COVER PAGE

Final Report on "Advanced Simulation of Metal Clusters" (Grant No. F49620-96-1-0211)

From: Dr. Xiao-Qian Wang (Principal Investigator)
Department of Physics
Clark Atlanta University
223 James P. Brawley Drive
Atlanta, Georgia 30314
Phone: (404) 880-8649
Fax: (404) 880-8360
Electronic Mail: xwang@ctsps.cau.edu

To: Dr. Michael Berman
AFOSR/NL
801 North Randolph Street
Arlington, VA 22203
(703) 696-7781

Grant: F49620-96-1-0211
Air Force Office of Scientific Research

Period: June 1, 1996 - November 30, 1999

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

0268

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPC
		Final -01 Jun 96 - 30 Nov 99

4. TITLE AND SUBTITLE
Advanced Simulation of Metal Clusters

5. FUNDING NUMBERS
F49620-96-1-0211

6. AUTHOR(S)
Dr Xiao-Qian Wang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Clark Atlanta University
223 James P. Brawley Drive
Atlanta GA 30314

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
801 N. Randolph St.,Rm 732
Arlington VA 22203-1977

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release: Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

In an effort to develop efficient O(N) first-principles calculation algorithms, we devised the approach using wavelets as basis functions fo relectronic structure calculation. The theory of wavelets allows one to apply a multi-scale (multiresolution) analysis to problems that exhibit widely varying length scales. Furthermore, the dual localization property of the wavelet basis is useful for improving the existing (N) methods that are yet based solely on the real-space locality. Our application of this idea to the density-functional molecular dynamics method leads to a robust algorithm, which holds potential to extend the applicability of the current first-principles methods to systems an order of magnitude large. On the other hand, we have developed an approach to the development of reliable "pair-functional" interatomic potentials for monoatomic metals based on fitting to a large set of experimental and ab initio data. In connection withthe construction of improved and accurate semi-empirical models, we have investigated the simulation tools such as hyper-Molecular Dynamics, generalized simulated annealing for global optimization, finite-difference method for calculating non-linear static third-order polarizabilities.

14. SUBJECT TERMS
Wavelets, Molecular Dynamics

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASS	UNCLASS	UNCLASS	

ADVANCED SIMULATION OF METAL CLUSTERS

Summary of effort

In an effort to develop efficient $O(N)$ first-principles calculation algorithms, we devised the approach using wavelets as basis functions for electronic structure calculation. The theory of wavelets allows one to apply a multi-scale (multiresolution) analysis to problems that exhibit widely varying length scales. Furthermore, the dual localization property of the wavelet bases is useful for improving the existing $O(N)$ methods that are yet based solely on the real-space locality. Our application of this idea to the density-functional molecular dynamics method leads to a robust algorithm, which holds potential to extend the applicability of the current first-principles methods to systems an order of magnitude larger. On the other hand, we have developed an approach to the development of reliable "pair-functional" interatomic potentials for monoatomic metals based on fitting to a large set of experimental and *ab initio* data. In connection with the construction of improved and accurate semi-empirical models, we have investigated the simulation tools such as hyper-Molecular Dynamics, generalized simulated annealing for global optimization, finite-difference method for calculating non-linear static third-order polarizabilities.

Accomplishments/New Findings

(i) Parallel and Distributed Molecular-Dynamics Simulations

Parallel Algorithm and Simulations

We have implemented a parallel and distributive algorithm for classical molecular dynamics using many-body "pair-functional" potentials, and tested a parallel version of *ab initio* molecular dynamics algorithm. The former parallel molecular dynamics algorithm was tested for systems consisting of 10^6-10^7 atoms, and was employed for the simulation of the epitaxial island growth on hexagonally reconstructed Au(100). The study for Au/Au(100) reveals that the stable islands of rectangular shape are hexagonally reconstructed in conformity with the patterns of the reconstructed Au(100) surface, and suggests the "magic" width of the islands in agreement with experimental observations. The associated study on transition states and adatom diffusions indicate that the experimentally observed strong anisotropic effect is attributed to the long-range exchange diffusion.

