Large-Scale, Long-Term Nonadiabatic Electron Molecular Dynamics for Describing Material Properties and Phenomena in Extreme Environments

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Abstract: We describe the first principle-based electron force field (eFF) methodology for modeling the simultaneous dynamics of electrons and nuclei (eMD) evolving nonadiabatically under transient extreme conditions. We introduce the parallel implementation of eFF (pEFF) that makes it practical to perform simulations of the nonadiabatic dynamics of materials in extreme environments involving millions of nuclei and electrons, over multi-picoseconds time scales, and demonstrate its application to: (i) accurately determine density and predict percent ionization of hydrogen at high pressure (∼61 GPa) and temperatures up to 15,300 K and (ii) determine, the single shock Hugoniot for lithium metal directly from the shock wave kinematics, i.e., mass velocities ($U_p$) and shock wave velocities ($U_s$), and shock density data. For (i), the density and ionization fractions of hydrogen atoms were calculated using the isobaric–isothermal ensemble at an isotropic pressure of 61.4 GPa and for temperatures between 300 K and 15,300 K. The results at 15,300 K describe a molecular fluid with density $\rho = 0.36 \text{ g/cm}^3$, in close agreement with existing experiments and theory, and ∼0.5% ionization. This result provides no indication of the existence of a critical plasma phase-transition point at this particular temperature and pressure, as previously predicted by others. For (ii), the relationship between $U_p$ and $U_s$ was characterized to be linear and plastic in the range 1–20 km/s, and the single shock Hugoniot was determined in close agreement with published results for experimentally reported $U_p$s. In addition to this, we provide a description of the materials’ behavior for large $U_p$s in terms of the appearance of a weak metallic plasma phase by $U_p = 10 \text{ km/s}$, with ∼8% ionization, gradually transitioning to a denser plasma with an estimated ∼35% ionization by $U_p = 15 \text{ km/s}$. Last but not least, we confirm the computational efficiency and scalability of pEFF by comparing its single processor performance against the fastest existing serial code, which results in a linear speedup $\sim 10\times$ faster for every 16,000 particles in favor of pEFF, and by evaluating its parallel performance in terms of its strong and weak scaling capabilities. Our results, on Los Alamos’s Lobo supercomputer (a 38TFLOPS Linux HPC with Quad-core AMD Opteron nodes interconnected with an Infiniband), show strong scaling with near ideal speedups for loads $>62$ particles per processor. Weak scaling is shown to be close to linear under the same per-processor load range. As an absolute reference, an NVT run with 2 million particle lithium bulk system (0.5 M nuclei and 1.5 M electrons) on Lobo takes $\sim 0.44 \text{ s/timestep}$ on 1024 processors ($\sim 1 \text{ day/ps}$ using an integration timestep of 0.005 fs).


Key words: hypervelocity impact of lithium; shock Hugoniot; nonadiabatic quantum mechanics; excited electron dynamics; high-density hydrogen; massively parallel molecular dynamics

Introduction

The Need for Materials Capable of Operating Under Extreme Conditions

Extreme environments may involve conditions of high dynamic or static pressure (>30 MPa), high strain, and high-strain rates (>1 km/s); low or high temperature (>1200 °C); highly corrosive or erosive conditions; high-radiation fluxes (>100 dpa); and high-intensity electromagnetic fields (>15 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. For example, the use of ultra-supercritical steam may allow increasing the efficiency of todays state-of-the-art coal-fired power plants from 35% to almost 60%, but this will involve raising operating temperatures by over 40% of their current capability (from 540 °C to 760 °C) and more than doubling the operating pressures, from 16.5 MPa to 37.9 MPa. Likewise, the next-generation nuclear reactors will require operating temperatures over 1000 °C, a significant increase from today’s 350 °C, which will bring neutron fluxes up an order of magnitude. Future ground, aerial and aquatic transportation vehicles will demand lighter and stronger structural materials capable of resisting large static and dynamic stresses, or materials for fast energy storage and release suited to work under extreme conditions of pressure, temperature, and chemical reactivity. Spaceships will need improved mechanical and thermal shielding materials to overcome the convective and radiative gas-surface flow conditions during atmospheric re-entry or during hypervelocity flight. At the same time, the next generations semiconductor electronics required to control and monitor such applications will require low-k dielectric materials capable of relatively extreme electric fields on nanometer-thin-gate geometries or novel material compositions that result in lossy permittivities and permeabilities to absorb electromagnetic interference from intense sources.

Consequently, understanding material properties and performance under extreme conditions, including their structure, morphology, and dynamic evolution over a broad set of length- (nanoscale to meters) and time-scales (femtoseconds to seconds), becomes an absolute imperative for their design, optimization, and use.

A common factor for all applications mentioned above, is that extreme operating environments accelerate the materials aging process, leading to reduced performance and reduced time to failure. High temperature lowers the chemical barrier for bond breaking and speeds up the chemical reactions of corrosion, sustained, or transient, extreme mechanical loading leads to accelerated propagation and growth of material defects and to subsequent failure, and extreme particle fluxes impinging on materials leads to radiation-induced embrittlement.

Major breakthroughs are required to elucidate the chemical, atomic, and molecular processes that occur within the bulk and at the surfaces of materials subjected to extreme operating conditions, requiring significant advances in experimental characterization, theory, and computation. Studying these states of matter through experimental observations has proved to be extremely challenging, if not impossible, mainly because they are hard to isolate and their time scales for changes are too rapid (<1 ps). It is only natural, then, that synergistic approaches from theory and computation have taken center stage in enabling predictive calculations or in steering experiments and material synthesis associated to extreme conditions.

First Principle Theory and Computation in the Characterization and Design of Materials for Extreme Environments

Over the last 20 years, improvements in computational quantum mechanics (QM) have revolutionized our understanding of processes ranging from homogeneous and heterogeneous catalysis to atmospheric and surface chemistry. However, most QM 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, due to the prohibitive scaling cost of propagating the total Schrödinger equation for a large number of atoms. 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, making it inefficient to work in a basis of stationary states for which the electron probability density has no time dependence. Under such conditions, the electronic kinetic energy is commensurate with the potential energy interactions between electrons and nuclei; therefore, a proper model capable of capturing and tracing the inherent processes would require describing nonadiabatic coupled electronic and nuclear motions for systems with 10s–100 s eV excitations over long enough periods of time (≫ ps).

Nonadiabatic Molecular Dynamics

One way to incorporate nonadiabatic effects is to describe nuclear motion via classical dynamics and electrons via time-dependent QM. Such an approach is termed a mixed quantum-classical approach. Because electrons are much lighter than nuclei, the electronic wavefunction spends most of its time evolving along stable adiabatic trajectories, except in small regions of phase space termed “avoided crossings,” where the wavefunction branches onto different adiabatic surfaces. When few states and only moderate excitations are present, it is essential in a mixed quantum-classical scheme that the electronic states are allowed to collapse onto one branch or the other, lest the nuclei are pulled “in between” states in an unphysical way. Curve hopping schemes of the sort introduced by Tully and Preston allow this collapse to one branch or the other, though a stochastic element is then added to the dynamics. On the other hand, when many states and high excitations are present, it becomes reasonable to allow the electrons to exist continuously in a linear combination of adiabatic states, and to move the nuclei in this mean field of states, i.e., an Ehrenfest approach.

In general, such mixed quantum-classical approaches combine (i) a particular scheme to deal with nonadiabaticity, (ii) an electronic structure method to deal with the multistate electronic structure, and (iii) classical molecular dynamics (MD) to propagate the nuclei. Aside from the specific compromises in accuracy for each approach, the major bottleneck is to first principle-based nonadiabatic MD simulations of large systems, during sufficiently long times, is the unavailability of efficient electronic structure methods that allow the evaluation of both gradients and nonadiabatic couplings for excited electronic states.

