Excited Electron Dynamics Modeling of Warm Dense Matter

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We present a model (the electron force field, or eFF) based on a simplified solution to the time-dependent Schrödinger equation that with a single approximate potential between nuclei and electrons correctly describes many phases relevant for warm dense hydrogen. Over a temperature range of 0 to 100,000 K and densities up to 1 g/cm³, we find excellent agreement with experimental, path integral Monte Carlo, and linear mixing equations of state, as well as single-shock Hugoniot curves from shock compression experiments. In principle eFF should be applicable to other warm dense systems as well.

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Warm dense matter appears in giant planetary interiors [1], inertial confinement fusion [2], and shock [3] or laser [4] heated solids that become plasmas. It is a challenging state to describe theoretically, as it lies in between the cold matter described well by ground state quantum mechanics [5,6], and the hot matter described well by classical plasma models [7]. Reactions, dissociations, and ionizations may occur simultaneously, and excited electron effects may be important.

As a prototype system, we consider the case of hydrogen, which at room temperature remains insulating at pressures as high as 342 GPa [8], but at 3000 K is already conducting at 140 GPa [9]. This enhanced conductivity of warm dense hydrogen may involve the participation of electronically excited mixtures of H₂ molecules, H atoms, and other species along with free protons and electrons [10].

We present a model (the electron force field, or eFF) based on a simplified solution to the time-dependent Schrödinger equation that with a single approximate potential between nuclei and electrons correctly describes many phases relevant for warm dense hydrogen. eFF computes the energy of a collection of point charge nuclei and single Gaussian function electrons [11] \( \psi = \exp[(r - x_i)²/s_i²] \) as a function of the nuclear and electron positions plus the electron sizes. It approximates the total energy as the sum of electron kinetic energies, electrostatic potential energies, and Pauli exclusion interactions.

We first assume that electrons move independently of each other, i.e., the wave function is a Hartree product. Then the kinetic energy and electrostatic potential energies of electrons have well-known analytic forms (e.g., \( E_{ke} = 3/(2s²) \), \( E_{nuc(i)-elec(j)} = -Z_i R_{ij}^{-1} \text{Erf}(\sqrt{2} R_{ij}/s_j) \), and \( E_{elec(i)-elec(j)} = R_{ij}^{-1} \text{Erf}(\sqrt{2}r_{ij}/\sqrt{s_i² + s_j²}) \)). Small electrons have higher kinetic energy, consistent with the Heisenberg uncertainty principle. The finite size of the hydrogen atom, for example, results from the balance between the kinetic energy of the electron and the electrostatic attraction of the electron to the proton.

However, as electrons are fermions, we make a correction to the independent electron assumption, and estimate a Pauli exclusion energy as a pairwise sum between electrons:

\[
E_{\text{Pauli}} = \sum_{\sigma_i \neq \sigma_j} E(\|i\rangle\langle j\|) + \sum_{\sigma_i \neq \sigma_j} E(\|i\rangle\langle i\|),
\]

with \( \sigma \) denoting the spin of the electrons, and

\[
E(\|i\rangle\langle j\|) = \left( S_{ij}^2 / \left( 1 - S_{ij}^2 \right) \right) \Delta T_{ij}.
\]

where \( \Delta T \) is a measure of the kinetic energy change upon antisymmetrization, and \( S \) is the overlap between two Gaussian functions:

\[
\Delta T_{ij} = \frac{3}{2} \left( \frac{1}{\bar{x}_i² + \bar{x}_j²} \right) - \frac{2(3\bar{x}_i² + \bar{x}_j²)}{(\bar{x}_i² + \bar{x}_j²)²},
\]

\[
S_{ij} = \left( \frac{2}{\bar{x}_i / \bar{x}_j + \bar{x}_j / \bar{x}_i} \right) ^{3/2} \exp(-\bar{x}_i²/(\bar{x}_i² + \bar{x}_j²)),
\]

where \( \rho = -0.2 \), \( \bar{x}_i = x_i \times 1.125 \), and \( \bar{x}_j = x_j \times 0.9 \). This expression was derived by considering the difference between the antisymmetric and symmetric combinations of valence bond states, and assuming that kinetic energy differences predominate; analogous approximations have been reported elsewhere [12–14].

