

OVERVIEW OF THE MURI PROJECT: Accurate Theoretical Predictions of the Properties of Energetic Materials

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RECENT RESEARCH HAS ENABLED THIS MURI

The overarching goal of this MURI project is to develop comprehensive theoretical/computational methods that can be used in the design of new energetic materials. The purpose here is to give an overview of how this will be accomplished – how the MURI is designed and organized to meet the intermediate and long-term goals, and how the MURI will transition the methods and results to DoD and DOE researchers. The specific and overall goals, strategy, and areas of expertise will be outlined as an introduction to the subsequent presentations.

Theoretical methods, particularly molecular dynamics (MD) simulation methods and *ab initio* electronic structure calculations, have undergone significant new developments in recent years. They can now provide accurate predictions of the energetics and rates for very large complex systems. This presents an opportunity for significant advances in energetic materials research and this MURI is designed to take advantage of this to develop practical predictive capabilities for use in the search for new materials. The thrust of the work is the development of atomic-level models and *ab initio* quantum chemistry methods that are generally applicable to physical changes and chemical decomposition of condensed-phase energetic materials under extreme conditions. Some of the work can be accomplished by relatively straightforward application of proven methods; however, for the realization of the full, long-term benefits of theoretical predictions to aid in the design of new materials, an important component of the proposed project is further development of the critical theoretical methods needed to meet the specific problems in this area.