Here, we describe a nonadiabatic wavefunction MD approach that overcomes this hurdle by balancing computational cost efficiency with near first principle accuracy in the electronic structure contributions — the electron force field (eFF), its parallel implementation (pEFF) over the LAMMPS MD framework, and demonstrate its applicability to challenging problems that require dynamics simulations of large-scale systems, over picosecond and higher time scales.

The rest of this document is organized as follows: Section “The electron force field approach” provides an overview of the fundamental theory behind the eFF approach, Section “Large-scale, long-term nuclei-electron mechanics/dynamics with the parallel
electron force field” describes the most salient features of pEFF, its support under LAMMPS, and other implementation details of interest to the specialized user. Section “Example applications” demonstrates the application of pEFF to two important problems, namely, (i) the prediction of thermodynamically accessible high-density states of hydrogen and (ii) the description of hypervelocity shock-dynamics of lithium metal, including plasma formation properties in the so-called warm dense regime. In Section “Single and multi processor performance,” we benchmark the single processor performance of pEFF against our fastest serial version, as well as exalt the multiple processor performance of pEFF for systems with millions of particles over multi-picosecond time scales. Section “Final observations and conclusions” provides some closing observations and conclusions regarding the use of this new theoretical and computational framework to enable further understanding of large-scale, long-term phenomena present in materials operating in extreme conditions.

The Electron Force Field Approach (eFF)

eFF Energies

In eFF, the N-electron wavefunction is described as a product of one-electron Gaussian functions, whose size is a dynamical variable and whose position is not constrained to a nuclear center. This form allows for straightforward propagation of the wavefunction, with time, using a simple formulation. The nuclei are described as point charges. The full Hamiltonian, shown in eq. (1), has a standard description for electrostatic interactions between a set of delocalized point and Gaussian charges which include, nuclei–nuclei (E_{NN}), electron–electron (E_{ee}), and nuclei-electron (E_{Ne}). In addition to the electrostatics, eFF introduces QM effects through an electron kinetic energy from the Gaussians (E_{KE}) and a spin-dependent Pauli repulsion potential term (E_{PR}) between Gaussians. Thus, eFF is a simplified QM method rather than a conventional force field method, in which electron motions are averaged out into ground state nuclear motions (i.e., a single electronic state) described by empirically parameterized interatomic potential functions. This makes eFF uniquely suited to simulate materials over a wide range of temperatures and pressures where electronically excited and ionized states of matter can occur and coexist.

\[
U(R, r, s) = E_{NN}(R) + E_{Ne}(R, r, s) + E_{ee}(r, s) + E_{KE}(r, s) + E_{PR}(\uparrow \downarrow, S) \tag{1}
\]

The Pauli principle tells us that the simplest antisymmetric wavefunction needed to compute the electronic energy contains N! product terms, and evaluating the energy of such a wavefunction would normally require \(N^4\) operations — mostly for the computation of four-center electron-electron repulsion integrals. To avoid this prohibitive scaling, eFF describes the wavefunction as a Hartree product one-particle wavefunction, which requires \(N^2\) operations to evaluate. We then add a spin-dependent correction term to account for the orthogonality that would have been imposed by the antisymmetrizer. This is evaluated as an \(N^2\) pairwise sum between electrons. Because the antisymmetry of the wavefunction is responsible for Pauli repulsion, this term is referred as the “Pauli repulsion” potential, \(E_{PR}\). The form of \(E_{PR}\) is consequently based on the effect on the kinetic energy of orthogonalizing Gaussians, i.e., on the difference in energy between a Slater determinant of orbitals and a Hartree product of the same orbitals, assuming the kinetic energy effects dominate and add in a pairwise fashion,

\[
E_{exch} = \frac{S_y^2}{1 - S_y^2} \left( t_i + t_j - \frac{2t_{ij}}{S_y} \right) \tag{2}
\]

where \(S_y = \langle \phi_i | \phi_j \rangle\) corresponds to the overlap between two wave packets, \(\phi_i\) and \(\phi_j\), and \(t_{ij} = \langle \phi_i | -0.5 \nabla^2 | \phi_j \rangle\). This energy difference is also a measure of the kinetic energy exchange upon antisymmetrization.

In eFF, we use a Valence-Bond (VB) wave function representation on eq. (2), which we will name \(E_u\), and combine it with the Pauli potential described by Klakow for same spin electrons, which is of the same form as eq. (2) and which we will name \(E_g\), using the following mixing rule,

\[
E(\uparrow \uparrow) = E_u - (1 + \rho)E_g, \quad E(\downarrow \downarrow) = \rho E_g \tag{3}
\]

where \(\rho\) corresponds to a mixing parameter.

Somewhat similar Pauli potentials, but with additional antisymmetry terms added, have been proposed in other fermionic MD methods; however, they fail to provide a reasonable description for molecules containing atoms beyond H or to accurately describe both ground and excited states. eFF is the first method applicable to a wide range of molecules.

The functional form for \(E_{PR}\) is depicted graphically in Figure 1. We allow the expression in eq. (2) to be modified with a total of three parameters, two for scaling which act on electron sizes (\(\bar{\epsilon}_i = 0.9\epsilon_i\) and distances (\(\bar{\epsilon}_{ij} = 1.125\epsilon_{ij}\)), and \((\rho = -0.2)\) to
account for the degree of mixing between the Klakow potential and our VB-derived potential. These were fixed to the shown values by comparing with structures of simple hydrocarbons, boron hydrides, and alkali hydride. Additional details into the functional form of the implemented potentials in pEFF is provided in Section “Potentials, kinetic energy of motion, temperature, and pressure expressions in pEFF”.

Equations of Motion

In eFF, we solve the time-dependent Schrödinger equation directly, propagating very cost-effective electron wavefunctions simultaneously with the nuclear motions. The nuclear point charges that move in the mean field of electrons (as in Ehrenfest dynamics) and the N-electron wavefunction is taken as a Hartree product of single-electron thawed floating spherical Gaussians expressed as,

$$\psi(r) \propto e^{-\frac{1}{4} \left( \frac{x^2}{\sigma^2} + \frac{r^2}{\sigma_e^2}\right)} \cdot e^{-\frac{i}{\hbar} p \cdot r},$$

where \(x\) and \(s\) correspond to the continuous wave packet positions and sizes (or widths), respectively, and \(p_x\) and \(p_s\) to its conjugate translational and radial momenta, which represent the translational motion and radial expansion/shrinking of the wave packet over time. Substituting the wavefunction from eq. (4), in the time-dependent Schrödinger equation and assuming a locally harmonic potential, \(V\), results in the semiclassical equations of motion for the wave packet,

\[
\begin{align*}
\dot{p}_x &= m_e \frac{dx}{dt} \rightarrow \dot{x} \equiv \frac{dx}{dt} = m_e^{-1} \dot{p}_x \\
\dot{p}_s &= d \frac{d}{dt} \frac{ds}{dt} \rightarrow \dot{s} \equiv \frac{d}{dt} \frac{ds}{dt} = (4/d) m_e^{-1} \dot{p}_s
\end{align*}
\]

where \(d\) corresponds to the dimensionality of the wave packet (\(d = 1, 2, 3\) for 1D, 2D, and 3D, respectively), and \(m_e\) to the adjustable effective electron mass — in a single particle system within a locally harmonic potential, \(m_e\) equals the true electron mass, but in a more complex system, we adjust \(m_e\) in an empirical fashion to tune the rate of energy exchange between multiple electrons, and to compensate for anharmonicities in the local potential.

