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NSSEFF - COMPUTATIONAL AND THEORETICAL DESIGN OF PHOTO- AND MECHANO-RESPONSIVE MOLECULAR DEVICES

Todd Martinez
LELAND STANFORD JUNIOR UNIV CA

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450 SERRA MALL
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14. ABSTRACT
This project developed GPU-based methods for electronic structure and ab initio molecular dynamics. We extended such approaches to include density functional theory, transition metal containing systems, large proteins, multireference wavefunction techniques, excited electronic states, and continuum solvation methods. During this project, we also discovered the tensor hypercontraction formalism which leads to orders of magnitude improvement in the performance of wavefunction-based electronic structure methods. We introduced the idea of interactive ab initio molecular dynamics and demonstrated a proof of concept. We also introduced the ab initio nanoreactor, which harnesses the GPU-based developments in electronic structure theory and ab initio molecular dynamics to perform discovery of new chemical reactions.

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Overview of project: The original goal of this project was to develop GPU-based approaches to electronic structure and ab initio molecular dynamics and to apply these to problems in mechanochemistry and photochemistry. The promise of the graphics processing unit (GPU) in quantum chemistry and ab initio molecular dynamics has been largely realized and as a consequence of this NSSEFF-funded research, it has now become routine to simulate molecules with hundreds of atoms for time scales of over 100 picoseconds from first principles (using only a single desktop machine in days). These simulations include all electrons treated quantum mechanically, and therefore can treat bond rearrangement, electron/proton transfer, and electronic excitation without constraints or foreknowledge. This new capability is revolutionizing molecular simulation and we have used it to study molecular behavior after photon excitation and/or under mechanical force. Below, we detail some of the advances in GPU-based first-principles molecular simulation achieved in this project. However, we also stress that there were three new areas which were incubated by this grant – advances which could not be anticipated when the grant was awarded, but which are themselves revolutionary. These are 1) the development of tensor hypercontraction which exploits ideas from recommendation systems (as used by Netflix and Amazon) to decrease the scaling of wavefunction methods, 2) the introduction of interactive ab initio molecular dynamics, where virtual reality interfaces are combined with quantum chemistry and first principles dynamics, and 3) the development of the *ab initio* nanoreactor which *discovers* new chemical reactions from first principles simulation.

Summary Outcomes: This NSSEFF project resulted in 34 peer-reviewed publications. It has supported 13 postdoctoral scholars/staff scientists and 8 graduate students. The PI has given more than 50 invited talks describing the NSSEFF-funded research in the US, Europe and Asia, including numerous plenary addresses.

GPU Acceleration of Electronic Structure and Ab Initio Molecular Dynamics: The main proposed goal of this project was to transform first principles simulation capabilities by leveraging GPUs. We redesigned algorithms for stream processors and made significant inroads compared to our first preliminary implementation. It is now possible to carry out calculations including *d* angular momentum basis functions[1] and effective core potentials[2] (opening up the possibility of treating organometallic complexes), continuum solvation[3] (enabling calculations that include both explicit and implicit solvent), multireference wavefunction methods[4-6] (enabling the calculation of dynamics involving diradical and other open shell species), excited electronic states,[4,7-9] and multiple levels of precision[10] (making consumer grade GPUs a viable option). We also introduced a method to exploit low cost methods and use them to increase the size of the time steps that can be used in

AIMD[11] and a method to increase the accuracy of electronic structure methods with small basis sets.[12] We demonstrated the new groundbreaking capabilities through application to numerous "firsts:" the first ab initio molecular dynamics of proteins,[13] large scale ab initio optimization to gauge accuracy in structure prediction/refinement,[14] ab initio calculations of electronic excitation energies and absorption spectra in proteins,[8] and ab initio dynamics including nonadiabatic surface crossing effects for a molecule with more than 50 atoms.[15] Using these tools, we were able to carry out numerous studies on excited state reactivity,[16-18] enzyme reactions,[19] and mechanochemistry of polymers.[20] We also exploited the ability to generate large amounts of electronic structure information to parameterize a new empirical potential for water.[21]

