

Ab initio molecular dynamics simulations of dense boron plasmas up to the semiclassical Thomas-Fermi regime

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We build an “all-electron” norm-conserving pseudopotential for boron which extends the use of *ab initio* molecular dynamics simulations up to 50 times the normal density ρ_0 . This allows us to perform *ab initio* simulations of dense plasmas from the regime where quantum mechanical effects are important to the regime where semiclassical simulations based on the Thomas-Fermi approach are, by default, the only simulation method currently available. This study first allows one to establish, for the case of boron, the density regime from which the semiclassical Thomas-Fermi approach is legitimate and sufficient. It further brings forward various issues pertaining to the construction of pseudopotentials aimed at high-pressure studies.

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INTRODUCTION

In *ab initio* molecular dynamics (MD) simulations [1], the electrons receive a full quantum mechanical treatment within finite-temperature density functional theory (DFT) while the ions are propagated classically on the resulting potential energy surface. The method has been extensively used in the past ten years to calculate the physical properties of dense plasmas [2]. When combined with linear response theory, this approach has been so far rather successful at reproducing the dynamical, electrical, and optical properties of various systems including metals, semiconductors, and molecular fluids in the warm dense matter regime [3–12]. In this regime, reached experimentally by shock compression in the Mbar range [13–15], laser heating of solid targets [16–19], or exploding wires [20–23], the matter is partially dissociated, ionized, and degenerate. This brings a rather challenging medium to model theoretically where many-body effects are important and perturbative approaches fail. The parameter-free nature of the *ab initio* MD approach is progressively making it the method of choice to study matter under these extreme conditions and to calibrate physical models such as the average atom [24–26], the chemical model [27,28], or even opacity calculations [29] at conditions not yet accessible experimentally.

The method is, however, computationally expensive and its application has been so far limited to low temperatures ($T < 10$ eV) and intermediate density situations ($\rho < 5\rho_0$). Unfortunately, this temperature-density regime is still far from the regime where semiclassical approaches are assumed to be valid [30]. As such, there is currently a need to extend the range of applicability of *ab initio* molecular dynamics simulations in both temperature and density. This would first allow one to establish the range of validity of semiclassical methods such as the Thomas-Fermi (TF) approach and, second, to fill the gap between the latter and current *ab initio* simulation results. We further note that the *ab initio* approach provides, in addition to the dynamical properties, consistent electrical and optical properties from the same simulations. To extend the range of applicability of the method would

also provide a useful benchmark as an additional layer of approximations, such as the Ziman formulation [31], is generally used to calculate these properties in the semiclassical regime.

The limitation of temperature is directly related to the number of bands that can be practically included into the calculation while the density range is limited by the cutoff and number of active electrons used in the pseudopotential (PSP). The latter is generally built for calculations to be performed around normal densities where only the outermost electronic shells are treated as active electrons. The inner-shell electrons can usually be approximated as atomic ones at normal densities and are generally treated within the frozen-core approximation. In addition, the cutoff radius is generally large in order to keep the plane-wave basis set as small as possible.

As a first step aimed at overcoming these limitations and reaching the regime where semiclassical approaches are valid, we relaxed the last two approximations and build a Troullier-Martins norm-conserving pseudopotential for boron where all the electrons are treated as active. We choose boron for its electronic structure and also because all the electrons can be treated as active with current computational capabilities. With two *s* and one *p* orbitals, boron exemplifies the issues encountered in building semilocal all-electron norm-conserving pseudopotentials for high-pressure studies.

Following previous work [32], we construct our all-electron pseudopotential by using the *1s* orbital as reference state for the *l=0* component. For boron, we further find that it is necessary to include components corresponding to empty atomic orbitals to ensure transferability at the highest pressures. We also suggest that the semiclassical Thomas-Fermi atomic model could be used to ensure the pseudopotential transferability at high pressure. With this pseudopotential, we perform *ab initio* molecular dynamics simulations for boron up to 50 times the normal density. These *ab initio* simulations of dense plasmas span from the regime where quantum mechanical effects are important to the regime where semiclassical methods such as the Thomas-Fermi approach are valid and justified.

PSEUDOPOTENTIAL CALCULATION

To simulate dense boron plasmas up to 50 times the normal density, we build a Troullier-Martins (TM) norm-conserving pseudopotential with a small cutoff radius and where all the electrons are active. These two conditions must be satisfied to enable accurate *ab initio* simulations at densities where the frozen-core approximation cannot be used and to prevent the “pseudoization” spheres from overlapping. We used the well-known FHI98PP pseudopotential generator developed by Fuchs and Sheffler [33]. This package is easily accessible and allows one to generate norm-conserving pseudopotentials for most elements throughout the periodic table and with a large array of DFT functionals.