It follows from (5), that electrons move classically, but with an additional “breathing” motion as they shrink and expand in size over time as a function of their degree of localization (Heisenberg’s uncertainty principle expressed via the kinetic energy of the electronic wavefunction). Nuclei also obey the classical equation of motion.

The Gaussian wave packets are propagated under the influence of the Hamiltonian. This procedure leads to very efficient calculations for interactions between thousands of nuclei and electrons.

eFF leads naturally to a shell structure, where for C, there are two tightly bound 1s core electrons near the nucleus, and the remaining valence electrons at normal distances. The form of \(E_{\text{PR}}\) term (shown in Fig. 1) was derived by assuming that the dominant energy change upon orthogonalizing overlapping Gaussians is a kinetic energy increase, which leads to a net repulsion that depends on the overlap of the electrons and their sizes.

Note that the electronic wave packets remain stably localized over long time by the Coulomb attraction to the nuclei (Fig. 1), and they only become ionized under extreme conditions (e.g., collision with protons, spin flipping, and Auger process). Stationary states are not explicitly computed in eFF, but, they can be recovered by applying a perturbation to the system, then taking the Fourier transform of the dipole moment, or other relevant quantity [as in time-dependent density functional theory (TDDFT) or time-dependent spectroscopy]. There will be limitations on how many states can be recovered from small systems, due to the small number of degrees of freedom per electron.

In general, the eFF method may be viewed as an elaboration of fermionic MD methods, using more sophisticated effective potentials that make studying condensed systems possible. Alternatively, eFF can be thought of as an approximate version of the floating spherical Gaussian orbital (FGSO) ab initio method, made time-dependent so that excited system dynamics can be studied. Properties such as bonding, hybridization, lone pairs, bond geometry preferences, steric effects, transition state energies, charge distributions, valence shell occupancies, spin multiplicity effects, and ionization potentials all appear in eFF as emergent properties of interactions between nuclei and electrons in eFF, and do not have to be explicitly entered into the model.

The following section describes the details of the pEFF development over the LAMMPS parallel MD framework. Interested users should contact the authors or refer to the LAMMPS website http://lammps.sandia.gov for up to date information regarding pEFF, and for further details on LAMMPS-specific functions that are available to pEFF simulations. Because eFF forces are at most pairwise, the method scales as \(N^2\) in computation time and \(N\) in memory, where \(N\) is the combined number of electrons and nuclei. Conventional molecular mechanics/dynamics techniques for speeding computations were used in pEFF, including, pairwise force cutoffs to achieve linear scaling, and spatial domain decomposition into multi-processors to achieve strong scaling (i.e., reduction of solution times, as a function of an increased number of processors for a constant problem size) and weak scaling (i.e., maintaining constant scaling efficiency for increased problem sizes). pEFFs overall performance, for single and multi-processors runs, are reported in Section “Single and multiprocessor performance”. The reported results on functionality, performance, and scalability make pEFF particularly well suited for simulating large-scale and long-term nonadiabatic dynamics: a critical enabler technology to study material systems and phenomena (periodic and finite) in extreme conditions.

Large-Scale, Long-Term Nuclei-Electron Mechanics/ Dynamics with the Parallel Electron Force Field

In general, pEFF follows the structure of conventional MD packages, except that it incorporates electrons explicitly into the data structures, energy expressions, forces, equations of motion, virials, and so on. For example, to compute the ground state properties of a system, minimization of the system’s total energy (or forces) leads to optimizing the nuclear and electron positions and the electron sizes simultaneously. To simulate the dynamics of materials at finite temperatures or pressures, including nonadiabatic excited electron dynamics, mixed quantum-classical equations of motion are propagated in time, allowing the positions of the nuclei and
electrons, as well as the sizes of the electrons, to change with time. With this considerations in mind, pEFF was developed as a LAMMPS user-package, using the same style and syntax of its core modules, and with the following features explicitly supported:

- All particles are explicitly declared as atoms, with electrons and nuclei distinguished by atom type (see Section “Data representations in pEFF”),
- Hybrid pairwise definitions, for systems with nuclei and electrons or with electrons only (see Section “Data representations in pEFF”),
- implicit handling of all parallel data MPI communications with appropriate hooks to the LAMMPS framework,
- computation of single point energies, forces, and pressure for a given configuration of nuclei and electrons (see Section “Potentials, kinetic energy of motion, temperature, and pressure expressions in pEFF”),
- computation of per atom energies and per atom forces, including nuclei and electrons,
- geometry optimization using force- and energy-based criteria for structures with nuclei and electrons or electrons only by fixing nuclear positions,
- dynamics ensembles to propagate excited electron motions, including microcanonic (NVE), canonical (NVT) with Nosé-Hoover thermostating, and isothermal-isobaric (NPT) with Nosé-Hoover thermostat and barostat (see Section “MD ensembles”),
- computation of instantaneous pressure and full pressure tensor, from analytical virial expressions,
- definition of constraints on nuclei and electron positions or on electron radii, applied during minimization and dynamics,
- definition of restraints on a variety of nuclear/electron distances and angles applicable during minimizations and dynamics,
- setting of initial translational (nuclei and electrons) and radial velocities (electrons) (see Section “Data representations in pEFF”),
- operations on orthorhombic and triclinic periodic simulation cells,
- long-range electrostatics and Pauli pairwise handled using seventh-order polynomial cutoff with implicit minimum image convention for large unit cells (>20 Bohr),
- pairwise cutoffs enable linear scaling dynamics for single- and multi-processor runs (see Section “single- and multi-processor performance”)
- different physical units supported, with defaults set by the units “electron” definition for Energy (Hartrees), mass (amu), time (femtoseconds), positions (Bohr), velocities (Bohr/amu), forces (amu · Bohr²/amu = Hartrees · Bohr), temperature (Kelvin), and pressure (Pascals),
- pre- and post-processing tools available for building a variety of molecules and periodic structures, and tools to enable full nucleus-electron visualization using packages like VMD,¹⁷
- numerous user examples included to demonstrate basic and advanced functionality, and
- installation and uninstallation through the LAMMPS user-package convention (user-eff).

Several key benefits from running pEFF over LAMMPS deserve explicit mention, including (i) its a tested MD framework available as open-source software under the GNU Public License (GPL), (ii) its modular object-oriented architecture design simplifies extension tasks, and (iii) having access to the added functionality and flexibility provided by its core and other user packages, which enables users, among other things, to:

- define simulation settings using a wide selection of: compute and fix styles; finite, periodic, and shrink-wraped boundaries; physical units; atom selection and manipulation commands for creation, replication, deletion and group definitions; I/O commands for handling logs, dumps, and restarts; among others, and to
- integrate complex simulation runs involving a wide range of methods and hybrid combinations of these as performing dynamic analysis and averaging over thermodynamic and user-defined data using an imperative scripting environment.

The following subsections describe the details of the pEFF implementation, regarding: input data formats, basic data structures, analytical functional forms involved in mechanics and dynamics calculations, ensemble declarations and settings, etc. and how these are exposed through the LAMMPS scripting environment.

