2004).
10. S. Ögüt and J.R. Chelikowsky: "Charge State Dependence Jahn-Teller Distortions of the E-center Defect in Crystalline Silicon," *Phys. Rev. Lett.* **91**, 235503 (2003).
11. F.-C. Chuang, C.Z. Wang, S. Ögüt, J.R. Chelikowsky and K.M. Ho: "Melting of small Sn clusters by *ab initio* molecular dynamics simulations," *Phys. Rev. B* **69**, 165408 (2004).
12. E. L. de la Grandmaison, S.B. Gowda, Y. Saad, M.Tiago, and J.R. Chelikowsky: "An Efficient Computation of the Coupling Matrix in Time Dependent Density Functional Theory," *Comp. Phys. Comm.* **167**, 7 (2005).
13. S. Li, M.M.G. Alemany and J.R. Chelikowsky: "*Ab initio* calculations for the photoelectron spectra of vanadium clusters," *J. Chem. Phys.* **121**, 5893 (2004).
14. L. Kronik, M. Jain, and J.R. Chelikowsky: "Electronic structure and spin-polarization of MnGaP," *Applied Phys. Lett.* **85**, 2014 (2004).
15. G. Neshet, L. Kronik and J.R. Chelikowsky: "*Ab initio* absorption spectra of Ge nanocrystals," *Phys. Rev. B* **71**, 035344 (2005).
16. X. Huang, E. Lindgren and J.R. Chelikowsky: "Surface passivation method for semiconductor nanostructures," *Phys. Rev. B* **71**, 165328 (2005).
17. S. Li, M.M.G. Alemany, and J.R. Chelikowsky: "*Ab initio* calculations of the photoelectron spectra of transition metal clusters," *Phys. Rev. B* **71**, 165433 (2005).
18. M.L. Tiago and J.R. Chelikowsky: "First-principles GW-BSE excitations in organic molecules," *Solid State Comm.* **136**, 333 (2005).
19. X. Huang, A. Makmal, J. R. Chelikowsky and L. Kronik: "Size dependent spintronic properties of dilute magnetic semiconductor nanocrystals," *Phys. Rev. Lett.* **94**, 236801 (2005).
20. C. Bekas, Y. Saad, M.L. Tiago and J.R. Chelikowsky: "Computing charge densities with partially re-orthogonalized Lanczos," *Comp. Phys. Comm.* **171**, 175 (2005).
21. Y. Zhou, Y. Saad, M. L. Tiago and J. R. Chelikowsky: "Self-consistent-field calculations using Chebyshev-filtered subspace iteration," *J. Comp. Phys.* **219**, 172 (2006).
22. M.L. Tiago and J.R. Chelikowsky: "Optical excitations in organic molecules, clusters and defects from first principles Green's function methods," *Phys. Rev. B* **73**, 205334 (2006).
23. L. Kronik, A. Makmal, M.L. Tiago, M.M.G. Alemany, M. Jain, X. Huang, Y. Saad and J.R. Chelikowsky: "PARSEC-the pseudopotential algorithm for real space electronic structure calculations: recent advances and novel applications to nano-structures," *phys. stat. sol. (b)* **243**, 1063 (2006).
24. G. Dalpian, M.L. Tiago, M. Lopez del Puerto and J.R. Chelikowsky: "Symmetry considerations for semiconductor nanocrystals," *Nano Letters* **6**, 501 (2006).
25. L. Kong, M. L. Tiago and J. R. Chelikowsky: "Real-space pseudopotential method for electron transport properties of nano-scale junctions," *Phys. Rev. B* **73**, 195118 (2006).
26. G. Dalpian and J.R. Chelikowsky: "Self-Purification in Semiconductor Nanocrystals," *Phys. Rev. Lett.* **96**, 226802 (2006).
27. S. Li, M.M.G. Alemany and J. R. Chelikowsky: "Real-space *Ab initio* pseudopotential calculations for anion clusters: Fe_n^- ($n = 3 - 6$)," *Phys. Rev. B* **73**, 233404 (2006).
28. S. Li, M.M.G. Alemany and J. R. Chelikowsky: "Real space pseudopotential calculations for copper clusters," *J. Chem. Phys.* **125**, 034311(2006).
29. Y. Saad, Y. Zhou, C. Bekas and J.R. Chelikowsky: "Diagonalization Methods in PARSEC," *phys. stat. sol. (b)* **243**, 2188 (2006).

