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DOE Computational Nanoscience Project:
Integrated Multiscale Modeling of Molecular Computing Devices

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## 1. BACKGROUND

Nanoscience has been one of the major research focuses of the U.S. and much of the world for the past decade, in part because of its promise to revolutionize many fields, including materials, medicine, and electronics. At the heart of this promise is the fact that nanostructured materials can behave radically differently than their macroscopic counterparts (e.g., bulk gold is such an inert metal that it has found applications in such diverse fields as jewelry, biomedical implants and dentistry, whereas gold nanoparticles are highly reactive and are thus useful as nanocatalysts) and have properties that are tunable due to a strong dependence on the size and surface area of the nanostructure. Thus, nanoscience offers a remarkable opportunity to develop new functional systems built around nanostructured materials with unusual and tunable properties and functionality.

The transition from nanoscience to nanotechnology becomes possible when nanostructured systems can be made reproducibly by processes that can be implemented on a large scale. The microelectronics industry is one example of an industry that has evolved into the realm of nanotechnology, since the exponential reduction in feature size in computer chips has resulted in feature sizes now under 50nm (45nm in production, 32nm demonstrated; feature size has been going down by a factor of approximately $1/\sqrt{2}$ every 18 months as chip density has doubled every 18 months according to Moore's law). Silicon-based microelectronics relies on etching features into a single-crystal silicon substrate by photolithography. As the feature size of silicon-based microelectronics continues to decrease, the continuation of Moore's law to below 20nm feature sizes is being questioned, due to limitations in both the physics of the transistors (leading to unacceptable power dissipation) and doubts about the scalability of top-down photolithography-based manufacturing to such small sizes.

There is no doubt that photolithography will some day reach a miniaturization limit, forcing designers of Si-based electronics to pursue increased performance by other means. Any other alternative approach would have the unenviable task of matching the ability of Si technology to pack more than a billion interconnected and addressable devices on a chip the size of a thumbnail. Nevertheless, the prospects of developing alternative approaches to fabricate electronic devices have spurred an ever-increasing pace of fundamental research. One of the promising possibilities is molecular electronics (ME), self-assembled molecular-based electronic systems composed of single-molecule devices in ultra dense, ultra fast molecular-sized components. This project focused on developing accurate, reliable theoretical modeling capabilities for describing molecular electronics devices. The participants in the project are given in Table 1.

## 2. OUTCOMES

The primary outcomes of this fundamental computational science grant are publications in the open scientific literature. As listed below, 62 papers have been published from this project. In addition, the research has also been the subject of more than 100 invited talks at conferences, including several plenary or keynote lectures. Many of the goals of the original proposal were completed. Specifically, the multi-disciplinary group developed a unique set of capabilities and tools for investigating electron transport in fabricated and self-assembled nanostructures at multiple length and time scales.

**Table 1**: Project participants. Key: AM = Applied Mathematics; CE = Chemical Engineering; CSM = Computer Science and Mathematics Division; M = Mathematics; P = physics

| Institution | Name | Project Role |
|---|---|---|
| Vanderbilt University (VU) | Peter T. Cummings (PI), CE | Atomistic and mesoscale simulation, non-equilibrium methods, self-assembly |
| | Sokrates T. Pantelides, P | Quantum transport in nano devices and the connection to macroscopic electrodes |
| | Ron Schrimpf, EECE | Transition from nanoscale devices to engineering-level device/circuit modeling |
| North Carolina State University (NCSU) | Jerzy Bernholc, P | Multigrid electronic structure, *O(N)* methods, quantum transport, multiscale, parallel computing |
| | Marco Buongiorno Nardelli, P | Quantum transport, optimized localized orbitals, electronic structure of nanoscale systems |
| Oak Ridge National Laboratory (ORNL) | Robert Harrison, CSM | Algorithms for large-scale electronic structure calculations, multiresolution methods |
| | George I Fann, CSM | Fast, $O(N)$, spectrally accurate, multiwavelet methods for computational chemistry |
| | Xiaoguang Zhang, CSM | Multiple scattering theory and Green's function method |
| | Vincent Meunier, CSM | Semi-empirical and first principles studies of nanoscopic materials |
| | Bryan Hathorn, CSM | Time-scale-spanning methods for atomistic simulations; Monte Carlo methods |
| | Phani Kumar Nukala, CSM | Multiscale methods in materials modeling |
| Princeton University (PU) | Weinan E., M and AM | Scale-spanning materials modeling, stochastic differential equations, complex energy landscapes |
| University of Colorado (CU) | Gregory Beylkin, AM | Multiresolution analysis, wavelet methods, non-uniform fast fourier transform |
| University of Michigan (UM) | Sharon Glotzer, CE | Atomistic and mesoscale materials modeling, hybrid materials, nano-interfaces |
| University of Tennessee Knoxville (UTK) | Tim Schultze, M | Kinetic Monte Carlo and related time-coarsening methods; mathematical analysis |