Tensor Hypercontraction: A key stumbling block in electronic structure theory (and therefore also in ab initio molecular dynamics) has been the steep scaling of wavefunction based methods for describing electron correlation. It is largely because of the perceived "scaling wall" that density functional theory has become so successful. DFT scales formally as $O(N^4)$, where N is the size of the molecule (or more accurately the number of basis functions used to describe the electronic density). The scaling of DFT is thus the same as Hartree-Fock (HF) theory, but DFT includes the electron correlation effects that HF ignores. Unfortunately, the exchange-correlation functional in DFT remains unknown and current approximations have numerous problems and deficiencies that have proven difficult to resolve. Wavefunction methods that include electron correlation scale as $O(N^5)$ or even worse – for example, CCSD(T) which is often called the "gold standard" for thermochemistry scales as $O(N^7)$. ***During the NSSEFF project, we discovered that it is possible to formulate wavefunction methods such as Moller-Plesset perturbation theory and coupled cluster such that their formal scaling is $O(N^4)$ – the same as DFT!*** This discovery was based on our investigation into recommendation systems used by Netflix and Amazon to determine what products should be suggested to consumers. The core idea in these recommendation systems is that one imagines a large matrix with consumers as rows and products as columns. Then one asks for an algorithm that can "complete" this matrix on the basis of several observations. This is of course impossible in general. However, it would be possible if the matrix in question contained very little information (for example, if consumers fell into groups where all members of the same group wanted the same products). Such information-deficient matrices are technically called "low-rank," and the recommendation system algorithms exploit this structure. We discovered how to apply this idea to high-dimensional tensors and then how to use this for the two electron repulsion integrals. We then discovered that the same idea could also be used for the electronic wavefunction. Effectively, we discovered that there are massive redundancies in *both* the quantum mechanical operators and wavefunctions that are encountered in most molecules. Recognizing this hidden structure and revealing it allows one to decrease the computational effort by up to two *powers* of the molecular size. A number of papers demonstrate the idea and show that it is quantitatively accurate and faster than conventional approaches already for small molecules (the accuracy and efficiency increase as larger molecules are treated).[22-31] We also implemented the method on GPUs for further acceleration[31] and applied it to electronic excitation energies with equation-of-motion coupled cluster (EOM-CC2).[26] Tensor hypercontraction has breathed

new life into wavefunction methods and is currently being pursued by numerous other groups as well as our own.

Interactive Ab Initio Molecular Dynamics: As our efforts to accelerate ab initio molecular dynamics on GPUs became more successful, we began asking ourselves what we might be able to do that was *qualitatively* different from "business as usual" in computational chemistry. Sure, larger molecules can now be simulated for longer time scales and this is bound to change the landscape considerably as the scope of problems that are amenable to computation is enlarged. But are there modes of use that were simply unthinkable before? Thinking about this led us to two ideas – interactive AIMD and the nanoreactor (see following paragraph). **The main idea in interactive AIMD is to allow the user to interact with an AIMD simulation in real time, i.e. *as the simulation progresses*.** We were successful in this venture, using a haptic input device with force feedback.[32] The user grabs an atom with the haptic device and then the haptic device resists the user according to the internal forces computed by AIMD. Bonds can be broken because the underlying simulation solves the electronic Schrodinger equation at each time step. When the user tries to break a strong bond, more force is required, compared to breaking a weak bond. This new technology allows users to experience chemistry in full three dimensions and with tactile response. We are exploring the use of this capability for both research and education.

The ab initio Nanoreactor: The second idea which arose from thinking about how to use GPU-accelerated AIMD in a disruptive manner was the "ab initio nanoreactor." We thought that it might be possible to begin using AIMD as a means to discover new reactions. The first attempts at this simply ran molecular dynamics at high temperatures with the molecules confined to remain within a sphere. We observed that reactions could be seen to progress on a time scale which was easily attained (tens of picoseconds, which consumed less than a day of real time on a desktop computer). This led us to realize that we could accelerate reactions in numerous ways, including not only high temperatures but also pulsing pressure (with a spherical piston). Once we discovered reactions in this way, we realized that the reactions could then be studied with traditional hypothesis-driven approaches – finding minimum energy paths and reaction barriers. This new tool[33-34] is a way to discover what reactions are possible and then these can be refined (possibly at a more accurate level of theory if desired), obtaining rates which can then be placed in a kinetic model (sometimes called a set of master equations). **This represents a major new direction in theoretical chemistry, which can now begin to unravel the mechanisms involved in complex reaction networks. Unlike traditional approaches, the nanoreactor is a *discovery* tool.** We are currently exploring the use of this and related strategies to discover new synthetic routes, to expose the mechanisms of combustion reactions, and to discover new catalysts for fundamental chemical reactions.

Summary: We accomplished many of the goals originally proposed for the NSSEFF project. Primarily, we exploited GPUs in ab initio molecular dynamics in a way that continues to transform the field. At the same time, we would like to emphasize the new directions that could not have been foreseen at the time the original proposal was written. Thanks to the flexibility of the NSSEFF funding, we were able to pursue these directions that have proven

to be transformative. We developed the tensor hypercontraction formalism that has resurrected wavefunction theories and may supplant DFT. We introduced a new technology for interactive ab initio molecular dynamics, which has now received funding through the STTR program and could be the beginning of a new effort to develop molecular computer-aided design (MolCAD) and perhaps ultimately also molecular computer-aided-manufacturing. We also introduced the ab initio nanoreactor which has attracted the attention of at least four major companies so far and is being developed in new directions. We are confident that the nanoreactor strategy will change our perception of the role of theory and computation in chemistry – from the traditional hypothesis-driven approach to one emphasizing discovery of chemical pathways and reactions.

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toddjmartinez@gmail.com

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Abstract

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New discoveries, inventions, or patent disclosures:

Do you have any discoveries, inventions, or patent disclosures to report for this period?

No

Please describe and include any notable dates

Do you plan to pursue a claim for personal or organizational intellectual property?

Changes in research objectives (if any):

No changes to the primary objectives, but we did pursue three new directions as specified in the report.

Change in AFOSR Program Officer, if any:

Extensions granted or milestones slipped, if any:

Grant was in no-cost extension for a year.

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Sep 06, 2016 04:09:45 Success: Email Sent to: toddjmartinez@gmail.com