Glassy Surfaces of Metallic Nanocrystals

The vibrational and elastic properties of metallic nanocrystals are studied using semi-empirical potentials of gold and lead. Our results on the density of vibrational states show that the experimentally observed linear-frequency dependence is attributed to the glass-like surface atomes, as a result of a thorough geometry optimization. The extracted elastic constants indicate a decrease of Young's moduli and an increase of the shear moduli with the increase of the nanocrystal size. The changes involved in the elastic

constants can be attributed to well-defined surgface layers, independent of the nanostructure size. The experimentally observed enhancement of low- and high-frequency modes are found to be spatially localized in two shells, a soft surface shell and a hard transition shell.

Nonlinear Optical Properties

We have devised a method for calculating valence electron contributions to the static molecular third-order polarizabilities. The method utilized is based on the finite-field approach coupled with semi-empirical polarization calculations on all-valence electrons. The static third-order polarizabilities of carbon-cage fullerenes are analyzed in terms of three properties, from a geometric point of view: symmetry; aromaticity; and size. The application to large fullerenes shows that the static linear polarizability depends almost exclusively on surface area while the third-order polarizability is affected by a combination of number of aromatic rings, length and group order, in decreasing importance.

Hyper Molecular Dynamics

Recently, based on the transition state theory, Voter has provided a method to accelerate the molecular dynamics (hyper-MD), which opens a window to simulate atomic dynamics for a microsecond or longer. In this scheme, a bias potential raises the potential energy except for the saddle points of the potential energy surface. The dynamics on the biased potential surface leads to accelerated evolution from one potential minimum to another. We have explored the possibility of using a local bias potential to speed up the hyper-MD. This approach is shown to be a good approximation to the real system. So far, the hyper-MD works only for interatomic potentials with continuous third order derivatives.

(ii) Multiresolution Analysis for Electronic Structures

Orthonormal Wavelet Bases for Electronic Structure Calculations

We have devised an approach utilizing compactly supported, orthonormal wavelet bases for *ab initio* molecular dynamics (Car-Parrinello) algorithm. A wavelet selection scheme is developed and tested for various atomic and molecular systems. The method shows systematic convergence with the increase of wavelet-selected grid size, along with improvement on compression rates. This method yields an optimal adaptive grid for self-consistent electronic structure calculations, and offers a realistic approach for the study of metal clusters.

The application involves the study of atomic and electronic shell structures for the experimentally characterized Al_{77}. The onion-like Al_{77} structure can be described as a stable Al_{13} inner core covered by a two-layer atomic shell. The stability of Al_{77} is confirmed by the structural optimization and electronic structure calculations. The interaction between Al_{77} and its ligand is found to be ionic-like. Our results on the electronic structure provide important information on the electronic shell structures in large metallic clusters.

Highly Accurate Electronic Structure Calculations

The structure and energies of the (1x2) and (1x3) missing-row reconstructed transition metal (110) surfaces are studied using first-principles density-functional theory with local-density and generalized gradient approximations. A detailed analysis of the multilayer relaxation shows that the heavy topmost-layer distortions are closely coupled with the change of kinetic energy of electrons. The first-principles results shed lights on the nature of roughening and deconstruction transitions of Au(110).

Personnel Supported

Faculty

Dr. Xiao-Qian Wang, P. I

Research Staff

Dr. D. Y. Sun, Research Scientist
Dr. Miki Nomura, Research Associate
Dr. C. J. Tymczak, Research Scientist
Dr. G. Jarparidze, Research Scientist
Dr. J. Niles, Research Staff

Visiting Research Scientists

Dr. M. Daw, Visiting scientist
Dr. M. Y. Chou, Visiting scientist
Dr. X. Y. Liu, Visiting scientist
Dr. X. G. Gong, Visiting scientist

Graduate Students

Dr. Julian Niles, Ph. D. student (successfully defended his Ph.D. thesis in March 1999).
Ms. Ako Emanuel, M.S. student
Mr. Ronald Hickson, M.S. student
Mr. Yonas Abraham, M. S. student
Ms. H. Liu, M.S. student

Undergraduate Students

Mr. John Maweu
Mr. M. Slater

Publications

The following relevant publications in referred journals have appeared:

- Miki Nomura and Xiao-Qian Wang, "Hexagonally reconstructed islands and anisotropic diffusion for Au/Au(100)", *Phys. Rev. Lett.* **81**, 2739 (1998).

