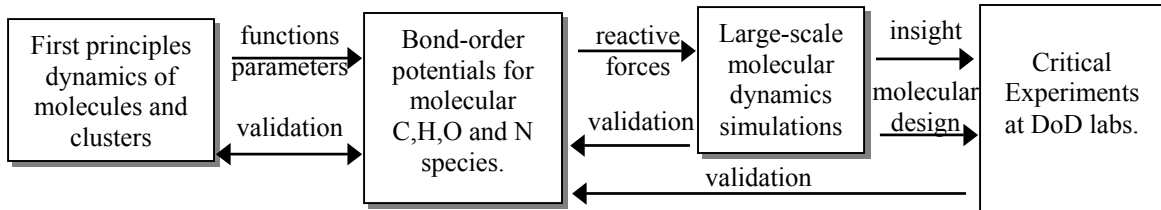


Quantum-Based, Reactive Potentials for Simulating Shock Dynamics of Condensed-Phase Energetic Materials: A Bridge Between *ab initio* Calculations and Experimental Shock Dynamics

D.W. Brenner, Department of Materials Science and Engineering, NC State University

Raleigh, NC 27695-7907

A transferable and robust analytic reactive potential for C, H, O and N containing species is being developed according to the scheme below:



The analytic functional form is based on a chemically sound bond-order formalism that has proven extremely powerful for describing reactivity in hydrocarbon systems.[1] Quantum-mechanical calculations, in particular those by MURI members Bartlett, Martin and Ceperley, will be used to 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, three-dimensional molecular dynamics simulations (to be carried out at OSU) 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.

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 - incorporates validation of the potentials across length scales by both comparisons between various theoretical methods as well as comparison to experimental results. A qualitative form of the proposed bond-order formalism was used to help establish the application of molecular dynamics methods to modeling self-sustaining reactive shock fronts that display properties reminiscent of macroscale detonation (see Fig. 1).[2] These properties include

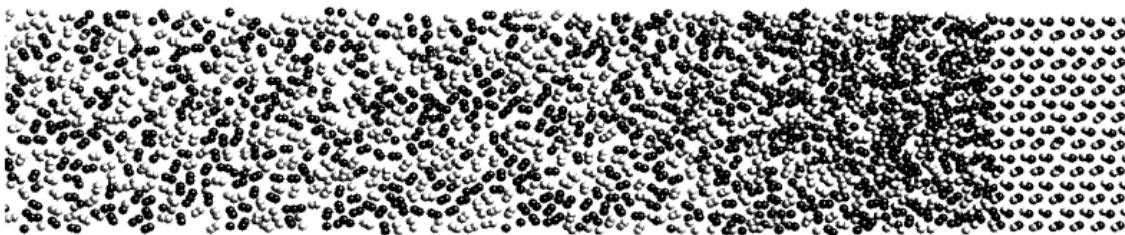


FIG. 1. Snapshot of a chemically sustained shock wave at 15 ps initiated by a four-layer flyer plate with an impact velocity of 6 km/sec. The two types of atoms are depicted in black and white. The shock front is propagating from left to right.

FIG 1: Figure from a paper describing a shock simulation using a generic form of the bond order potential.

initiation at defects behind shock fronts, detonation speeds that become independent of initiation, split shocks from phase transitions, and anisotropic shock speeds. The reactive potentials and associated simulations being developed in this MURI are a natural extension of these efforts, as well as related efforts by Rice and coworkers at the ARL, to specific energetic materials. These potentials also compliment other molecular modeling approaches for simulating reactivity undertaken by MURI members and their collaborators that are based on more traditional valence-force field/molecular mechanics-type formalisms.[3]

The bond-order formalism, which can be derived from the Harris functional form of density functional theory, is based on a second moment approximation that connects broadening of the local densities of states and associated energy changes with increasing number of neighbors.[4] Assuming that the total energy of a collection of atoms is the sum of the energy of individual atoms (i.e. the total density of states is the sum of the local density of states), the following equation can be derived for the total energy E^{tot} of a system of atoms

$$E^{\text{tot}} = \sum_i \sum_{j>i} [V^{\text{R}}(r_{ij}) - b_{ij} V^{\text{A}}(r_{ij})]$$

where the sums are over atoms i and j , $V^{\text{R}}(r)$ and $V^{\text{A}}(r)$ are repulsive and attractive pair terms representing core-core repulsion and attraction from valence electrons, respectively, and b_{ij} is a bond-order function. In this formalism, the repulsive and attractive pair terms are independent of bonding environment and in principle are transferable between different coordination numbers and molecular structures. ***This is the key element in producing a robust and transferable potential that can model chemical reactivity as well as the range of low and high pressure structures (i.e. in front of, inside and behind high-pressure shocks) typical of strongly shocked systems.***

In a strict second moment approximation, the bond order function b_{ij} between a pair of atoms is proportional to the sum of the inverse of the square root of the number of nearest neighbors N of each atom. For practical modeling applications, empirical bond order functions are needed whose values depend on more detailed aspects of local bonding environments. In our prior work on hydrocarbons, for example, a bond order function was developed that depends on local coordination, bond angles, degree of conjugation, and the presence of radical structures.[1] It was shown that with appropriate coupling to this empirical bond-order function, pair potentials for C and H could be developed that (1) are highly transferable between bonding environments, (2) can model appropriate changes in atomic hybridization during molecular dissociation and recombination, and (3) are sufficiently computationally efficient that the potential function can be used in large-scale molecular simulations.