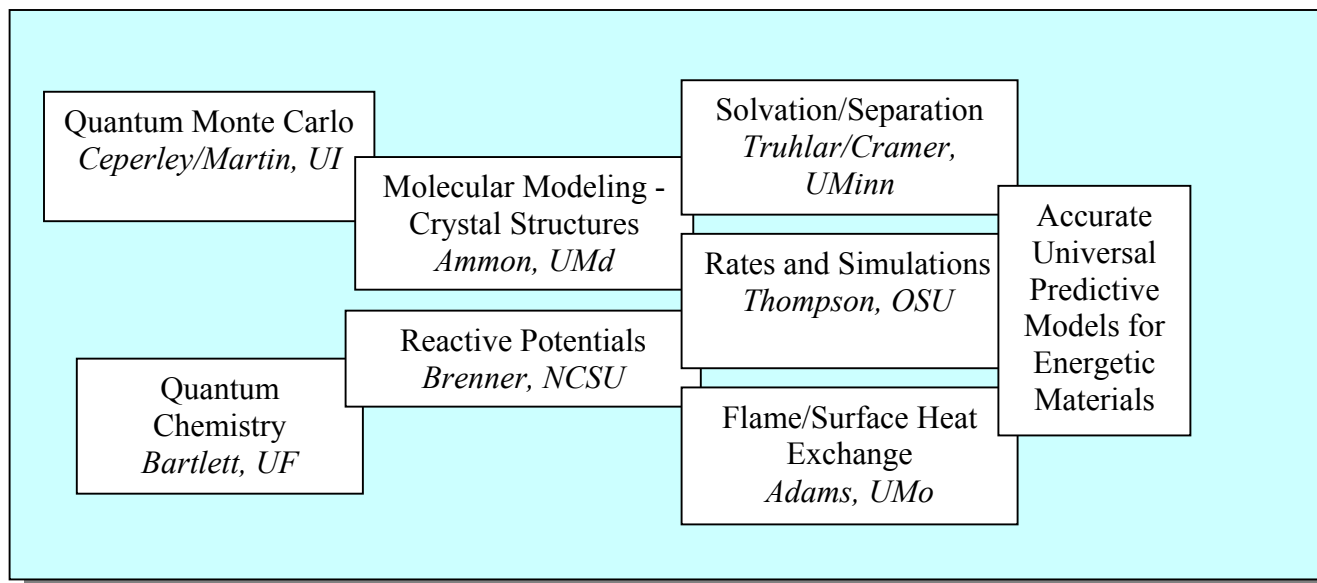
MURI GOALS

The major goals of the project are (a) Models that describe phase transitions and chemical reactions in condensed materials. (b) *Ab initio* predictions of structures and properties of solids at high temperatures and pressures. (c) Methods to predict mechanical properties and physical changes in condensed phases. (d) Simulation methods to predict chemical decomposition in condensed phases, particularly ignition and sensitivity in response to heating and shocking. (e) Methods for predicting temperatures of the condensed phases and flames resulting from physical and chemical changes, including a predictive model for the “heat feedback” from the flame to burning surface. This will provide a direct link between the atomic-level condensed phases models to the continuum models for flames. (f) Methods for predicting solvation and separation for energetic materials in supercritical fluids. The focus is materials containing H,C,N,O – particularly, nitro and nitramine compounds.

MURI ORGANIZATION

The MURI team comprises all the critical requisite areas of expertise, including quantum mechanics, molecular modeling, Monte Carlo, and MD, to yield state-of-the-art methods specifically designed for and tailored to target DoD energetic materials research needs. They

are: John Adams (U. Mo.) *Gas-liquid heat transfer*; Herman Ammon (U. Md.) *Crystal models*; Rod Bartlett (U. Fla.) *Quantum Chemistry*; Don Brenner (NCSU) *Reaction potentials*; David Ceperley/Richard Martin (U. Ill.) *Solid-state quantum mechanics*; Don Thompson-PI (OSU) *Reactions dynamics and simulations*; Don Truhlar/Chris Cramer (U. Minn.) *Solvation models*. While integration of the overall research project into a cohesive, focused effort is necessary to achieve the goals, much of the critical work will be carried out by the team members at their respective universities. Thus, there are clearly defined sub-projects, which are the responsibilities of the particular experts on the team. How the various components contribute to the goals of the project is illustrated in the following diagram.



The group at the University of Illinois, headed by Professors Ceperley and Martin, are working on a long-term project to enable first-principles simulations of energetic materials. The overall goal is to develop accurate methods that will become robust tools for prediction of the properties of materials under extreme conditions, especially high temperature and pressure. The primary applications will be materials containing first row elements H, C, N, and O, for which they will carry out selected benchmark calculations for definitive comparison with experiments, and for predictions beyond the capabilities of experiments. Their work focuses primarily upon quantum Monte Carlo (QMC) methods, the only known approaches that can simulate materials directly from the fundamental equations for interacting nuclei and electrons. They will provide benchmarks that can be used in constructing universal force field models, in conjunction with the work of Professors Ammon, Brenner, and Thompson. Ultimately, they expect to treat reactions in nitromethane (CH_3ONO) and the simpler analogue HONO, which decomposes in a way similar to CH_3ONO , *i.e.*, $\text{HONO} \rightarrow \text{HO} + \text{NO}$.

The focus of the work by Professor Bartlett's group at the University of Florida is the development and application of quantum and classical mechanical methods to condensed phase energetic materials. Professor Bartlett's group will provide the highly accurate potential energy surfaces (PES), activation barriers, and spectroscopic identification required as the first stage in developing the predictive models. Equally important, they continue work on developing better methods that will ensure that the full benefits of *ab initio* calculations are realized in future refinements of the model. These *ab initio* results will provide critical data for the classical potentials that will be developed by Professor Brenner. Also, Professor Bartlett will collaborate

with Professor Thompson to develop methods for doing direct dynamics simulations to bypass the fitting of analytical potentials. And, of course, Professor Bartlett's work complements the solid-state quantum Monte Carlo studies of Professors Martin and Ceperley.

The primary goals of the work being carried out by Professor Ammon's group at the University of Maryland are the development of procedures for the prediction of the crystal structures, accurate densities and heats of formation of energetic materials, and investigations of the relationships between crystal structure/microstructure and sensitivity, compressibility, polymorphism and crystal shape. This work is being closely coordinated with that by the groups at the University of Illinois, North Carolina State University, and Oklahoma State University. Also, Professor Ammon is maintaining a close interaction with Dr. Betsy Rice as the methods and models are incorporated into her simulation codes.

