REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-
G469

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		FINAL 01 May 95 To 28 Feb 98

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
DENSITY FUNCTIONAL THEORY FOR LARGE MOLECULAR SYSTEMS AND APPLICATIONS TO METCARS	F49620-95-1-0203

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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING / MONITORING AGENCY REPORT NUMBER
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19980514 152

11. SUPPLEMENTARY NOTES

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

13. ABSTRACT (Maximum 200 words)

During the grant period, we developed a major improvement in the calculation of the Coulomb term appearing in ab initio electronic structure methods based on Gaussian orbitals. Our efficient implementation of the Gaussian very Fast Multipole Method (GvFMM) combines speed, accuracy, and linear scaling properties. The method is clearly superior to state-or-the-art analytic integration techniques of Gaussian functions. Our benchmarks on graphitic sheets containing more than 400 atoms and 3,500 basis functions showed that the GvFMM dramatically reduces the computational requirements of the Coulomb problem. We implemented analytic first and second derivatives of the energy with respect to nuclear displacements using our GvFMM method for the efficient calculation of forces and frequencies in large molecules. We developed and implemented a linear scaling exchange correlation quadrature which dramatically speeds up another of the computational bottlenecks of state-of-the-art DFT programs. The combination of fast quadratures and GvFMM yielded substantial improvements in the calculation of harmonic frequencies. In order to obtain linear scaling with the Hartree-Fock method, we developed and implemented a linear scaling method termed 'near-field exchange' for exact exchange calculations of large molecules.

14. SUBJECT TERMS			15. NUMBER OF PAGES
	DTIC QUALITY INSPECTED 4		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT (U)	18. SECURITY CLASSIFICATION OF THIS PAGE (U)	19. SECURITY CLASSIFICATION OF ABSTRACT (U)	20. LIMITATION OF ABSTRACT (UL)

The remaining cubic-scaling computational bottleneck, the Hamiltonian diagonalization, was dealt with using a direct search for the density matrix. Our method is called the conjugate gradient density matrix search (CGDMS) method and replaces the Hamiltonian diagonalization for both Hartree-Fock and DFT methods. CGDMS was implemented for tight-binding, semiempirical, and ab initio methods.

FINAL TECHNICAL REPORT

I. General Information:

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Grant Number:

F49620-95-1-0203

Period Covered by this Report:

01 March 95 through 28 February 98

II. Objectives:

(a) The development of methodological and computational tools for the quantum chemistry study of large molecular systems.

(b) The development of the fundamental understanding of the bonding, structure, and reactivity of metal-carbon clusters.

III. Publications Acknowledging AFOSR Support:

1. Achieving Linear Scaling for the Electronic Quantum Coulomb Problem, M. C. Strain, G. E. Scuseria and M. J. Frisch, Science **271**, 51 (1996).

2. Analytic Energy Gradients for the Gaussian Very Fast Multipole Method (GvFMM), J. C. Burant, M. C. Strain, G. E. Scuseria and M. J. Frisch, Chem. Phys. Lett. **248**, 43 (1996).

3. Achieving Linear Scaling in Exchange-Correlation Density Functional Quadratures, R. E. Stratmann, G. E. Scuseria and M. J. Frisch, Chem. Phys. Lett. **257**, 213 (1996).

4. Kohn-Sham Analytic Energy Second Derivatives with the Gaussian Very Fast Multipole Method (GvFMM), J. C. Burant, M. C. Strain, G. E. Scuseria, and M. J. Frisch Chem. Phys. Lett. **258**, 45 (1996).

5. The Use of Density Matrix Expansions for Calculating Molecular Exchange Energies, R. M. Koehl, G. K. Odom and G. E. Scuseria, Mol. Phys. **87**, 835 (1996).

6. An ab initio Study of TiC: A Comparison of Different Levels of Theory Including Density Functional Methods, M. D. Hack, R. G. A. R. Maclagan, G. E. Scuseria and M. S. Gordon, J. Chem. Phys. **104**, 6628 (1996).

7. Ab Initio Calculations of Fullerenes, G. E. Scuseria, Science **271**, 942 (1996).

8. Crystalline Ropes of Metallic Carbon Nanotubes, A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer and R. E. Smalley, Science **273**, 483 (1996).

9. An ab initio Study of VC: A Comparison of Different Levels of Theory Including Density Functional Methods, R. G. A. R. Maclagan and G. E. Scuseria, Chem. Phys. Lett. **262**, 87 (1996).

10. An O(N) Tight-Binding Study of Carbon Clusters up to C_{8640}: The Geometrical Shape of the Giant Icosahedral Fullerenes, C. H. Xu and G. E. Scuseria, Chem. Phys. Lett. **262**, 219 (1996).

11. A Linear Scaling Method for Hartree-Fock Exchange Calculations of Large Molecules, J. C. Burant, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **105**, 8969-8972 (1996).

12. An ab initio Study of CrC: A Comparison of Different Levels of Theory Including Density Functional Methods, R. G. A. R. Maclagan and G. E. Scuseria, J. Chem. Phys. **106**, 1491 (1997).