To compute the ground state, we minimize the energy of the system, optimizing the nuclear and electron positions and the electron sizes simultaneously [15]. We chose the Pauli potential to obtain stable bonds between elements from \( Z = 1–6 \). The specific form selected for the Pauli potential distinguishes eFF from a method such as wave packet molecular dynamics (WPMD [12]), which does not produce stable molecules with elements \( Z > 1 \) and does not describe the equation of state (EOS) of dense hydrogen accurately. We optimized the three universal parameters of the Pauli potential to reproduce the bond lengths of small molecules such as CH₄ [1.143 (1.094) Å, exact values in

[1.143 (1.094) Å]
potential produces the semiclassical equations of motion:

\[ \begin{align*}
\dot{\mathbf{r}} & = -\nabla \tilde{V}, \\
\dot{\mathbf{p}} & = m_{\text{elec}} \mathbf{\dot{x}}, \\
\dot{\mathbf{p}}_s & = -\partial \tilde{V}/\partial s, \quad p_s = (3m_{\text{elec}}/4)\dot{s}.
\end{align*} \]

Thus the average position of a wave packet obeys classical dynamics (Ehrenfests' theorem) with the addition that the size of the wave packet obeys classical dynamics as well [13]. With this method, the size and position of each electron evolves independently, and we can obtain nonadiabatic electron dynamics if desired.

We extract thermodynamic parameters from the simulations using classical virial expressions, e.g., \( \frac{3}{2} k_B T = \frac{1}{N_{\text{nuc}}} \times (\sum_i \frac{1}{2} m_i \mathbf{v}_i^2) \) and \( PV = N_{\text{nuc}} k_B T + \frac{1}{3} \left( \sum_i \frac{\partial^2 \tilde{V}}{\partial x_i^2} \right) \), where we sum over all nuclear and electronic degrees of freedom and take \( m_{\text{elec}} = m_{\text{nuc}} \). In order to compute quantities dependent solely on the electronic degrees of freedom, such as plasma oscillation frequencies or electrical conductivity, a more rigorous separation of nuclear and electronic time scales is likely required.

Figure 1 shows the equation of state of solid deuterium at 300 K computed using semiclassical dynamics with eFF. We indicate density with the Wigner-Seitz radius \( r_s \), where each atom occupies a volume \( \frac{4}{3} \pi r_s^3 \). Pressure versus density data has been measured up to 120 GPa \( (r_s = 1.52 \text{ bohr}) \) at 300 K using diamond anvil apparatuses.

FIG. 1 (color online). Equation of state for solid deuterium at 300 K and varying density. We show here that the pressures from eFF dynamics are in good agreement with diamond anvil experiments. Here constant number/volume/energy (NVE) dynamics were performed in a cubic periodic box with 64 H atoms. Electrostatics were computed using Ewald summation, and \( E_{\text{Pauli}} \) was computed using the minimum image convention. Thermodynamic parameters were averaged over 1 ps following a 200 fs equilibration period, with the time step set to min (0.02, \( 1/\sqrt{\langle f \rangle} \)) fs. Masses were set to \( m_{\text{nuc}} = m_{\text{elec}} = 1.008 \text{ amu} \); reducing the electron mass to \( m_{\text{nuc}} = 0.5 \text{ amu} \) and increasing the nuclear mass by the same amount had a negligible effect on the equations of state.

We now consider the behavior of hydrogen at higher temperatures. At 1 atm, \( H_2 \) dissociates into atoms at 3960 K and the atoms ionize at 15 870 K (from the Saha equation [19], which assumes an ideal gas). In the ideal gas limit, the dissociation and ionization temperatures increase with density, remaining separate events. To study the nonideal behavior of warm dense hydrogen, Saumon and Chabrier constructed a linear mixing EOS [20] taking into account contributions from molecular, atomic, ionized, and metallic phases. Their model predicts that the ionization temperature lowers to coincide with the dissociation temperature in a plasma phase transition at \( r_s = 2 \text{ bohr} \) and \( T = 15 300 \text{ K} \).

Figure 2 shows the pair distribution predicted from eFF as deuterium is heated from 9100 to 30 720 K at \( r_s = 2 \text{ bohr} \). We find that deuteron gradually dissociates from fluid molecules to fluid atoms over this temperature range. Fluid molecules are characterized by strong peaks in the proton-proton pair distribution at the \( D_2 \) bond distance and first solvation shell (0.74 and 2.3 Å), while fluid atoms are characterized by a pair distribution that rises gradually as \( r \) increases from 0.5 to 1.5 Å and then is a constant for longer distances. The eFF midpoint of dissociation is at \( T = 16 500 \text{ K} \) (where \( r_{\text{min}}/r_{\text{max}} = 0.5 \)), comparable to the dissociation temperature (15 300 K) predicted by Saumon and Chabrier.
From eFF dynamics, the average electron size increases with temperature, from 1.74 bohr at 4200 K to 2.32 bohr at 33 000 K. At temperatures exceeding ~50 000 K, some electrons begin to expand past the dimensions of the periodic box, which we consider to represent ionization [21]. This suggests that at \( r_s = 2 \) bohr, dissociation and ionization occur in separate temperature ranges, 16 500 K and 50 000 K, respectively.