30. J.R. Chelikowsky, E. Kaxiras and R.M. Wentzcovitch: "Theory of Spintronic Materials," *phys. stat. sol. (b)* **243**, 2133 (2006).
31. M. Lopez del Puerto, M.L. Tiago, and J.R. Chelikowsky: "Excitonic effects and optical properties of passivated CdSe clusters," *Phys. Rev. Lett.* **97**, 096401 (2006).
32. M.L. Tiago and J.R. Chelikowsky: "Confinement effects in the optical properties of semiconductor nanocrystals," *phys. stat. sol. (b)* **243**, 2151 (2006).
33. S. Beckman, J. Han, and J.R. Chelikowsky: "Role of Quantum Confinement in Ge Nanowires," *Phys. Rev. B* **74**, 165314 (2006).
34. M.L. Tiago, Y. Zhou, M.M.G. Alemany, Y. Saad, and J.R. Chelikowsky: "The Evolution of Magnetism in Iron from the Atom to the Bulk," *Phys. Rev. Lett.* **97**, 147201 (2006).
35. N.S. Norberg, G.M. Dalpian, J.R. Chelikowsky, and D.R. Gamelin: "Vacuum Pinning of Magnetic Impurity Levels in Quantum Confined Semiconductors," *Nano Letters* **6**, 2887 (2006).
36. J.R. Chelikowsky: "The Role of Self-Purification and the Electronic Structure of Magnetically Doped Semiconductor Nanocrystals," *Phase Transitions* **79**, 739 (2006).
37. Y. Zhou, Y. Saad, M.L. Tiago, and J.R. Chelikowsky: "Parallel Self-Consistent-Field Calculations via Chebyshev-Filtered Subspace Acceleration," *Phys. Rev. E* **74**, 066704 (2006).

Invited Talks: Professional Society Meetings or Workshops

1. J.R. Chelikowsky: "Optical Excitations in Molecules, Clusters and Nanocrystals," Mardi Gras Conference: Frontiers of Grid Computing at the Nano-Bio Interface," Baton Rouge, LA, February 2003.
2. J.R. Chelikowsky: "Predicting the optical and electronic properties of semiconductors at the nanoscale," IGERT Nanoparticle Science and Engineering Summer Symposium, Minneapolis, MN, July, 2003.
3. J.R. Chelikowsky: "Optical properties and doping of semiconductor nanocrystals," Grand Challenges in Modeling the Assembly and Properties of Nanomaterials, DOE workshop at Argonne National Labs, August, 2003.
4. J.R. Chelikowsky: "Quantum confinement in nanocrystals: Optical excitations and doping. Computational Approaches towards the Electronics Properties of Quantum Workshop sponsored by DARPA-DSO, Chicago, September, 2003.
5. J.R. Chelikowsky: "Point Defects in Silicon: Modeling the Infinite with the Finite," Mardi Gras Conference: Materials and Modeling for Information Technology, Baton Rouge, LA, February 2004.
6. J.R. Chelikowsky: "Computational Methods for Predicting the Optical Properties of Matter at the Nanoscale," EC-NSF Workshop on Computational Methods in Materials Science, San Francisco, CA, April, 2004.
7. J.R. Chelikowsky: "Predicting the Optical and Structural Properties of Matter at the Nanoscale," Fourth SIAM Conference on Mathematical Aspects of Materials Science, Los Angeles, CA, May, 2004.
8. J.R. Chelikowsky: "Ab Initio Simulation of the Properties of Nanoclusters," 3rd International Conference on Computational Modeling and Simulation of Materials, Sicily, Italy, June, 2004.
9. J.R. Chelikowsky: "Numerical Methods for Predicting the Optical Properties of Nanocrystals," ACS/PRF Summer School on "Time-Dependent Density-Functional Theory and the Dynamics of Complex Systems," Santa Fe, NM, June, 2004.
10. J.R. Chelikowsky: "Optical Properties in Quantum Dots and Clusters Using Time Dependent Density Functional Theory," First-principles computational materials mini-school, Taipei, Taiwan, May, 2005.
11. J.R. Chelikowsky: "Magnetically Doped Quantum Dots," Grid Applications in Nanoscience, Nara, Japan, June 2005.

12. J.R. Chelikowsky: “Magnetism in Semiconductor Quantum Dots,” Electronic structure workshop at Cornell, Ithaca, NY, June, 2005.
13. J.R. Chelikowsky: “Magnetic Doped Nanocrystals,” International Symposium on Structure and Dynamics on the Nanometer Scale, Duisburg, Germany, November, 2005.

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- Dr. Claudia Troparevsky, Oak Ridge National Laboratory
- Dr. Shen Li, Computational Biology, Public Health Sciences, Fred Hutchinson cancer research center
- Dr. Lingzhyu Kong, Rutgers University
- Professor Marie Lopez del Puerto, Department of Physics, St. Thomas University
- Dr. Hyunwook Kwak, Applied Sciences Laboratory Materials Modeling and Simulations Group, Washington State University