Table 2. Publications from grant DE-FG02-03ER15385.


1. Hernandez, E., Meunier, V., Smith, B. W., Rurali, R., Terrones, H., Nardelli, M. B., Terrones, M., Luzzi, D. E. and Charlier, J. C., "Fullerene coalescence in nanopeapods: A path to novel tubular carbon," Nano Letters, 3, 1037-1042 (2003).
2. Krstic, P. S., Dean, D. J., Zhang, X. G., Keffer, D., Leng, Y. S. and Cummings, P. T., "Computational chemistry for molecular electronics," Computational Materials Science, 28, 321-341 (2003).
3. Leng, Y. S., Keffer, D. J. and Cummings, P. T., "Structure and dynamics of a benzenedithiol monolayer on a Au(111) surface," J. Phy. Chem. B, 107, 11940-11950 (2003).
4. Bernholc, J., Nardelli, M. B., Lu, W. C., Meunier, V., Nakhmanson, S. M. and Zhao, Q., "Simulations of nanotube-based structures and devices," In Foundations of Nanoscience 2004: Proceedings of Self-Assembled Architectures and Devices. Snowbird Cliff Lodge, Snowbird, UT, April 21-23, 2004.; J. Reif, Ed.; ScienceTechnica: 2004; pp 367-372.
5. Bernholc, J., Nardelli, M. B., Lu, W. C., Meunier, V., Nakhmanson, S. M. and Zhao, Q., "Large-scale quantum-mechanical simulations of nanoscale devices and new materials," In Users Group Conference (DOD-UGC '04); R. E. Peterkin, Ed.; IEEE Computer Society: 2004; pp 34.