### Data Representations in pEFF

To simplify the definition of atomic related data structures in pEFF, both nuclei and electrons are declared and reserved via dynamic memory allocations using a LAMMPS atom_style, which determines the corresponding attributes associated to, and stored by, nuclei or electrons during a simulation. An atom_style electron introduces the electronic degrees of freedom in pEFF, which include attributes such as: wave packet position in Cartesian coordinates \(x, y, z\) of type \([\text{double,double,double}]\), up/down electron spin \([-1,1]\), and electron radius of type \([\text{double}]\) in addition to the conventional \(ID\) of type \([\text{integer}]\) and atom type as \([\text{integer}]\) declarations. The atom type is defined in LAMMPS from the mass attribute declarations, i.e., every mass declaration has an integer index associated to the type, and the \(ID\) corresponds to the tag that uniquely identifies the particle in the system. pEFF nuclei are defined using the already built-in atom_style charge in LAMMPS, which describes these with a point charge attribute of type \([\text{double}]\).

An atom_style hybrid charge electron definition enables the declaration of systems with both nuclei and electrons. The format for such a hybrid atom_style declaration is: \(ID\) type \(x\ y\ z\ q\ spin\ radius\), or conversely \(ID\) type \(x\ y\ z\ spin\ radius\ q\) if the user prefers an atom_style hybrid electron charge definition. The syntax for invoking this atom style in a LAMMPS script can take the following forms,

```
atom_style electron
atom_style hybrid charge electron
```

where the hybrid definition order can be switched for the second form as described previously.

For system setups that require \textit{a priori} defined initial velocities, their declaration in a LAMMPS format data file would involve the conventional attributes, i.e., \(ID\) \(vx\ vy\ vz\) for all nuclei and electrons, plus an extra \([\text{double}]\) attribute corresponding to the electronic radial velocity, \(s\ (vr)\).

Preparation of input structure data files (i.e., structure and composition) for running pEFF on LAMMPS is then a straightforward

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¹⁷ Note: VMD (Visual Molecular Dynamics) is a popular visualization tool for molecular dynamics simulations.
task. A general example of such a data file, for \( n \) particles and \( m \) atom types declared as atom_style hybrid charge electron, follows:

User-defined header line

\[
\text{[int]} \text{ atoms} \\
\text{[int]} \text{ atom types} \\
\]

# Simulation cell boundaries

\[
\text{[double]} \ [\text{double}] \ xlo, xhi \\
\text{[double]} \ [\text{double}] \ ylo, yhi \\
\text{[double]} \ [\text{double}] \ zlo, zhi \\
\]

# for triclinic systems, include tilts

\[
\text{xy} \ \text{xz} \ \text{yz} \\
\]

Masses

# type mass

1 [double]

2 [double]

::

m [double]

Atoms

# ID type x y z q spin radius

1 [int] [int] [double] ... [double] [+/-1] \\

2 [int] [int] [double] ... [double] [+/-1] \\

::

n [int] [int] [double] ... [double] [+/-1] \\

[double]

Velocities

# (optional) ID vx vy vz vr

1 [int] [double] [double] [double] [double] \\

2 [int] [double] [double] [double] [double] \\

::

n [int] [double] [double] [double] [double] [double]

Potentials, Kinetic Energy of Motion, Temperature, and Pressure Expressions in pEFF

The standard electrostatic interactions between nuclear point charges, nuclei-electrons, and electrons–electrons are written, respectively, as follows:

\[
E_{\text{nuc-nuc}} = \frac{1}{4\pi \varepsilon_0} \sum_{i<j} \frac{Z_i Z_j}{R_{ij}},
\]

(6)

\[
E_{\text{nuc-elec}} = -\frac{1}{4\pi \varepsilon_0} \sum_i \frac{Z_i}{R_{ij}} \text{Erf} \left( \frac{\sqrt{2} R_{ij}}{s_j} \right),
\]

(7)

and,

\[
E_{\text{elec-elec}} = \frac{1}{4\pi \varepsilon_0} \sum_{i<j} \frac{1}{R_{ij}} \text{Erf} \left( \frac{\sqrt{2} R_{ij}}{s_j} + \frac{\sqrt{2} R_{ij}}{s_j'} \right),
\]

(8)

where \( i \) and \( j \) correspond to the pair of interacting particles, \( Z \) to the nuclear point charges, \( R \) to the inter-nuclear or nuclear-electron distances, \( r \) to the inter-electron distances, and \( s \) to the electrons size. Here \( \varepsilon_0 \) converts the units of charge and distance to energy (e.g., \( \varepsilon_0 = 1/14.4 \) if the unit of charge is the electron, the unit of distance is Å and the unit of energy is eV).

The full Hamiltonian expressed in eq. (1) involves two quantum mechanical terms: (i) the kinetic energy of the wave packet (or electronic kinetic energy) defined as,

\[
E_{\text{KE}} = \frac{\hbar^2}{m_e} \sum_i \frac{3}{2 s_i^2},
\]

(9)

and the Pauli Repulsion potential defined as,

\[
E_{\text{Pauli}} = \sum_{\sigma_i = \sigma_j} E(\uparrow \uparrow)_{ij} + \sum_{\sigma_i \neq \sigma_j} E(\uparrow \downarrow)_{ij},
\]

(10a)

where,

\[
E(\uparrow \uparrow)_{ij} = \frac{S_{ij}^2}{1 - S_{ij}^2} + (1 - \rho) \frac{S_{ij}^2}{1 + S_{ij}^2} \Delta T_{ij},
\]

(10b)

and,

\[
E(\uparrow \downarrow)_{ij} = \rho S_{ij}^2 \frac{\Delta T_{ij}}{1 + S_{ij}^2},
\]

(10c)

correspond to the same-spin and opposite-spin portions, respectively, of the Pauli potential in eq. (10a), and

\[
\Delta T_{ij} = \frac{\hbar^2}{m_e} \left[ \frac{3}{6} \left( \frac{1}{s_i^2} + \frac{1}{s_j^2} \right) - \frac{6 (s_i^2 + s_j^2) - 4 s_i^2 s_j^2}{(s_i^2 + s_j^2)^2} \right].
\]

(10d)
and
\[
S_{ij} = \left( \frac{2}{\tilde{x}_i/\tilde{z}_i + \tilde{z}_j/\tilde{x}_j} \right)^{3/2} e^{-r_{ij}^2/(\tilde{x}_i^2 + \tilde{z}_j^2)},
\]
(10e)
correspond to the kinetic energy change upon antisymmetrization, and \(S\) to the overlap between two wavepackets, \(i\) and \(j\). The scaling parameters for size and position, \(\tilde{x}\) and \(\tilde{z}\), and the mixing parameter, \(\rho\), in \(E_{\text{FF}}\) were already defined in Section "eFF Energies".

Eqs. (6)–(9) constitute the total analytical potential energy forms expressed in eq. (1).

**LAMMPS pEFF Pairwise Extensions**

The total potential energy components for pEFF were implemented in LAMMPS as a new pair_style called eff/cut. The syntax for invoking this command in a LAMMPS script is,

```
pair_style eff/cut cutoff
pair_style eff/cut cutoff limit yes/no
```

where `cutoff` corresponds to a real number for the global cutoff in eFF interactions, and `limit` to a flag that can be set (yes) to restrain electrons from becoming unbound at very high temperatures.

The restraining harmonic potential takes the form \(E = 1/2k_s x^2\) for \(s > L_{\text{box}}/2\), where \(k_s = 1\) Hartrees/Bohr\(^2\). We should note that the equation of state is insensitive to the value of \(k_s\) — it is simply set large enough to keep the electrons bound.

As pEFF uses the minimum image convention, the `cutoff` value should be set to be at least half of the minimum simulation box dimension. Furthermore, to accurately account for the long-range electrostatics interactions, the system size under simulation should be large enough (i.e., \(L_{\text{box}}/2 \geq 20\) Bohr). For atom type pairs \(i,j\), and \(i \neq j\), the cutoff distance for the `eff/cut` style can be mixed. The default mix value is geometric, but using the LAMMPS `pair_modify` command gives the user additional options.

