

Electronic Structure Theory for Energetic Molecules

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Our part of the MURI effort is to develop and use our state-of-the-art methods for accurate quantum mechanical solution of molecular problems as the starting point for condensed phase simulations. Over some years we have developed the coupled-cluster theory to offer the best available results for molecules up to ~15 atoms. In fact, today it is well established that many-body methods offer a converging series of approximations MBPT(2)<CCSD<CCSD(T)<CCSDT<CCSDT(Qf)<CCSDTQ<Full-CI that enable us to converge efficiently with correlation and basis set extensions to the exact solutions for a problem. We have also formulated and implemented analytical gradients to enable us to obtain the forces on atoms to conveniently locate minima and saddle points (transition states) on potential energy surfaces. Activation barriers remain one of the most difficult quantities to obtain, but no better solution than CC exists. We also have developed CC methods for excited, ionized, and electron attached states via our EOM-CC approach, and can readily provide all kinds of spectroscopy, vibrational (IR and Raman), UV-vis, photoelectron, ESR, and NMR for identification and detection purposes.

Other contributions from our effort that will complement other parts of this project should include further developments of our new ab initio dft methods, our transfer Hamiltonian approach to providing quantum mechanical forces for MD in a tractable way; and semi-classical flux-flux autocorrelation methods as a complementary approach for rate constants.

More specifically, in Figure 1 are shown a series of target systems that we believe should be studied during this project.

POTENTIAL TARGETS

GASES

NO, NNO, H₂N-NO₂
HN₃, HNCO, HCNO
HONO, O₃,...

LIQUIDS

H₃C-NO₂
H₂N-NH₂,...

SOLIDS

H₃C-N(NO₂)-CH₃
ADN, FOX-7, RDX, ...

fig1.

Some choices will serve as tests of the theory, either because of the existence of excellent molecular level experimental data, or because it offers a demanding case for some of the theoretical approaches being developed. For example, O_3 is well known to be an extremely difficult system to get its vibrational[1] and electronic excited states[2] right. Dimethylnitramine is a prototype solid explosive where substantial data exists. We expect to study several of these, and have begun by investigating the unimolecular decomposition in the series nitramine, methylnitramine, and dimethylnitramine. As the methyl groups are added, we open new pathways for decomposition which we would like to compare. We would expect to obtain accurate transition states and comparative activation barriers at the coupled-cluster and lower levels.

Another issue of great concern for condensed phases is the prevalence of bimolecular reactions. Unlike in the gas phase, bimolecular reactions may well be the dominant mechanism encountered in the initial stages of detonation. Hence, we have to devote considerable effort to addressing this issue. Doubling the size of molecule means a high-level CC calculation is some 2^7 times as difficult as it is for the single molecule, potentially forcing more compromises in the quality of the description, while also opening a plethora of new pathways.

Another aspect of the condensed phase that might require attention is the effect of long-range interactions. Attention needs to be paid to how such effects can modify the TS and activation barriers for the unimolecular and bimolecular reactions. Just as a solvent can greatly modify the kinetics of a reaction, the condensed phase might have a similar effect that needs to be introduced. I propose to look at these issues with some kind of dielectric function viewpoint

After the basic quantum chemistry is done, the next step is to provide a representation of those results into a classical, adaptive, or some other type of potential, for subsequent dynamics in the gas and condensed phase. Classical potentials are the easiest to use, but our particular approach to this problem is to use the concept of a transfer Hamiltonian, that is a low-rank Hamiltonian that allows us to describe complicated potential energy surfaces conveniently, and readily obtain first and second derivatives on the surface. This offers a fully quantum mechanical approach with electronic state specificity, yet within a framework that should be competitive with some classical potential simulations. We have had success with this approach in large-scale simulations [3] as well as in dynamics [4]. Fig. 2 summarizes our proposed quantum chemical approach.

My research group already has substantial interactions with Drs. Cary Chabalowski, Steve Bunte, and Shashi Karna at ARL, which will continue and be enhanced. In this project we also expect to broaden the scope of our interactions with other ARL scientists significantly.

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