6. Bernholc, J., Nardelli, M. B., Lu, W. C., Meunier, V., Schmidt, W. S., Wang, S. and Zhao, Q., "Large-scale simulations of advanced materials and nanoscale devices," In Users Group Conference (DOD-UGC '04); R. E. Peterkin, Ed.; IEEE Computer Society: 2004; pp 41-45.
7. Calzolari, A., Cavazzoni, C. and Nardelli, M. B., "Electronic and transport properties of artificial gold chains," Phys. Rev. Lett., 93, Art. No. 096404 (2004).
8. Calzolari, A., Marzari, N., Souza, I. and Nardelli, M. B., "Ab initio transport properties of nanostructures from maximally localized Wannier functions," Phys. Rev. B, 69, Art. No. 035108 (2004).
9. Meunier, V., Kalinin, S. V., Shin, J., Baddorf, A. P. and Harrison, R. J., "Quantitative analysis of electronic properties of carbon nanotubes by scanning probe microscopy: From atomic to mesoscopic length scales," Phys. Rev. Lett., 93, Art. No. 246801 (2004).
10. Rocquefelte, X., Rignanese, G. M., Meunier, V., Terrones, H., Terrones, M. and Charlier, J. C., "How to identify Haeckelite structures: A theoretical study of their electronic and vibrational properties," Nano Letters, 4, 805-810 (2004).
11. Shin, J., Meunier, V., Baddorf, A. P. and Kalinin, S. V., "Nonlinear transport imaging by scanning impedance microscopy," Appl. Phys. Lett., 85, 4240-4242 (2004).
12. Varga, K., Zhang, Z. Y. and Pantelides, S. T., ""Lagrange functions": A family of powerful basis sets for real-space order-N electronic structure calculations," Phys. Rev. Lett., 93, Art. No. 176403 (2004).
13. Bernholc, J., Lu, W. C., Nakhmanson, S. M., Meunier, V. and Nardelli, M. B., "Multiscale simulations of quantum structures," In Users Group Conference (DOD-UGC '05); D. E. Post, Ed.; IEEE Computer Society: 2005; pp 18-24.
14. Calzolari, A. and Buongiorno Nardelli, M., "First principles theory of artificial metal chains on NiAl(110) surface," Phys. Rev. B, 72, Art. No. 045146 (2005).
15. Cummings, P. T. and Leng, Y. S., "Integrated multiscale modeling of molecular computing devices," Journal of Physics: Conference Series, 16, 269 (2005).
16. Evans, M. H., Zhang, X. G., Joannopoulos, J. D. and Pantelides, S. T., "First-principles mobility calculations and atomic-scale interface roughness in nanoscale structures," Phys. Rev. Lett., 95, Art. No. 106802 (2005).
17. Ferretti, A., Calzolari, A., Di Felice, R., Manghi, F., Caldas, M. J., Nardelli, M. B. and Molinari, E., "First-principles theory of correlated transport through nanojunctions," Phys. Rev. Lett., 94, Art. No. 116802 (2005).
18. Lee, Y. S., Nardelli, M. B. and Marzari, N., "Band structure and quantum conductance of nanostructures from maximally localized wannier functions: The case of functionalized carbon nanotubes," Phys. Rev. Lett., 95, Art. No. 076804 (2005).
19. Leng, Y. S., Krstic, P. S., Wells, J. C., Cummings, P. T. and Dean, D. J., "Interaction between benzenedithiolate and gold: Classical force field for chemical bonding," J. Chem. Phys., 122, Art. No. 244721 (2005).
20. Lu, W. C., Meunier, V. and Bernholc, J., "Nonequilibrium quantum transport properties of organic molecules on silicon," Phys. Rev. Lett., 95, Art. No. 206805 (2005).
21. Lu, Z. Y., Zhang, X. G. and Pantelides, S. T., "Spin-dependent resonant tunneling through quantum-well states in magnetic metallic thin films," Phys. Rev. Lett., 94, Art. No. 207210 (2005).
22. Meunier, V., Lu, W. C., Bernholc, J. and Sumpter, B. G., "Electron transport in molecular electronics systems," Journal of Physics: Conference Series, 16, 283 (2005).
23. Meunier, V. and Sumpter, B. G., "Amphoteric doping of carbon nanotubes by encapsulation of organic molecules: Electronic properties and quantum conductance," J. Chem. Phys., 123, Art. No. 024705 (2005).
24. Tsetseris, L. and Pantelides, S. T., "Atomic-scale mechanisms of selective adsorption and dimerization of pentacene on silicon surfaces," Appl. Phys. Lett., 87, Art. No. 233109 (2005).
25. Tsetseris, L. and Pantelides, S. T., "Atomic-scale mechanisms of selective adsorption and dimerization of pentacene on Si surfaces," Appl. Phys. Lett., 87, Art. No. 233109 (2005).
26. Zhao, Q., Nardelli, M. B., Lu, W. and Bernholc, J., "Carbon nanotube-metal cluster composites: A new road to chemical sensors?," Nano Letters, 5, 847-851 (2005).
27. Bernholc, J., Nardelli, M. B., Lu, W., Meunier, V., Nakhmanson, S. M. and Zhao, Q., "Atomic Scale Design of Nanostructures," In Proceedings of the Indo-US workshop on Nanoscale Materials: From Science to Technology; S. N. Sahu; R. K. Choudhury and P. Jena, Ed.; Nova Science Publishers, in press: 2006.
28. Du, S. X., Gao, H. J., Seidel, C., Tsetseris, L., Ji, W., Kopf, H., Chi, L. F., Fuchs, H., Pennycook, S. J. and Pantelides, S. T., "Selective nontemplated adsorption of organic molecules on nanofacets and the role of bonding patterns," Phys. Rev. Lett., 97, Art. No. 156105 (2006).
29. Lambin, P., Triozon, F. and Meunier, V., "Electronic transport in nanotubes and through junctions of

nanotubes," In Theory of Quantum Transport in Metallic and Hybrid Nanostructures: Proceedings of the NATO Advanced Research Workshop on Theory of Quantum Transport in Metallic and Hybrid Nanostructures, St. Petersburg, Russia, 25-29 August 2003; A. Glatz; V. I. Kozub and V. M. Vinokur, Ed.; Kluwer Acad.: 2006; Vol. 230.