**Molecular Mechanics and Dynamics in pEFF**

To simulate materials at finite temperatures and pressures, we propagate the mixed quantum-classical electron equations of motion, allowing the positions of the nuclei and electrons and the sizes of the electrons, to change over time. The corresponding equations of motion were given in eqs. (4) and (5).

The kinetic energy of motion \((K)\) for the particles is given by,
\[
K = \sum_i \frac{1}{2} m_i \dot{x}_i^2 + \sum_j \frac{1}{2} \frac{3}{4} m_e \dot{z}_j^2,
\]
(11)
where \(m_i\) corresponds to the nuclear or effective electron mass, \(m_e\) exclusively to the effective electron mass, \(\dot{x}\) to the translational velocity for nuclei and electrons, and \(\dot{z}\) to the electron radial velocities. Each electron has two kinetic energies, as given by eqs. (9) and (11), which can interconvert, e.g., a localized electron in free space expands radially outward over time, transforming its size-dependent kinetic energy into a radial-dependent motion kinetic energy.

It should be noted that the electron mass appears in three different places: First, in the electronic kinetic energy, eq. (9), second, in the Pauli potential, eq. (10a), and third, in the kinetic energy of motion, eq. (11). Changing \(m_e\) in the Hamiltonian terms [Eqs. (9) and (10a)] affects the sizes of electrons in atoms and the lengths of bonds in molecules, hence, for these terms, it remains fixed at all times to the true value of the electron mass thereby avoiding any disruption to the chemistry of the system. On the other hand, \(m_n\) is a general parameter in the equations of motion [i.e., eq. (11)] and changing it may prove to be useful to alter the overall time scale of excited electron motions (e.g., simulating adiabatic systems or Auger processes), with the time scale of excitation relaxations and energy transfer proportional to \(1/\sqrt{m_n}\). For this reason, the option to vary \(m_n\) in eq. (11) is provided through the LAMMPS `mass` command.

It follows that the total energy \(E = K + U\) for the system is a constant of motion and, from eq. (11), that the kinetic temperature may be written as,
\[
T = \frac{2}{3k_B N_{\text{nuc}}} (K)
\]
(12)
where \(i\) and \(j\) correspond once more to the interacting particles, \(N_{\text{nuc}}\) to the nuclear degrees of freedom, and \(k_B\) to the Boltzmann constant. The virial expression essentially sets the kinetic contribution to the heat capacity to \(\frac{2}{3} k_B N_{\text{nuc}}\) (where only the nuclear degrees contribute). This is valid for temperatures well below the Fermi temperature. At intermediate temperatures, the kinetic contribution to the pressure from the electrons is recovered indirectly through the Pauli potential, i.e., as temperature increases, the electrons become excited, which causes their average size to increase, in turn raising the pressure via the Pauli potential. At temperatures comparable with or higher than the Fermi temperature, a separate ideal gas electron pressure corrective term is required.

The pressure is also extracted from dynamical simulations in pEFF as,
\[
P = \frac{1}{V} \left[ N_{\text{nuc}} k_B T + \frac{1}{d} \sum_{i<j} r_{ij} \cdot f_{ij} \right]
\]
(13)
where \(V\) corresponds in this case to the volume, \(T\) to the instantaneous temperature from eq. (12), \(d\) to the dimensionality of the system (2 or 3, for 2D and 3D), \(N_{\text{nuc}}\) to the interparticle distance, \(f\) to the interparticle force as a function of position, electron size, and spin (if electrons are involved in the corresponding pairwise interaction).

It must be noted that the equivalence between the virial and the potential energy, for pairwise potential forms proportional to \(-1/r\), as in eFF, will not hold true — for the most part — when using a cutoff scheme, for example, for a potential given as \(U = -1/r\), a polynomial cutoff \(s_c\), and virial \(v\), it follows,
\[
s_c U = -s_c/r
f = -\partial(s_c U)/\partial r
= -[(U \partial s_c)/\partial r + s_c \partial U/\partial r]
\]
(14)
where \( x \) corresponds to a user-assigned name for the \( \mathit{fix} \), and \( \mathit{group-ID} \) to the identification tag for the group of atoms to apply the \( \mathit{fix} \) to.

A \( \mathit{fix} \) in LAMMPS is an operation that is applied to the system during timestamping or minimization. Additional \( \mathit{fixes} \) include, a canonical (constant \( \mathit{NVT} \); \( T \) is the temperature) integration to update positions and velocities each timestep for all atoms (or a subgroup) using a Nosé-Hoover temperature thermostat,\(^{21} \) and an isothermal-isobaric (constant \( \mathit{NPT} \); where \( P \) is pressure) integration to update positions and velocities each timestep for all atoms (or a subgroup) using a Nosé-Hoover temperature thermostat\(^{21} \) and a Nosé-Hoover pressure barostat,\(^{22} \) implemented as described in ref. 23. Once again, all the electron-specific quantities are updated accordingly at each timestep,

\[
\begin{align*}
&\mathit{fix ID group-ID nvt/eff Tstart Tstop Tdamp} \\
&\mathit{keyword value} \ldots
\end{align*}
\]

where the desired temperature at each timestep is a ramped value during the run from \( \mathit{Tstart} \) to \( \mathit{Tstop} \) using a Nosé-Hoover thermostat, the \( \mathit{Tdamp} \) parameter determines how rapidly the temperature is relaxed (using the corresponding temperature and time units, as selected by the user through the \( \mathit{units} \) command), and \( \mathit{keyword value} \) corresponds to one of two options in the \( \mathit{nvt/eff} \) case, namely, \( \mathit{drag factor} \) or \( \mathit{chain yes/no} \), and \( \mathit{drag factor} \) or \( \mathit{dilate all/partial} \) in the \( \mathit{npt/eff} \) case. The chain \( \mathit{keyword} \) determines whether Nosé-Hoover chains are used or not, the use of chains helps overcoming non-ergodic sampling issues and energy oscillations found with ordinary Nosé-Hoover dynamics, and the \( \mathit{p-style args} \) provides control over the pressure conditions, for isotropic \( xz \) \( \mathit{Psstart Psstop Pdamp} \), or \( xy \) or \( yz \) or \( xz \) or aniso for partially coupled pressure directions or fully anisotropic, respectively, with the corresponding \( \mathit{Px_start Px_stop Py_start Py_stop Pz_start Pz_stop Pdamp} \) as a pressure damping parameter in the selected time units. The drag option will damp undesirable oscillations in pressure (volume) and temperature in an \( \mathit{ad hoc} \) fashion, but the resulting equations no longer sample the canonical or isothermal-isobaric ensembles, respectively. The nonisotropic \( \mathit{NPT} \) conditions should be used with caution at high pressures due to limitations in the spherical Gaussian electronic wavefunction representation.