A survey of first-principles calculations available in the literature suggests relations between bond length, energy and force constant for bonding combinations involving N, C, O and H atoms exist that are necessary for a universal bond-order description of systems containing these species. Plotted in the figures below, for example, are bond energies and force constants as a function of equilibrium bond length for C-N bonds derived from a wide range of molecular and solid structures. The smoothly decreasing bond energies and force constants with increasing bond length suggest that a potential that is transferable between bonding environments can be developed using a bond-order formalism for a wide-range of prototypical energetic materials containing CN bonds. Initial fitting studies in the MURI will focus on using the

results of first principles simulations of nitrogen systems under pressure being carried out by Martin to parameterize the nitrogen pair potentials and bond-orders. The data being generated by Martin goes significantly beyond comparable literature studies, and the synergy within the MURI team resulting from accurate first principles data and well-parameterized potential functions will produce robust and reasonably accurate potential energy functions.

One challenge to be addressed in these MURI studies is the incorporation of long-range non-bonded interactions into the bond-order formalism. Effectively accomplishing this goal will require combining expertise in charge-transfer formalisms available from Truhlar and Cramer, accurate non-bonded force parameterizations by Ammon, and experience in developing potentials brought to the MURI by Brenner, Thompson and Rice.

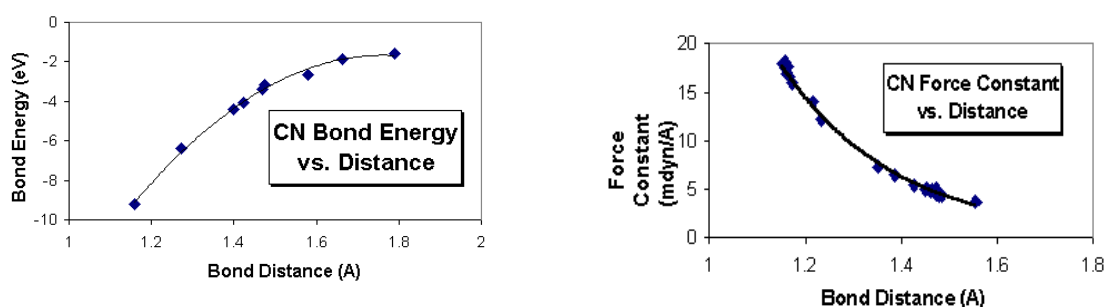


FIG 2: Bond energy-bond length-force constant relations for CN bonds. The well-behaved trends suggest that with proper parameterizations these bonds can be accurately described by a bond order potential.

- [1] D.W. Brenner, 'Empirical Potential for Hydrocarbons for Use in Simulating the Chemical Vapor Deposition of Diamond Films', *Phys. Rev. B* **42**, 9458 (1990); D.W. Brenner, 'The Art and Science of an Analytic Potential', *Physica Status Solidi B* **217**, 23 (2000).
- [2] D.W. Brenner, M.L. Elert and C.T. White, 'Incorporation of Reactive Dynamics in Simulations of Chemically-Sustained Shock Waves', in *Shock Compression of Condensed Matter*, S.C. Schmidt, J.N. Johnson and L.W. Davison, Ed. (North-Holland, Amsterdam), 263 (1990); D.W. Brenner, D.H. Robertson, M.L. Elert and C.T. White, 'Detonations at Nanometer Resolution Using Molecular Dynamics', *Phys. Rev. Lett.* **70**, 1821 (1992).
- [3] See for example B.M. Rice, G.F. Adams, M. Page, and D.L. Thompson, 'Classical Dynamics Simulations of Unimolecular Decomposition of CH₂NNO₂- HONO Elimination vs. N-N Bond Scission', *J. Phys. Chem.* **99**, 5016 (1995); B.M. Rice, J. Grosh and D.L. Thompson, 'Vibrational Mode Selectivity in the Unimolecular Decomposition of CH₂NNO₂', *J. Chem. Phys.* **102**, 8790 (1995); B.M. Rice, C.F. Chabalowski, G.F. Adams, R.C. Mowrey, M. Page, 'A Comparative Study of the Reaction Dynamics of a Model System Using Different Criteria in Parameterizing the Potential Energy Function', *Chem. Phys. Lett.* **184**, 335 (1991);
- [4] D.W. Brenner, O.A. Shenderova and D.A. Areshkin, 'Quantum-Based Analytic Interatomic Forces and Materials Simulation', in *Reviews in Computational Chemistry*, K.B. Lipkowitz and D.B. Boyd, Eds., (VCH Publishers, New York, 1998), pp 213-245.