Professor Brenner's group at North Carolina State University is developing a transferable analytic reactive potential for C, H, O and N containing species. The analytic functional forms are based on a chemically sound bond-order formalism that has proven extremely powerful for describing reactivity in hydrocarbons. Accurate first principles quantum-mechanical calculations are being used to both determine appropriate functional forms and parameters entering this formalism, and to validate specific chemical reaction paths and rates for unimolecular dissociation and recombination produced by the analytic potential. These computationally efficient potentials will enable large-scale, 3-D molecular dynamics (MD) simulations that will predict system properties related to shock initiation and detonation of a wide range of both existing and potentially safer and more powerful high explosives (*i.e.*, molecular design). The proposed scheme - which represents an essential bridge between the accurate *ab initio* studies of molecular dissociation and the macroscale properties of shocked, condensed-phase molecular energetic materials, incorporating validation of the potentials across length scales by both comparisons between various theoretical methods as well as comparison to experimental results. The initial focus is on validating the potential for RDX and HMX. The models are being developed by working closely with other team members; especially, Professor Bartlett, who is providing *ab initio* results for parameterization; Professors Ceperley and Martin, whose calculations will be used as benchmarks for the formulation of universal force fields; Professor Ammon, who will provide basic structural and energetic models that will serve as the framework for the reactive models; and Professor Thompson, who has developed realistic potential energy surfaces for the unimolecular decomposition of several important energetic materials, including RDX and nitromethane. This phase of the work will be done in collaboration with Professor Thompson's group at OSU and Dr. Rice at ARL as it brings together most of the components that will make up the final general condensed-phase, chemical decomposition model.

The research by Professor Adams' group at the University of Missouri, Columbia, is concerned with developing more accurate models to aid in the prediction of the burning rate of solid-phase energetic materials, which strongly depends on the temperature of the fluid layer that forms between the flame and the underlying solid surface. The heating of this fluid surface depends on energy feedback from the combustion reactions. The absence of a molecular description of this energy transfer has required the development of "interim" descriptions of the kinetics. The goal is to link the condensed-phase models being developed by the MURI team with the steady-state continuum model of Drs. Miller and Anderson, and Professor Adams is working closely with the rest of the MURI team, particularly, Professors Brenner and Thompson, to make his modeling and simulations consistent with the overall models. The prediction of a burning propellant surface temperature will be based on molecular simulations that will be

carried out by Dr. Rice (ARL). Furthermore, he will be working closely with Drs. Anderson and Miller at ARL to ensure that the atomic modeling accurately weds to the continuum modeling.

The goal of the work the group at the University of Minnesota, headed by Professors Cramer and Truhlar, is to achieve a better understanding of the solubility and other properties of substances in supercritical fluids and to employ that understanding in the development of supercritical fluid technologies for recycling and reclamation of energetic materials. They are developing models for computing free energies of transfer of molecules between the gas phase, the liquid phase, and the solid phase, and into supercritical fluids. The model development effort is being pursued simultaneously from both semiempirical and first-principles standpoints.