The thermostat is only applied to the translational degrees of freedom for the particles, nuclei or electrons, which can also have a bias velocity removed from them before thermostating takes place (e.g., for removing a center of mass velocity from a group of, or all, atoms). In such cases, the LAMMPS \( \mathit{option fix modify} \) should be used to assign a temperature compute to this fix that includes such a bias term. If the user is interested in computing the e\( \mathit{ff} \) temperature to store, dump, or use as a variable for other calculations within a simulation script, without integrating the equations of motion, a

\[
\begin{align*}
&\mathit{compute ID group-ID temp/eff} \\
&\mathit{is available for this purpose (see Section ‘Other pEFF operations for further details’).}
\end{align*}
\]

\( \mathit{Other pEFF Operations} \)

Additional \( \mathit{pEFF LAMMPS compute} \) styles are available to the user, including:
compute ID group-ID temp/eff
compute ID group-ID ke/eff
compute ID group-ID ke/atom/eff

Computes in LAMMPS create computations to be performed on a group of atoms, including nuclei and electrons for the above cases, to produce instantaneous values (i.e., calculated from information about atoms on the current timestep or iteration). The first two computes listed above correspond to global computes that calculate the eFF temperature and the eFF kinetic energy, respectively, for all or a subgroup of atoms. The third compute corresponds to a per-atom compute that calculates the kinetic energy of motion for each nucleus or electron in the group. The results of global computes can be output via the LAMMPS thermo_style custom or the fix ave/time commands, or the values can be referenced in a variable equal for the temp/eff and ke/eff cases, or the variable atom command for the KE/atom/eff case. The results of computes that calculate a global temperature or pressure can be used by LAMMPS fixes that do thermostating or barostatting (e.g., nvt/eff or npt/eff), and when atom velocities are created. Likewise, the results of the per-atom compute ke/atom/eff can be output via the dump custom command or the fix ave/spatial command, or they can be time-averaged via the fix ave/atom command and then output via the dump custom or the fix ave/spatial commands, or they can be referenced in a variable atom command. The value of per-atom compute ke/atom/eff will be 0.0 for atoms (nuclei and electrons) not in the specified group.

In general, a significant majority of the standard global and per-atom computes in LAMMPS are available for pEFF simulations, without any change in their syntax, including those associated with pressure, potential energy, atom/stress, among others.

The following sections present two different example applications that demonstrate the capabilities of pEFF, one involving the dynamics and properties of high-density hydrogen, and the other involving large-scale simulations of the warm dense plasma regime that appears during hypervelocity impact of lithium metal.

**Example Applications**

**High-Density Hydrogen**

Hydrogen is the simplest molecule, yet its properties at high pressures (10–1000s GPa) and moderate temperatures (10s–1000s K) remain poorly understood, due to the experimental challenges of producing and characterizing it under such conditions. On the other hand, it has also been a challenge to model Hydrogen under such conditions due to the complex mixtures of molecules, atoms, ions, and excited electrons that may be present at the different regimes of pressure and temperature. Having an accurate equation of state (EOS) for dense hydrogen would be useful to diverse fields ranging from astrophysics — e.g., understanding the internal structure of giant planetary cores, or designing fuel pellets for inertial confinement fusion.

The similarities between hydrogen and alkali metals suggest that pressure-ionized hydrogen would behave like a conducting monovalent “metal” and that a first-order phase transition must occur between the insulating molecular and the conducting metallic states given the large density difference between the two. Saumon and Chabrier predicted the existence of a plasma phase transition (PPT) with a critical point at $T_c = 15,300$ K, $P_c = 61.4$ GPa, and $\rho_c = 0.35$ g/cm$^3$ using a Helmotz free-energy model for nonideal mixtures of hydrogen atoms and molecules. Although the existence of a PPT is uncertain, we expect our chemical model to be accurate in its extremes, i.e., the limits of purely molecular or weakly coupled plasma phases.

We use the NPT capabilities in pEFF to calculate the density, $\rho$, and ionization percentage of isotropically compressed hydrogen at a pressure of 61.4 GPa and a temperature of 15,300 K. A system with 15,625 hydrogen molecules in a lattice with P6/m symmetry and Wigner-Seitz radius $r_s = 1$ Bohr was prepared, and saved into an ASCII file `data.h_plasma`, using an orthorhombic unit cell of size $40.3 \times 40.3 \times 40.3$ Bohr. As a reference, liquid H$_2$ at atmospheric pressure has $r_s = 3.16$ Bohr and at the selected starting density and room temperature it is a solid. The structure was then optimized at 0 K using a conjugate gradient scheme with convergence thresholds set at 0 energy change and 1.0e−4 RMS force, and subsequently equilibrated at 15,300 K under 61.4 GPa of pressure during 1.0 ps. Data collection for calculating the density and the ionization percentage averages started after equilibration and involved 3 ps. The following summarized LAMMPS-pEFF script describes the general settings and procedure used for this calculation.

```plaintext
units electron boundary p p p atom_style hybrid charge electron read_data data.h_plasma pair_style eff/cut 20.15 pair_coeff * *
neigh_modify one 20000 page 200000 communicate single vel yes thermo_style custom step etotal pe thermo_style custom step pe temp press vol
# npt fix 1 all npt/eff 15300.0 15300.0 1.0 xyz 61.4e09 61.4e09 10.0 variable rho equal 11.2058851*mass (all)/vol thermo_style custom step pe temp press vol v_rhoe
compute peatom all pe/atom compute keatom all ke/atom/eff

variations for calculating the density and the ionization percentage averages started after equilibration and involved 3 ps. The following summarized LAMMPS-pEFF script describes the general settings and procedure used for this calculation.