Figure 3 shows the pressure versus temperature of \( \text{D}_2 \) at \( r_s = 2 \) bohr. Since no experimental data are available, we compare eFF to equations of state from the most accurate \textit{ab initio} theories. Path integral Monte Carlo (PIMC) is in principle exact but in practice the accuracy is limited by the step size, which is inversely proportional to temperature. PIMC predicts that the midpoint of molecular dissociation occurs at 10 000 K; however it also predicts that \( dP/dT < 0 \) at this temperature, which initially [22] was taken as evidence of a first-order phase transition. But later [6] this result was concluded to be an unphysical artifact of the simulation. Thus currently PIMC can capture accurately only the thermodynamics of higher temperature dissociated states [6]. At lower temperatures (<10 000 K), we compare our results against the Saumon-Chabrier EOS, which used parameters fitted to describe the molecular phase.

Thus eFF provides a unified and continuous description of both the molecular and atomic regimes, including the ionized regime above 50 000 K. It matches the pressures from the Saumon-Chabrier EOS well at low temperatures, and it matches the slope of PIMC computations [23] at higher temperatures. At higher temperatures the eFF EOS inflects slightly upward while the PIMC and chemical models both inflect downward over the dissociation regime. We believe that the upward inflection is physically reasonable, since the doubling in the number of free particles resulting from dissociation should increase the pressure. While eFF describes the dissociation of molecules into atoms as the temperature increases, it does not show the discontinuous first derivative in the equation of state that would characterize a first-order plasma phase transition.

The good agreement of eFF with PIMC persists to ~100 000 K, above which point the eFF EOS slope becomes too small, with the pressure becoming 20% too low by 120 000 K. Thus the simple eFF, with no adjustable parameters, provides a consistent description of hydrogen over the 0 to 100 000 K temperature range.

Figure 4 shows the eFF computed pressure-density relation (Hugoniot curve) of shocked liquid deuterium, where deuterium is heated from 20 K to tens of thousands of degrees within tens of nanoseconds. The single-shock Hugoniot curve for liquid deuterium is by now well established, with experimental data from diverse shock sources such as gas guns [24], exploding wires (Z machine [25]), and imploding hemispheres (convergent geometry [26]), as well as theoretical results from PIMC in impressive accord with each other. These data support a curve that sharply inflects upward at a maximum compressibility of \( \rho/\rho_0 \sim 4 \), consistent with the limiting compressibility of other diatomics such as CO and \( \text{N}_2 \) [27]. The redundant experiments were spurred by controversy over an anomalously
large compressibility $\rho/\rho_0 = 6 \pm 1.8$ observed using laser ablation as a shock source (Nova laser [28]). The latest convergent geometry experiments have the smallest error bars, and definitively support a maximum compressibility of $4 \pm 0.6$.

The eFF Hugoniot passes through the gas gun and Z machine data points, and shows a stiff upward bend, but predicts a maximum compressibility of 4.8, which lies slightly above the limits of 3.4 to 4.6 from the convergence geometry experiments. Below 50 GPa, the eFF Hugoniot curve leads pressures and temperatures that are slightly too low (eFF $P = 13$ GPa, $T = 2510$ K at $r = 2.00$ bohr versus gas gun $P = 25$ GPa, $T = 4650$ K at $r = 2.10$ bohr), but the upward slope matches experiment. Above 120 GPa, the eFF Hugoniot curve bends upward to form a stiff curve with a minimum and maximum $\rho/\rho_0$ of 4.8 and 5.0. In this pressure range, the PIMC Hugoniot curve is shaped like a backward C, with a maximum $\rho/\rho_0$ of 4.3 which decreases to 4.1 at $P = 5608$ GPa ($T = 10^6$ K). Hence the eFF Hugoniot curve has the correct overall shape, but the maximum compressibility is slightly too high.

The encouraging results obtained with warm dense hydrogen, as well as the correct ground state geometries obtained for molecules with elements from $Z = 1$ to 6, suggest that eFF could be a valuable and general method for studying the excited electron dynamics of systems with diverse combinations of elements and bonding. The eFF potential contains terms no more complex than those used in traditional force fields involving only nuclei. Thus it should be practical to use eFF to study large scale excited systems beyond the reach of current quantum mechanics. We anticipate further developments will be required for applications to atoms beyond carbon.

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