30. Lu, J. Q., Zhang, X. G. and Pantelides, S. T., "Tunable spin Hall effect by Stern-Gerlach diffraction," Phys. Rev. B, 74, Art. No. 245319 (2006).
31. Meunier, V., Lu, W., Sumpter, B. G. and Bernholc, J., "Density Functional Theory Studies of Quantum Transport in Molecular Systems," International Journal of Quantum Mechanics, 106, 3334 (2006).
32. Meunier, V., Lu, W. C., Sumpter, B. G. and Bernholc, J., "Density functional theory studies of quantum transport in molecular systems," Proceedings of (2006), pp. 3334-3342,
33. Rodriguez, B. J., Jesse, S., Meunier, V. and Kalinin, S. V., "Scanning Frequency Mixing Microscopy of High Frequency Transport Behavior at Electroactive Interfaces," Appl. Phys. Lett., 88, Art. No. 143128 (2006).
34. Tsetseris, L. and Pantelides, S. T., "Encapsulation of floating carbon nanotubes in SiO2," Phys. Rev. Lett., 97, Art. No. 266805 (2006).
35. Wang, S., Lu, W., Zhao, Q. and Bernholc, J., "Resonant Coupling and Negative Differential Resistance in Metal/Ferrocenyl-Alkanethiolate/STM structures," Phys. Rev. B, 74, Art. No. 195430 (2006).
36. Zhao, X. C., Leng, Y. S. and Cummings, P. T., "Self-assembly of 1,4-benzenedithiolate/ tetrahydrofuran on a gold surface: A Monte Carlo simulation study," Langmuir, 22, 4116-4124 (2006).
37. Bernholc, J., Lu, W., Nakhmanson, S. M., Hahn, P. H., Meunier, V., Buongiorno Nardelli, M. and Schmidt, W. G., "Atomic Scale Design of Nanostructures," Molecular Physics, 105, 147 (2007).
38. Calzolari, A., Ferretti, A. and Buongiorno Nardelli, M., "Ab initio correlation effects on the electronic and transport properties of metal(II)-phthalocyanine based devices," Nanotechnology, 18, Art. No. 424013 (2007).
39. Caussanel, M., Schrimpf, R., Tsetseris, L., Evans, M. and Pantelides, S., "Engineering model of a biased metal–molecule–metal junction," Journal of Computational Electronics, 6, 425–430 (2007).
40. Fuentes-Cabrera, M., Meunier, V. and Sumpter, B. G., "Benzo-homologated nucleobases in a nanotube-electrode set-up for DNA sequencing," Nanotechnology, 18, Art. No. 424019 (2007).
41. Hodak, M., Wang, S., Lu, W. and Bernholc, J., "Implementation of ultrasoft pseudopotentials in large-scale, grid-based electronic structure calculations," Phys. Rev. B, 76, Art. No. 085108 (2007).
42. Leng, Y. S., Dyer, P. J., Krstic, P. S., Harrison, R. J. and Cummings, P. T., "Calibration of chemical bonding between benzenedithiolate and gold: the effects of geometry and size of gold clusters," Molecular Physics, 105, 293-300 (2007).
43. Lu, J.-Q., Zhang, X.-G. and Pantelides, S. T., "Standing Friedel waves: a quantum probe of electronic states in nanoscale devices," Phys. Rev. Lett., 99, Art. No. 226804 (2007).
44. Meunier, V., Kalinin, S. V. and Sumpter, B. G., "Nonvolatile memory elements based on the intercalation of organic molecules inside carbon nanotubes," Phys. Rev. Lett., 98, Art. No. 056401 (2007).
45. Meunier, V. and Sumpter, B. G., "Tuning the conductance of carbon nanotubes with encapsulated molecules," Nanotechnology, 8, Art. No. 424032 (2007).
46. Pu, Q., Leng, Y. S., Tsetseris, L., Park, H. S., Pantelides, S. T. and Cummings, P. T., "Molecular dynamics simulations of stretched gold nanowires: The relative utility of different semiempirical potentials," J. Chem. Phys., 126, Art. No. 144707 (2007).
47. Pu, Q., Leng, Y. S., Zhao, X. C. and Cummings, P. T., "Molecular simulations of stretching gold nanowires in solvents," Nanotechnology, 18, Art. No. 424007 (2007).
48. Romo-Herrera, J. M., Terrones, M., Terrones, H., Dag, S. and Meunier, V., "Covalent 2D and 3D networks from 1D nanostructures: Designing new materials," Nano Letters, 7, 570-576 (2007).
49. Souza, A. G., Meunier, V., Terrones, M., Sumpter, B. G., Barros, E. B., Villalpando-Paez, F., Mendes, J., Kim, Y. A., Muramatsu, H., Hayashi, T., Endo, M. and Dresselhaus, M. S., "Selective tuning of the electronic properties of coaxial nanocables through exohedral doping," Nano Letters, 7, 2383-2388 (2007).
50. Sumpter, B. G., Meunier, V., Valeev, E. F., Lampkins, A. J., Li, H. and Castellano, R. K., "A new class of supramolecular wires," J. Phy. Chem. C, 111, 18912-18916 (2007).
51. Tsetseris, L., Hadjisavvas, G. and Pantelides, S. T., "First-principles studies of isomerization processes of silicon clusters," Physical Review B (Condensed Matter and Materials Physics), 76, Art. No. 045330 (2007).
52. Tsetseris, L. and Pantelides, S. T., "Intercalation of oxygen and water molecules in pentacene crystals: First-principles calculations," Phys. Rev. B, 75, Art No. 153202 (2007).
53. Tsetseris, L. and Pantelides, S. T., "Probing the nanoscale with first-principles calculations," Materials Science and Engineering B, 152, Issues 1-3, 25 August 2008, Pages 109-113 (2008).