```

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neigh_modify one 20000 page 200000 communicate single vel yes thermo_style custom step etotal pe thermo_style custom step pe temp press vol
# npt fix 1 all npt/eff 15300.0 15300.0 1.0 xyz 61.4e09 61.4e09 10.0 variable rho equal 11.2058851*mass (all)/vol thermo_style custom step pe temp press vol v_rhoe
compute peatom all pe/atom compute keatom all ke/atom/eff
```

The following sections present two different example applications that demonstrate the capabilities of pEFF, one involving the dynamics and properties of high-density hydrogen, and the other involving large-scale simulations of the warm dense plasma regime that appears during hypervelocity impact of lithium metal.
Figure 2. Radii distribution for high-density hydrogen at 0 K-minimized (circles), 300 K (diamonds), and 15,300 K (boxes) shows there is a gradual increase in both the center and the bandwidth of the distribution as the system is heated (i.e., the distribution no longer has a sharp peak at $\sim$ radius = 1.15 Bohr). As the temperature increases up to 15,300 K, we also observe a small number of electrons shifting from bond-centered positions in the H$_2$ molecular fluid, to atom-centered positions. This is indicative of a partial transition toward an atomic fluid. At higher temperatures, 30,000–100,000 K, hydrogen atoms gradually separate into protons and electrons to form a dense plasma.

Figure 3. Depicts variations in ionization fraction as a function of temperature and pressure for hydrogen. Inset figure corresponds to a snapshot of the molecular-atomic fluid system after 1.25 ps with electrons (transparent blue), nuclei (gray), and a single delocalized electron (shown in red). A $\sim$0.5% of ionized hydrogen atoms is predicted by pEFF at 61.4 GPa of pressure and a temperature of 15,300 K calculated from NPT dynamics with pEFF. Note that the system starts off highly compressed and unequilibrated, hence the initial fluctuations in ionization fraction (and volume expansion). These results are consistent with those reported for H Hugoniots in ref. 31.

Shock Dynamics of Lithium Metal

Systems with a mixture of molecules, atoms, ions, and electrons at temperatures ranging from 0.1–100s eV [$10^3$–$10^6$ K] and densities up to 10 times standard value are referred to as warm dense matter. Such systems have been most difficult to characterize theoretically and experimentally. Conventional weakly coupled plasma physics models break at high densities, whereas condensed-matter physics models are unable to precisely describe high and commensurate electronic and nuclear energetics. Figure 4 depicts the different regimes of interest, namely, condensed matter with highly localized electrons (i.e., mostly ground state), an interfacial intermediate region with partially ionized electrons (warm dense region with a portion of highly excited electronic states), and a...
regime with predominant delocalized electrons (high proportion of loose electrons, plasma). Reactions, dissociations, and ionization/recombination can occur simultaneously in warm dense matter, and the complex interplay of partial degeneracy, excited electronic states, charge screening, and strong coupling in the behavior of materials under this regime.

To describe these regimes of matter, we have used eFF to study the single shock response of hydrogen\(^{10}\) and lithium metal\(^{32}\), assuming that a thermodynamic equilibrium is established in the bulk solid as the shock front passes through. Under such conditions, the pressure \(P\), volume \(V\), and internal energy \(E\) satisfy the Rankine-Hugoniot equation:

\[
E - E_0 + \frac{1}{2} (V - V_0)(P + P_0) = 0, \tag{16}
\]

where the subscript zero denotes the initial state before the compression for each material. The procedure used involved performing eFF \(NVE\) dynamics equilibration on systems of varying densities (i.e., \(V\)) and temperatures to determine the corresponding \(P(V)\) and \(T\) that would satisfy eq. (16). The initial structure in each case was taken to be the structure with lowest internal energy at the given density (for lithium, the fcc structure was used as starting configuration). Using the capabilities in pEFF, we performed large-scale, long-term simulations on the dynamics of lithium nonequilibrium shock, involving much higher temperatures and pressures than the conventional static shock experiments. The system was prepared in fcc configuration (see Fig. 5) with 480,000 electrons and 160,000 nuclei, using fully periodic boundary conditions on a unit cell size of \(\sim 177 \times 4.5 \times 4.5 \text{ nm}\) (with the long direction corresponding to that of the translational impact). The structure was then minimized, using a conjugate gradient scheme with quadratic line search to a convergence of 0 in energy difference and 1.0e\(^{-6}\) RMS force, and to dumping a snapshot of the resulting structure at a timestep of 0.005 fs, before proceeding with 3 ps of thermal equilibration and to dumping a snapshot of the resulting structure with id type x y z spin radius vx vy vz vr. To make the system finite in the impact direction \(x\), we proceeded to cut the \(\pm x\) surfaces manually to avoid delocalized electrons, and to perform an additional 1 ps of \(NVT\) dynamics at \(T = 298 \text{ K}\) to relax any remaining strain on the free surfaces before writing the restart file used for the dynamic shock simulations (\textit{lithium.restart}). The procedure used consists of impacting an fcc lithium slab at varying particle velocities (for simplicity, we drive the slab into a fixed wall at \(U_p = 1, 2, 5, 10, 15\), and \(20 \text{ km/s}\) in the \(-x\) direction). To explore the shock dynamics, in this case, we calculate the single shock Hugoniot relationship directly from \(P, U_s\), initial \((\rho_0\), uncompressed\) and final \((\rho_1\), compressed regime\) density, as follows,

\[
P = \rho_0 U_s U_p, \quad \rho_1 = \rho_0 [U_s/(U_s - U_p)]. \tag{17}
\]

Other setups were tested, including opposing slab impacts, and small clusters impacting on slabs, for studying welding, melting, and atomic fluid formation, but these results will be a subject of a different publication. The corresponding LAMMPS input script for the single slab impact follows:

