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REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	03/18/1999	Final Progress Report 01/16/96-12/24/98

4. TITLE AND SUBTITLE
Advanced Simulation of Electronic Materials:
A Paradigm for Distributive Computing and Simulations

5. FUNDING NUMBERS
DAAH04-95-1-0651

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 34939.9-MA-SDI

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The researchers have developed parallel and distributed algorithms for classical molecular dynamics and first-principles molecular dynamics methods for electronic structure calculations. An effective multivariable optimization scheme is employed for the construction of semi-empircal models. An innovative approach to apply the wavelet theory to electronic structure calculations is devised and implemented. A new iterative approach for solving quantum chemistry problems is discovered and tested for prototype atomic and molecular systems. In addition, a finite field method for calculating non-linear optical properties of molecules is developed and applied to the study of third-order polarizability of carbon-cage fullerenes. These developments in parallel and distributive algortihms have greatly enhanced the efficiency of simulating material properties.

Moreover, under the support of the grant, three graduate students have completed their thesis, one for Ph.D, and two others for M.S.

14. SUBJECT TERMS	15. NUMBER IF PAGES
Final Progress Report	6
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

FINAL REPORT ON "ADVANCED SIMULATION OF ELECTRONIC MATERIALS: A PARADIGM FOR DISTRIBUTIVE COMPUTING AND SIMULATIONS"

ARO Proposal Number: 34939-MA-SDI
Grant Number: DAAH04-95-1-0651
Period Covered By This Report: 01/30/96-12/24/98

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The final report for the project "Advanced Simulation of Electronic Materials: A Paradigm for Distributive Computing and Simulations" covers the period 01/16/96-12/24/98). In this report we summarize the achievements and results, consistent with the research activities outlined in the original proposal.

Recently, several groups have developed methods for performing first-principles electronic structure calculations that scale linearly with system size (the $O(N)$ methods). The fundamental idea behind the $O(N)$ techniques is the utilization of the spatial locality or "near-sightedness" of the system, a consequence of the sparse density matrix. 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 primary application of this idea to the density-functional molecular dynamics (Car-Parrinello) 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, in spite of the greatly increased computer power, the use of empirical or semi-empirical interatomic potentials is the only practical way for simulating much larger systems (up to 10^7-10^8 atoms) for much longer times (up to nanoseconds). For this reason there is always a demand for realistic interatomic potentials. We have developed an approach to the development of reliable many-body potentials for monoatomic metals based on fitting to a large set of experimental and *ab initio* data. The new features of this approach are as follows: (1) The database used for the development of the potential includes both experimental data and a large set of energies of various alternative structures of the materials generated by *ab initio* calculations. (2) The multivariable optimization scheme is employed to achieve the best accuracy of fitting within the intrinsic limitations of the potential model. (3) The theoretical basis of the

"pair-functional" potential is investigated using the density matrix method, which provides insight into the consistent approximation for applying the "pair-functional" functional form to intermetallic alloys. As an application of this approach we have developed accurate many-body potentials for Au, Pt, Pd, and Al. 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.

The following relevant publications in referred journals have appeared:

- 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).
- C. J. Tymczak and Xiao-Qian Wang, "Orthonormal wavelet bases for quantum molecular dynamics", *Phys. Rev. Lett.* **78**, 3654 (1997).
- 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).
- 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).

In addition, several papers are under review and in preparation. The related results were also represented at various conferences. Among the six minority graduated students supported under this project, three have completed their research thesis.

(i) Parallel and Distributed Molecular-Dynamics Simulations

The objectives of the parallel and distributive simulation thrust were: (1) Develop parallel and distributive codes for classical molecular dynamics and *ab initio* molecular dynamics; (2) Develop simulation tools for nonlinear optical properties, transition states, and global optimizations; and (3) Apply the algorithms to realistic problems, specifically the structure, dynamics, and transitions of metal clusters.

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.

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. Work is in progress to incorporate this feature into the construction of man-body force models.

Generalized Simulated Annealing

Many problems in materials theory and quantum chemistry involve the determination of the global minimum of a certain multidimensional function. In this context, many algorithms, such as the simplex, conjugate gradient relaxation, steepest descent, Monte Carlo, and genetic algorithm were developed. Among these, the simulated annealing is considered to be the key idea in finding the global minimum.

Recently, a generalized simulated annealing algorithm based on the generalized statistical mechanics of Tsallis is tested and developed. This approach unifies the conventional classical simulated annealing and the fast simulated annealing as corresponding visiting distributions stand for the limiting cases of the Tsallis statistics. We have tested this approach for a prototype problem, the Thomson model. The approach is shown to be efficient in drastically reducing the fluctuation in energy, and is capable of finding a new global minimum in comparison with the genetic algorithm. This method was applied to realistic problems such as the equilibrium structure of large clusters,

(cluster) island growth on surfaces, and the reconstruction pattern of the complicated herringbone Au(111) surface.

(ii) Multiresolution Analysis for Electronic Structures

Recently, it has been recognized that the wavelet bases with dual localization characteristics in real and reciprocal spaces are desirable for electronic structure calculations. By employing non-uniform grids, it is possible to add resolution adaptively. This leads to drastic savings in the basis size and thereby total computational workload. One of the important features of the wavelet bases is its ability to reduce the number of components needed for solving the Kohn-Sham equation, reminiscent of compression in applying wavelets to image processing. Furthermore, multi-resolution analysis associated with orthonormal wavelets provides automatic preconditioning on all length scales, which increases the rate of convergence of the electronic wave functions.

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 transition metal clusters.

Continuous Wavelet Analysis for Quantum Mechanics

We have discovered an efficient scheme of applying non-orthogonal wavelets to quantum chemistry calculation. This is based on the observation that in a power-series type expansion of the electronic wave function (such as Gaussian or Slater functions commonly used in quantum chemistry calculations), the converging zeros of the coefficient functions approximate the exact energies of atomic and molecular levels. Since the space of polynomials is invariant under affine maps, it facilitates the application of continuous wavelet analysis to quantum mechanics. This approach is shown to be equivalent to a convergent variational determinant quantization procedure. This method has been applied, with remarkable success, to various quantum-mechanical problems, including the electron correlation of molecular dimers and the Regge pole positions and residues (complex angular momentum) associated with the inelastic molecular collisions and reactive scattering.

Personnel Supported

List professional personnel supported and/or associated with the research project

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Mr. John Maweu, Department of Physics

All the students supported are minority students.

Interactions/Transitions

Participation/presentations at meetings, conferences, 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", 6th 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 surfaces, clusters, grain boundaries, and diffusions", Univ. Penn., March 1998.
- Y. Abraham, 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.
- G. S. Japaridze, "Highly accurate solutions to quantum problems", XXI International Workshop on the Fundamental Problems of Physics", June 23-25, 1998, Protvino, Russia.