54. Varga, K. and Pantelides, S. T., "Quantum transport in molecules and nanotube devices," Phys. Rev. Lett., 98, Art. No. 076804 (2007).
55. Zhang, X. G., Kalman, V. and Pantelides, S. T., "Generalized Bloch theorem for complex periodic potentials: A powerful application to quantum transport calculations," Physical Review B (Condensed Matter and Materials Physics), 76, Art. No. 035108 (2007).
56. Beste, A., Meunier, V. and Harrison, R. J., "Electron transport in open systems from finite-size calculations: Examination of the principal layer method applied to linear gold chains," J. Chem. Phys., 128, Art. No. 154713 (2008).
57. Meunier, V. and Krstic, P. S., "Enhancement of the transverse conductance in DNA nucleotides," J. Chem. Phys., 128, Art. No. 041103 (2008).
58. Ribeiro, F. J., Lu, W. and Bernholc, J., "Doping-dependent negative differential resistance in hybrid organic/inorganic Si-porphyrin-Si junctions," ACS Nano, 2, 1517-1522 (2008).
59. Romo-Herrera, J. M., Terrones, M., Terrones, H. and Meunier, V., "Electron transport properties of ordered networks using carbon nanotubes," Nanotechnology, 19, Art. No. 315704 (2008).
60. Saraiva-Souza, A., Sumpter, B. G., Meunier, V., Souza, A. G. and Del Nero, J., "Electrical rectification in betaine derivatives," J. Phy. Chem. C, 112, 12008-12011 (2008).
61. Pu, Q., Leng, Y. S. and Cummings, P. T., "Rate-Dependent Energy Release Mechanism of Gold Nanowires under Elongation," Journal of the American Chemical Society, 130, 17907–17912 (2008).
62. Teich-McGoldrick, S. L., Bellanger, M., Caussanel, M., Tsetseris, L., Pantelides, S. T., Glotzer, S. C. and Schrimpf, R. D., "Design considerations for CdTe nanotetrapods as electronic devices," Nano Letters, 9, 3683-3688 (2009).