

## Large-Scale, Quantum-based Non-Adiabatic Molecular Dynamics Simulation of Materials in Extreme Conditions

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Extreme environments may involve conditions of high dynamic or static pressure ( $>30\text{MPa}$ ), high strain, and high-strain rates ( $>1\text{km/s}$ ); low or high temperature ( $>1200^\circ\text{C}$ ); highly corrosive or erosive conditions; high-radiation fluxes ( $>100\text{dpa}$ ); and high intensity electromagnetic fields ( $>15\text{T}$ ), alone or in combination. Developing materials that can operate reliably in such environments is critical to enabling technologies required for the next-generation of energy, spatial, transportation, medical, and military systems and devices, among many others. But major breakthroughs are required in theory, computation and experiments to elucidate the chemical, atomic and molecular, processes that occur within the bulk and at the surfaces of materials subjected to extreme operating conditions. Studying these states of matter through experimental observations has proven to be extremely challenging, if not impossible, primarily because they are hard to isolate and their time scales for changes are too rapid ( $<1\text{ps}$ ).

Consequently, synergistic approaches from theory and computation have taken center stage in enabling predictive calculations capable of steering experiments and material synthesis associated to extreme conditions. Yet, first-principles quantum mechanics simulation methods are inadequate for accurately describing the effects of thermal, mechanical, chemical or radiative excitations that may occur in materials operating under extreme conditions, or are impractical to use, except for very small systems ( $<100$  atoms) over short timescales ( $10\text{ps}$ ); including time-dependent Density Functional Theory or TDDFT. Furthermore, in the regime of a large number of electronic excitations, the electronic portion of the wavefunction contains contributions from many stationary states, and the Born-Oppenheimer approximation breaks down quickly. Therefore, a proper model capable of capturing and tracking the inherent processes would require describing non-adiabatic coupled electronic and nuclear motions for systems with  $10\text{'s}$ - $100\text{'s}$  eV excitations over long enough periods of time ( $>>\text{ps}$ ).

With this in mind, we developed the electron Force Field method (Su et al, 2007) and demonstrated it is iso-efficiently scalable to millions of atoms (and electrons) over  $10\text{'s}$  of ns timescales (Jaramillo-Botero et al, 2011) on massively parallel processing architectures. In eFF, the electrons are defined explicitly as self- and pairwise-interacting particles via potentials derived from quantum mechanics and classical electrostatics, and their motions are propagated independently, making it possible to go beyond adiabatic dynamics. Unlike other fermionic molecular dynamics methods, our approach achieves a balanced description of both ground- state condensed systems and highly excited systems containing ionized electrons. eFF is uniquely suited to simulate the dynamics of materials in which many electronically excited states of matter can occur and coexist, and overcomes salient limitations of quantum mechanics methods.

We have successfully demonstrated its use in describing the thermodynamics of dense hydrogen over 0 to  $100,000\text{K}$ ; the real-time dynamics of Auger fragmentation of diamond nanoparticles over fs ranges; electron stopping potentials in bulk materials; the dynamics of cascaded valence electron ionizations in shocked materials (e.g. polyethylene, silicon carbide and hydrocarbon molecules) during hypervelocity impact; and the electronic emissions during high strain rate brittle fracture of silicon; among others.

Yet, eFF is limited to low-Z elements of the periodic table ( $Z<6$ ) and the simplicity of its Gaussian basis formulation has several limitations, including 1) the omission of the true electron exchange between same spin electrons, and 2) the lack of cusp conditions and nodal structures, which complicates scaling to higher Z's. This leads to incorrect descriptions for double and triple bonds, lone pairs, and aromatic pi electron systems. To address these problems rigorously, we have now developed the Gaussian Hartree Approximated (GHA) kernel within the eFF concept (Jaramillo-Botero, Xiao et al 2015). GHA incorporates formal energy penalties for singlet and triplet pairs and angular momentum projected effective core pseudo-potentials that account for cusp conditions and missing nodal structures.

I will present the underlying theory behind the new kernel and demonstrate its application on open challenges.