In this scheme, the norm-conserving pseudopotential is first written in terms of an l -dependent and semilocal operator [33,34]

$$\hat{V}_l^{ps} = V_{loc}^{ps}(r) + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{m=l} |Y_{lm}\rangle [V_l^{ps}(r) - V_{loc}^{ps}(r)] \langle Y_{lm}|. \quad (1)$$

In Eq. (1), $V_{loc}^{ps}(r)$ is the local pseudopotential and $V_l^{ps}(r) - V_{loc}^{ps}(r)$ is the l -dependent component which is expected to vanish for $l > l_{max}$. In the present study, we choose $l_{loc} = l_{max}$ for all pseudopotentials constructed except when explicitly stated.

A first difficulty encountered in constructing an all-electron norm-conserving pseudopotential for boron using this semilocal formulation comes from the two s orbitals. This semilocal formulation, in effect, restricts the pseudopotential to one projector or component per angular momentum. We further recall that, in this scheme, the pseudo-wavefunctions $\Psi_{lm}^{ps}(\mathbf{r}) = [u_l(\epsilon_l^{ps}; r)/r] Y_{lm}(\Omega_r)$ do not contain any radial nodes. With this requirement, the resulting pseudo-wavefunctions are necessarily of type $1s, 2p, 3d, \dots$. The unscreened pseudopotential components are obtained by solving and inverting the Schrödinger equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{ps,scr}(r) - \epsilon_l^{ps} \right] u_l^{ps}(\epsilon_l; r) = 0. \quad (2)$$

A fully separable ionic pseudopotential is then constructed using the Kleinman-Bylander form [35]. As pointed out by Blöchl [36] and Vanderbilt [37], a separable pseudopotential can be directly constructed without using the semilocal form (1). In this case, the pseudopotential is fully nonlocal and one can then have several reference levels per angular momentum [38].

To construct the boron all-electron pseudopotential using the procedure summarized above, we use the all-electron $1s$ state as the reference state for the $l=0$ component [32]. In this scheme, the $2s$ eigenstate is now an excited state for the pseudo-Hamiltonian. We recall that for a standard boron pseudopotential with three active electrons and where the $1s$ orbital is treated in the frozen-core approximation, the $2s$ all-electron orbital is used as a reference state and agrees beyond the cutoff radius with the $1s$ pseudo-orbital.

To assess the validity of this approximation for boron and the accuracy of the resulting pseudopotential, we first compare the all-electron energies and pseudoenergies obtained

TABLE I. Boron atomic energies.

	All electron	3e pseudopotential $2s^2 2p^1$	5e pseudopotential $1s^2 2s^2 2p^1$
E_{1s} (eV)	-178.6714086		-178.6728144
E_{2s} (eV)	-9.3837355	-9.3837937	-9.2036065
E_{2p} (eV)	-3.7152605	-3.7152674	-3.7146330

with a cutoff value of $r_c = 0.5a_B$ and calculated in the PW92 [39] formulation of the local density approximation (LDA). Table I shows that the energy of the $2s$ orbital is still reproduced within 2% in this scheme. We also show, in Table I, the result obtained with a pseudopotential using three active electrons and a cutoff radius $r_c = 1.7a_B$. Furthermore, we find that the logarithmic derivatives $D_l(\epsilon, r^{diag})$, defined as

$$D_l(\epsilon, r^{diag}) = \left. \frac{d}{dr} \ln u_l(\epsilon, r) \right|_{r=r^{diag}}, \quad (3)$$

are in good agreement over the energy range corresponding to the $1s$ and $2s$ orbitals and for energies up to 2 hartrees. For both pseudopotentials, we choose $l_{max} = 3$.

