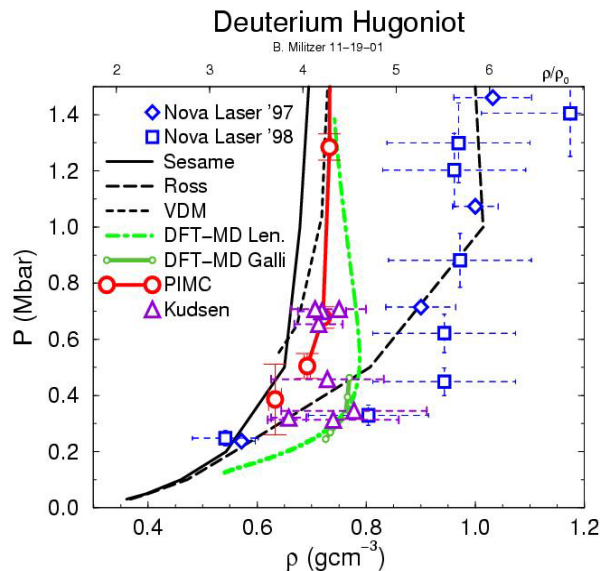


First Principles Simulations of Energetic Materials

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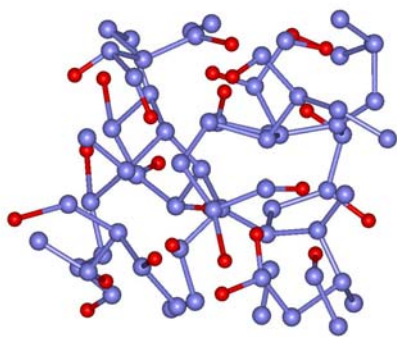
The group at the University of Illinois is working on a long-term project to enable first-principles simulations of energetic materials. The overall goal is to develop accurate methods that will become robust tools for prediction of the properties of materials under extreme conditions, especially high 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. The 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. Two QMC methods are under development: Path Integral Monte Carlo and Coupled Electron Ion Monte Carlo.

The last few years we have developed PIMC codes to simulate systems of electrons and protons at high pressures and temperatures down to 0.5eV. We have made detailed comparisons[1] with other types of models and approaches and have predicted the results of shock wave experiments carried out at Livermore. This year our PIMC calculations were verified by a new shock compression experiment at Sandia National Laboratory [2]. We were in disagreement with the previous laser shock experiments NOVA (Livermore) and ONR. The work is a good, timely example of the inroads that quantum simulation is making on equation of state problems where experiment is costly or unreliable.



We have recently developed another QMC method to do coupled electronic-ionic Monte Carlo (CEIMC) simulations[3]. In this method, one moves the ions classically while calculating the electronic potential (i.e. Born-Oppenheimer)with QMC. In the last 2 years this method has been tested on molecular and metallic hydrogen composed of up to 100 atoms at temperatures as low as 300K. Our impression is that the method applied to hydrogen, has the same order of computational demands but can be much more accurate than Car-Parrinello plane-wave methods for some applications. The processing power of current multi-processors is enough that significant applications can already be envisioned. Tests for non-hydrogenic systems are needed to find the performance of the algorithms on a broader spectrum of applications. We will apply the CIEMC method to energetic materials at finite temperatures.

We have also carried out density functional theory (DFT) and QMC studies of other first row materials. As an example of cases where we have had a long term interest in nitrogen under widely varying conditions. The phases of nitrogen at high pressure have presented a major challenge for many years. Over ten years ago we carried out DFT and QMC calculations that predicted a metastable phase of nitrogen[4]. However, the QMC was limited to very simple structures. recently, experiments[5] have observed the phase and established the exciting possibility that it is sufficiently stable that it could be a candidate energetic material with very high energy per unit mass. We have carried out new DFT simulations[6] to study the high pressure and temperature properties and ways to stabilize the compound. The figure shows a typical quenched network structure for which the range of metastability has been increased by passivation of dangling bonds by H.



The DFT simulations have been done with the linear scaling local-orbital program named SIESTA that is now widely used. This program is based upon work started at Illinois and developed by our collaborators in Spain. This is an example of a general DFT simulation method that can be combined with a full QMC simulation for truly first-principles predictions of properties of energetic materials.

Within the granting period, the above calculations will provide benchmarks that can be used in constructing universal force field models, in conjunction with the work of Professors Ammon, Brenner, and Thompson. We expect to treat reactions in nitromethane (CH_3ONO) and the simpler analogue HONO.

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