```bash
units electron
boundary s p p
atom_style hybrid charge electron
read_restart lishock.restart
pair_style eff/cut 37.73585
neigh_modify one 30000 page 300000
timestep 0.005
pair_coeff * *
thermo_style custom step etotal pe ke temp press
thermo 100
thermo_style custom step etotal pe ke ...
fix 1 all nve/eff
fix xwalls all wall/reflect xlo
thermo 200
thermo_style custom step etotal pe ...
velocity all set -2.9274E-01 NULL NULL
sum yes units box
compute peatom all pe/atom
compute keatom all ke/atom/eff
dump 1 all custom 5000 lishock.nve.
lammpstrj id type x y z spin ... radius vx vy vz vr mass c_peatom c_keatom
run 200000 # 1 ps
```

Figure 5. NaCl-like bonds for lithium fcc with lattice constant \(a = 4.42 \text{ Å}\) and bulk modulus of 12.2 GPa. The larger dark and light gray filled circles indicate the position of +1 and −1 spin electrons, respectively, and the black dots the nuclear positions.
Figure 6. (a) Shows a side view of the shock wave propagating to the right with a velocity $U_s$ after the lithium slab is hit by the piston wall at a velocity $U_p$, and color coded electrons (nuclei are barely visible) depicting a fraction of ionized electrons (toward red) and a fraction of higher kinetic energy localized electrons (toward blue) in the compressed region. The shock front is seen at the interface between cooler electrons to the right and hotter electrons closer to the piston wall, some of which are fully ionized with a large radii. (b) Shows a front view from the piston wall of the same snapshot in (a), where large ionized electrons can be distinguished (note: the electron size limit flag was set to “no” in the pair_style definition to allow these to expand beyond half the box length size), and (c) gives the color coding according to the electron radii between 0 Bohr [e.g., blue nuclei] and 4 Bohr [e.g., red ionized electrons].

The thermodynamic pressure, volume and energy ($P, V, E$) behind the shock front are related to the initial properties ($P_0, V_0, E_0$) in front of the shock wave by the dynamic variables $U_s$ and $U_p$ through the Rankine-Hugoniot equations in eq. (16) (see Fig. 6a for further details). Figure 7 shows the resulting shock wave kinematic parameters for the mass velocities in the abscissa and the wave velocities in the ordinate. The velocity profile is in close agreement with available experimental data from Bakanova et al.,$^{33}$ Rice,$^{34}$ van Thiel,$^{35}$ and Marsh,$^{36}$ showing a linear relationship between $U_p$ and $U_s$ between $U_p = 1 - 20$ km/s given by $U_s = 6.0581 + 1.0807U_p$.

We believe the eFF data for $U_p = 1, 2$ km/s results in larger pressures than those found experimentally because the simulations were performed starting from the fcc crystal of Lithium, which does not correspond to its lowest energy phase used by experiments (i.e., bcc). A larger energy change at lower shock speeds leads to an increase in the virials of the pressure expression in eq. (13). Analyzing the structural characteristics for the system in the uncompressed state and within the shock-compressed region for the $U_p = 15$ km/s case shows a transformation of the system from an fcc lithium crystal into an atomic liquid (see the corresponding radial distributions functions and coordination numbers for the pairs nuclei–nuclei in Figures 8c and 8d compared with the corresponding uncompressed state in Figures 8a and 8b. Similar RDFs and CNs to those in Figures 8c and 8d can be shown for the nuclei-electron and electron–electron cases.

The preliminary shock dynamics data on lithium metal is useful to characterize the stages of plasma formation, during the compressive and tensile-expansive regimes. Analyzing the compressive regime for a $U_p = 15$ km/s provides clear evidence of the energetic contributions of the excited electronic states on the material structure, including the formation of a plasma phase in the compressed region with an ionization percentage of $\sim 35\%$ (see Fig. 9), as well as an increased fraction of localized (compressed) high-kinetic energy valence electrons from the visual grading of colors shown in Fig. 6.

This regime is characterized by plastic deformation in the transition from solid to an atomic fluid. The temperature in the shocked region reaches 39,317.4 K and the pressure in the shocked direction is $\sim$300 GPa with a corresponding density of 1.74 g/cm$^3$.

From Figure 10, we believe a significant rise in the pressure takes place after the system density reaches $\sim 1.5$ g/cc, mainly due to an increase in temperature and ionization effects that appear $>10$ km/s, before reaching a compressibility limit. Once again, the single shock Hugoniot curve matches closely those from experiments and to our own previous results using a static compression approach to fit

Figure 7. Shock wave kinematic parameters showing the mass velocities in the abscissa and the shock wave velocities in the ordinate, with linear relationship for $p_{EFF}$ results given by $U_s = 6.0581 + 1.0807U_p$ for $U_p = 1, 2, 5, 10, 15, \text{ and } 20$ km/s.
the Rankine-Hugoniot equation. We are currently exploring higher velocity regimes to elucidate this phenomena.

As mentioned before, the ability to scale pEFF computations over single and multiple processors is of utmost importance when simulating the large-scale, long-term dynamics of materials and phenomena under extreme conditions. The next section describes the overall performance and scalability of pEFF.

**Single- and Multi-Processor Performance**

All parallel calculations, unless noted otherwise, were done on the Los Alamos Lobo supercomputer (38TFLOPs system with Quad-core AMD Opteron nodes with infiniband interconnect), whereas the single processor calculations were done on a PowerBook, Intel Mac OS 10.5.8. Figure 11 shows the comparative performance between pEFF and the current serial implementation of eFF (named eFF1).

![Figure 8. Unscaled radial distributions functions (RDF) and coordination numbers (CN) for uncompressed and shock-compressed regions at \( U_p = 15 \text{ km/s} \), respectively. (a) The corresponds to the nuclei–nuclei RDF and (b) CN for the uncompressed region, whereas (c) to the nuclei–nuclei RDF and (d) CN for compressed region. Similar RDFs and CN are found for nuclei-valence, and valence–valence electrons in the compressed region, confirming the transition from a solid to an atomic fluid.](image)

The improved single-processor performance of pEFF is due to a more efficient definition of data structures, nuclei and electron using a single atom type class to reduce the cost of pairwise interactions, optimized I/O costs, among others. Figure 12 shows the parallel scalability of pEFF using a log–log plot. For the most part, ideal weak and strong scaling can be maintained with a CPU load between 62 and 128 particles, with >90% parallel efficiency up to 500 processors, and reasonably good scaling up to 1024 processors (a higher number of processors was not tested due to allocation restrictions). Communication and synchronization overheads become proportionally relevant to overall performance (compared with compute cost) for loads above 128 particles per processor. Nevertheless, this performance can vary depending on the type of HPC used (e.g., memory hierarchy, interconnect latency, and bandwidth, etc.), the density of the system being simulated, and cutoff values used, among other things.
Figure 9. Shows the percentage of lithium atoms being ionized, due to excited valence electrons, within the compressed region during the first $\sim 0.1$ ps at a 15 km/s impact velocity converges to $\sim 35\%$ leading to the formation of a metallic plasma phase. For 5 km/s, there was no significant ionization and for 10 km/s $\sim 8\%$.

Final Observations and Conclusions

The currently implemented pEFF gives a reasonably accurate description for systems containing nuclei from $z = 1 \sim 6$. For the purpose of this article, we restrict ourselves to systems where electrons are $s$-like, or contain $p$ character only insofar as a single lobe of electron density is shifted away from the nuclear center. We have demonstrated concrete examples for Hydrogen and Lithium. Work is underway to extend it to higher $Z$ elements with increasingly non-spherical electrons with $p$-like and $d$-like character, and to improve its computational efficiency for atoms with a large number of core electrons using core approximating pseudo-potentials.

Figure 10. Shock Hugoniot calculated directly from the planar shock velocity $U_s$, particle(mass) or piston velocity $U_p$, and initial ($\rho_0$) and final ($\rho_1$) densities obtained from our simulations, using eq. (17), compared with existing experiments.

Figure 11. Performance of pEFF running on a single processor compared against the serial eFF1 implementation from http://www.electronforcefield.com shows superior scalability of pEFF for a single point energy calculation using the minimum image convention and a cutoff, half the box length. The case depicted above corresponds to a lithium bulk system with increasing number of nuclei and electrons (particles).

Figure 12. Strong and weak scaling in pEFF for lithium bulk systems with 16,000 particles (4000 nuclei and 12,000 electrons), 32,000 particles (8000 nuclei and 24,000 electrons), and 128,000 (32,000 nuclei and 96,000 electrons) particles in an NVE dynamics calculation over 1000 iterations demonstrate ideal parallel efficiency, under such conditions, for $N/P > 62$. Single timestep performance for 512 processors is 0.071 sec for the 32,000 particle system. Weak scaling is demonstrated from the approximate linear scaling in the relative performance between systems with 16,000–32,000 particles, $2 \times$, and between systems with 16,000–128,000 particles, $8 \times$, indicated by the upward arrows in the figure. These results use a cutoff of 30 Bohr and include a trajectory dump every 1000 steps, and a restart file writing every 100 steps.
pEFF excels computing the properties of materials in extreme conditions and tracing the system dynamics over multi-picosecond time scales, this is, particularly relevant where electron excitations can change significantly the nature of bonding in the system. The eFF method can capture with surprising accuracy the behavior of such systems because it describes consistently and in an unbiased manner many different kinds of bonds, including covalent, ionic, multicenter, ionic, and plasma, and how they interconvert and/or change when they become excited.

pEFF also excels in computing the relative thermochemistry of isodemic reactions and conformational changes, where the bonds of the reactants are of the same type as the bonds of the products. For materials, eFF assumes that kinetic energy differences dominate the overall exchange energy, which is true when the electrons present are nearly spherical and nodeless and valid for covalent compounds such as dense hydrogen, hydrocarbons, and diamond; alkali metals (e.g., lithium), alkali earth metals (e.g., beryllium), and semimetals such as boron; and various compounds containing ionic and/or multicenter bonds, such as boron dihydride.

The results reported here for high-pressure hydrogen and lithium shock dynamics are in close agreement with experimental data, and consistent with observations provided. We succeeded in reproducing the single shock Hugoniot for lithium from actual kinematics data, in close analogy to experimental settings, as opposed to satisfying the Rankine-Hugoniot equation from static compression simulations reported elsewhere.

On the other hand, the user should be cautioned before using the current pEFF implementation liberally to describe,

- cases where the differences in the adiabatic potential energy landscapes are pronounced — given that eFF is a mean-field approach, it will be unable to describe all reaction channels adequately,
- rare events using transition state theory, because these cannot be applied rigorously under eFF (it violates the principle of microscopic reversibility9),
- materials having electrons with substantial p character are poorly described, both because of limitations in the underlying wave packet representation, and also because kinetic energy differences no longer dominate exchange, so that the Pauli potential becomes inaccurate; hence, multiple bonds, radical electrons, and lone pairs are not properly represented — they are too diffuse, too easily ionized, and generally less stable than they should be (work is underway to extend the wavepacket representation in eFF),
- when electrons have substantial density on both sides of the nucleus, as in the lone pairs of neon, the bond of ethylene, or the unpaired electron of methyl radical. In those cases, the p electrons are already orthogonal to each other, their overlap is zero, and the kinetic energy contribution to the Pauli interaction becomes zero. Other terms then dominate and a more complex Pauli potential is needed; this will be the subject of a future paper.
- systems at very high temperatures (100s–1000s K), the Gaussian wave packets become very diffuse and no longer interact with the remainder of the system; hence, all pressure contribution from the electrons is lost (unless, the electron size limit flag is set, see Section “LAMMPS pEFF pairwise extensions”). This may be corrected to recover the correct EOS, by adding an ideal gas correction in the weakly coupled regime.

- highly accurate bond dissociation energies or relative transition state energies for reactions where bonds are being broken and reformed, given the relatively simple basis functions used in eFF,
- applications that require distinguishing electronic energy levels (e.g., emission spectra), because these are not available in the current implementation.

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