- C. J. Tymczak, G. S. Japaridze, C. R. Handy, and Xiao-Qian Wang, "Iterative solutions to quantum-mechanical problems", *Phys. Rev.* **A58**, 2708 (1998).
- C. E. Moore, B. H. Cardelino, D. O. Frazier, J. Niles, and X. Q. Wang, "Molecular static third-order polarizabilities of carbon-cage fullerenes and their correlation with three geometric properties: symmetry, aromaticity, and size", *J. Molecular Structure (THEOCHEM)* **454**, 135 (1998).
- C. J. Tymczak, G. S. Japaridze, C. R. Handy, and Xiao-Qian Wang, "New perspective on inner product quantization", *Phys. Rev. Lett.* **80**, 3673 (1998).
- C. J. Tymczak and Xiao-Qian Wang, "Orthonormal wavelet bases for quantum molecular dynamics", *Phys. Rev. Lett.* **78**, 3654 (1997).
- Craig E. Moore, Beatriz H. Carderlino and Xiao-Qian Wang, "Static third-order polarizability calculations for C_{60}, C_{70}, and C_{84}", *Letter, J. Phys. Chem.* **100**, 4685 (1996).

The following papers have been submitted for publication and are currently under review:

- X. G. Gong, D. Y. Sun, and X. Q. Wang, "Relative Stability of Missing-Row Reconstructed (110) Surfaces", *Phys. Rev. Lett.* (1999).
- X. G. Gong, D. Y. Sun, and X. Q. Wang, "Atomic and Electronic Shells of Al_{77}", *Phys. Rev. Lett.* (1999).
- X. Q. Wang, "Universal Singularities of Two-Dimensional Superconductor-Insulator Transitions", *Europhys. Lett.* (1999).
- D. Y. Sun, X. G. Gong, and X. Q. Wang, "Soft and Hard Shells in Metallic Nanocrystals", *Phys. Rev. Lett.* (2000).

The following papers are in preparation:

- D. Y. Sun, X. G. Gong, and X. Q. Wang, "Glassy Surfaces of Metallic Nanocrystals", *Phys. Rev.* B, to be submitted (1999).
- Y. Abraham, D. Y. Sun, and X. Q. Wang, "Integrating the Bases of Pair Functional Interatomic Potential Models", *Phys. Rev. Lett.*, to be submitted (1999).

Interactions/Transitions

a. Participation/presentations at meetings, confernces, seminars, etc.

- C. E. Moore, B. H. Cardelino, D. O. Frazier, J. Niles, and X. Q. Wang, "Molecular static third-order polarizabilities of carbon-cage fullerenes and their correlation with three geometric properties", Sixth Conference on Current Trends in Computational Chemistry, Vicksburg, MS, November 1997.

- C. J. Tymczak and X. Q. Wang, "Application of wavelets to electronic structure calculations", Los Alamos National Laboratory, December 1997.
- Miki Nomura and X. Q. Wang, "Molecular-dynamics simulations of metal suraces, clusters, grain boundaries, and diffusions", Univ. of Penn. March 1998.
- Y. Abriham, X.Y. Liu, M. Nomura, and X. Q. Wang, "The construction of optimal many-body interatomic potentials for transition metals", National Society of Black Physicists Conference, University of Kentucky, March 4-7,1998.
- X. Q. Wang, posters at AFOSR Molecular-Dynamics Contractor's Review, Monterey, California, "Wavelet bases for quantum chemistry calculations", and "Reconstruction, island growth, and surface diffusion for Au/Au(100): parallel and distributed molecular dynamics simulations", May 1998.
- G. S. Jarparidze and X. Q. Wang, "Highly accurate solutions to quantum problems", XXI International Workshop on the Foundamental Problems if Physics", June 23-25, 1998, Protvino, Russia.
- X. Q. Wang, "Wavelet bases for electronic structure calculations", January 1999, Emory University, and American Physical Society March Meeting at Atlanta, 1999.

b) none

c) none

New Discoveries, inventions, or patent disclosures

None.

Honors/Awards

None.