13. Linear Scaling Conjugate Gradient Density Matrix Search for First Principles Electronic Structure Calculations, J. M. Millam and G. E. Scuseria, J. Chem. Phys. **106**, 5569 (1997).

14. Improving Harmonic Frequencies Calculations in Density Functional Theory, R. E. Stratmann, J. C. Burant, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **106**, 10175 (1997).

15. Semiempirical Methods with Conjugate Gradient Density Matrix Search to Replace Diagonalization for Molecular Systems Containing Thousands of Atoms, A. D. Daniels, J. M. Millam, and G. E. Scuseria, J. Chem. Phys. **107**, 425 (1997).

16. Exchange Energy Functionals Based on the Density Matrix Expansion of the Hartree-Fock Exchange Term, T. van Voorhis and G. E. Scuseria, Mol. Phys. **92**, 601 (1997).

17. Ab Initio Calculations on Met-Cars: A Comparison of Different Levels of Theory on Model Compounds, R. G. A. R. Maclagan and G. E. Scuseria, in *Advances in Metal and Semiconductor Clusters*, Vol. IV, pp 253-261 (1998), M. A. Duncan, ed., JAI Press Inc.

IV. Interactions/Transitions

The basic research developed under objective (a) of this AFOSR contract has been incorporated as software technology by the private sector. In particular, Gaussian, Inc., one of the leading commercial vendors of ab initio computational chemistry programs, has implemented some of our recent methodological developments into *Gaussian 98*, the most recent release of their software package. The PI has not provided the company with a finished product for commercial use but has rather advised and consulted with Gaussian, Inc., on aspects related to the basic research that are in the public domain. The company itself is solely responsible for implementing and incorporating into their package the methods, ideas, and computational tools which we have made available to the general public by the standard procedure of disseminating results in the peer-reviewed scientific articles listed in section III above.

V. Accomplishments under objective (a)

During the grant period, we developed a major improvement in the calculation of the Coulomb term appearing in ab initio electronic structure methods based on Gaussian orbitals. Our efficient implementation of the Gaussian Very Fast Multipole Method (GvFMM) [1] combines speed, accuracy, and linear scaling properties. The method is clearly superior to state-of-the-art analytic integration techniques of Gaussian functions. Our benchmarks on graphitic sheets containing more than 400 atoms and 3,500 basis functions showed that the GvFMM dramatically reduces the computational requirements of the Coulomb problem. Our method is one order of magnitude faster than existing techniques in a 3-21G $C_{384}H_{48}$ LDA calculation. Our method becomes faster than standard techniques for as few as 300 basis functions, and given its linear scaling properties, it removes the major obstacle in the quest for ab initio electronic structure calculations of truly large molecular systems.

We implemented analytic first [2] and second derivatives [4] of the energy with respect to nuclear displacements using our GvFMM method for the efficient calculation of forces and frequencies in large molecules. We developed and implemented a linear scaling exchange correlation quadrature [3] which dramatically speeds up another of the computational bottlenecks of state-of-the-art DFT programs. The combination of fast quadratures and GvFMM yielded substantial improvements in the calculation of harmonic frequencies [14]. In order to obtain linear scaling with the Hartree-Fock method, we developed and implemented a linear scaling method termed 'near-field exchange' for exact exchange calculations of large molecules [11].

The remaining cubic-scaling computational bottleneck, the Hamiltonian diagonalization, was dealt with using a direct search for the density matrix. Our method is called the conjugate gradient density matrix search (CGDMS) method and replaces the Hamiltonian diagonalization for both Hartree-Fock and DFT methods. CGDMS was implemented for tight-binding [10], semiempirical [15], and ab initio methods [13].

In this grant, we have not only focused on the required speed up of DFT methods and algorithms to make calculations on very large molecules feasible, but also on improving the accuracy of existing exchange-correlation functionals. A new exchange functional [5,16] based on density matrix expansions, which shows great promise as an alternative to other functionals currently in use, was developed for this purpose.

VI. Accomplishments under objective (b)

We carried out a series of theoretical studies on the TiC molecule employing standard ab initio Hartree-Fock, multi reference configuration interaction, coupled cluster, and density functional theory methods [6]. The objective was not only to predict the fundamental properties of the molecule but also to calibrate with the highest levels of theory the more approximate techniques to be later used in the large cluster calculations. A series of theoretical studies on other met-car dimers (CrC and VC) using a variety of methods were also carried out for calibration purposes [9,12]. Work on Ti_2, TiC_2, and Ti_2C was presented in Ref. [17], together with a comprehensive summary of our results.

Fullerene and carbon nanotubes are materials with many interesting properties and our research group has been active in theoretical predictions of these systems for many years [7]. A breakthrough [8] in the large yield macroscopic production of single wall nanotubes of uniform diameter has facilitated experimental applications of these tubes as proximal probes and in composite materials. Our calculations [8] played a central role in understanding the outcome of the carbon nanotube macroscopic production experiment.