The focus of the research of Professor Thompson's group at Oklahoma State University is the development of methods for simulations and rate calculations for the physical changes and chemical reactions in the gas and condensed phases. The challenge here is the development of methods particularly suited to the particular problems in energetic materials. Given the nature of the processes of interest here, the focus is on classical and semiclassical approaches for the near term (although methods such as those being developed by Professors Martin and Ceperley are clearly the ultimate approach). The particular challenges are simulations of relatively slow processes and methods for treating complex problems such as shock-induced chemical reactions. The need to rely upon the classical approximation requires careful assessments of its validity in descriptions of energy transfer and chemical reactions in the kinds of systems of interest here. The models will be based on those developed by the MURI team, thus the models will evolve over time along with increasing complexity of the processes being simulated. The aim is accurate simulations of the decomposition of energetic materials such as cyclic nitramines in the gas and condensed phases corresponding to the various practical conditions. A critical aspect of this work is the development of methods for theoretical rate calculations for and simulations of the complex chemical reactions occurring along parallel, branching sequential pathways for the decomposition; *e.g.*, such as those predicted in mechanisms of TNAZ, RDX, and HMX decompositions. While the focus of the MURI is the chemistry in condensed phases, it is important that the resulting models accurately describe the gas-phase reactions. The OSU group is developing new ways of formulating the potentials to take greater advantage of *ab initio* results and that are consistent with the reaction models for the condensed-phase chemistry. This entails close interactions with the groups of Professors Bartlett and Brenner. The models are being formulated such that they are consistent with those for the condensed phases that are being developed by the composite effort of the MURI team. Since the gas-phase reactions produce the species and energy contributing to heat feedback from flames, the OSU group will do this with strong interactions with Professor Adams' group. They will also provide information that can be useful in refining the continuum flame models developed by Drs. Miller and Anderson at ARL, and thus there will be continuing interactions with them. The OSU group assumes a central role in the development of the general models for predicting the properties of energetic materials and is collaborating with Dr. Rice at ARL to incorporate these into practical simulation codes. The proposed models will be the practical result of the combined efforts of the MURI team, and the OSU group will be responsible for bringing together the various contributions to produce the practical models that will be the final product of the project.

MURI WHOLE IS GREATER THAN THE SUM OF THE PARTS

The success of the project depends on the integration of the various components into a seamless whole that works towards a "solution" that is comprehensive and targeted. This

pertains to both the interactions within the MURI team, but also to the interactions of the team (collectively and individually) with DoD and DOE researchers to identify the critical problems, frame the right approaches, and finally to “transition” the methods and models to practical applications. Thus, the members of this MURI team were selected not only because they bring to the project the needed expertise but also because they have demonstrated their abilities to work in collaborations while making creative, independent contributions. Also, many of them have past and ongoing interactions and collaborations with DoD and DOE researchers. This will facilitate the interactions of the MURI team the DoD and DOE researchers who will contribute to the theoretical efforts, provide data for testing of the models, or aid in the transition of the MURI results and models to DoD applications. The MURI team will work closely with DoD researchers to continuously transition the methods and models to Army applications. A crucial part of the work will be to make extensive and detailed comparisons with experimental data to prove the accuracy of the methods and models. *The end result of this project will be a set of methods and computer codes that provide DoD researchers with predictive theoretical tools to aid in the search for new energetic materials and in the study, handling, and modification of current materials.*

COMMITMENT TO EDUCATION

It is important to point out that this project is providing opportunities to educate a number of young scientists in research of high relevance to DoD missions. Many of the team members have outstanding records in this regard, having produced graduate and postdoctoral students who have gone on to work in DoD relevant areas in national and military laboratories as well as universities. The MURI will support 14 graduate students each year. These students will be trained in fundamental theoretical chemical physics with strong components of computational methods. They will gain a solid understanding of important DoD relevant research. Similarly, the 7 postdoctoral research associates supported by the project will gain expertise in critical areas of DoD interests. Most of the MURI groups comprise a number of students and postdoctoral fellows working on a wide range of problems that will provide an excellent environment for the MURI students and postdocs. All of the academic departments have strong graduate programs. Several of them are associated with research centers that will enhance the education of the students.

MURI BUDGET

Finally, we will discuss how the funding is being spent. The bulk of the funding is devoted to student and postdoctoral researchers’ salaries, with only a small percent going to faculty salaries. Aside from the Indirect Charges (based on University-Government contracts), which accounts for approximately 40% of the costs, the largest single expenditure is for training young scientists: 20.6% of the budget is allocated for student support and 23.6% for postdocs (for a total of 44.2%). Only 7.1% will be spent on PI salaries. Most of the MURI team members have access to adequate facilities for performing the research; thus only 2.6% of the funding is being used for equipment, mainly to purchase additional PCs to accommodate the students and postdocs. Travel expenses account for another 2.5%, with the remainder going to fringe, supplies, publication costs, communication, etc.