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-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. 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.
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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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:


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 C384H48 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 Ti2, TiC2, and Ti2C 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.