We show, in Fig. 1, the calculation of the fcc equilibrium volume with the $3e$ and $5e$ pseudopotentials. At normal density, boron has a rather complex crystallographic structure. For convenience, the transferability test is performed on the fcc structure as its properties are well documented in the literature. The calculations are performed using the plane-wave electronic structure code ABINIT [40]. The calculations are done using an fcc elementary cell with 6^3 k points. The plane-wave cutoff is set to 50 and 180 hartrees for, respectively, the $3e$ and $5e$ pseudopotentials. This increase in plane-wave cutoff, and, consequently, in the resulting calculation time, is a direct consequence of the reduction in cutoff radius from $1.7a_B$ to $0.5a_B$. We see, in Fig. 1, that the equilibrium volume is slightly shifted to higher values when the $1s$ electrons are included in the pseudopotential. This value is, however, in good agreement with previous calculations performed by Mailliot *et al.* [41]. They obtained V_0

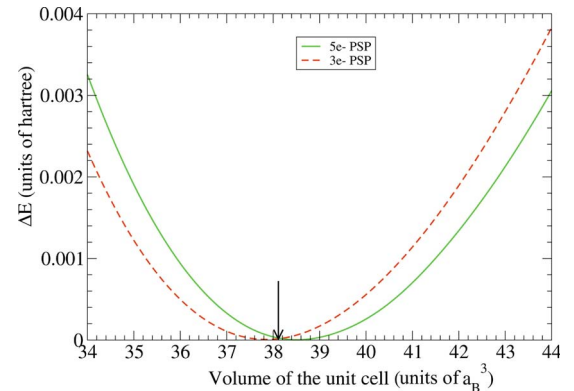


FIG. 1. (Color online) Energy variation around the equilibrium volume calculated with the $3e$ and $5e$ pseudopotentials. The arrow indicates the equilibrium volume obtained by Mailliot *et al.* [41]

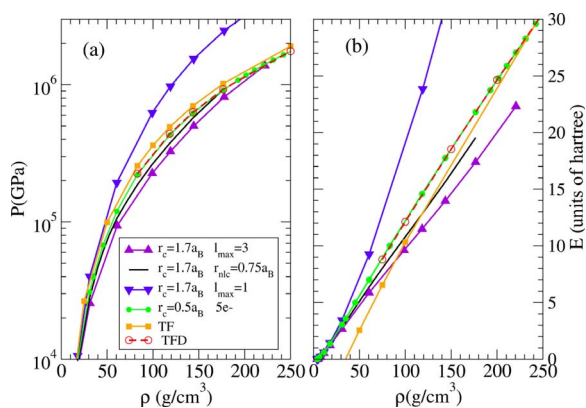


FIG. 2. (Color online) Variation of pressure and energy as a function of density for fcc boron.

$=38.12a_B$ with a norm-conserving pseudopotential calculated using the Ceperley-Alder LDA functional.

To further test the transferability at very high pressures, we show, in Fig. 2, the pressure and energy variations as a function of densities and, as before, for an fcc structure. Figure 2 shows the calculations performed with the two pseudopotentials described above ($r_c=1.7a_B$, $l_{max}=3$ and $r_c=0.5a_B$, $l_{max}=3$). We also show calculations performed with a $3e$ pseudopotential which contains only two l components ($l_{max}=1$) and where we used $l_{loc}=0$. We also performed calculations with a pseudopotential where a nonlinear core correction is introduced beyond a radius $r_{nlc}=0.75a_B$ in the $3e$ pseudopotential described in the previous section (with $l_{max}=3$).

Around normal densities, these various pseudopotentials agree and give rather similar equilibrium volumes. As the density increases to $100\rho_0$, we see, in Fig. 3(a), that the various pressure predictions deviate substantially. The $3e$ pseudopotential gives slightly higher pressures around 50 g/cm^3 when nonlinear core corrections are included. We interpret this result as the manifestation of the hybridization of the $1s$ orbital at these densities and the need to treat the $1s$ electrons as active electrons. In agreement with this interpretation, we find that the $5e$ pseudopotential where the $1s$ elec-

trons are treated as active progressively gives higher pressures beyond this density.

It is also interesting to note that the pseudopotential which only includes components corresponding to occupied atomic orbitals, with $l_{max}=1$, rapidly diverges as the density increases. While the effect is the most spectacular when the calculations are performed with and without a d component, we find it necessary to include the d and f components to achieve the best description over the whole density range. While we used $l_{loc}=0$ in this case, we further point out that a similar result is obtained when the p component is used as the local one.

Using Eq. (1), we see that this result implies that the short part of the d and f components cannot be approximated by either the s or p component at high densities. We recall that Eq. (1) implies, in this case, that $V_l^{ps}(r)=V_{l=0/1}(r)$ for $l > l_{max}$. In the present situation, these components correspond to empty atomic orbitals. This result suggests that it is necessary to include l components higher than the occupied atomic ones to obtain converged results at high densities. We believe that this result is rather general and is not limited to norm-conserving pseudopotentials, but will be also encountered with ultrasoft [37] or projected augmented wave (PAW) pseudopotentials [37,42].

To validate the $5e$ pseudopotentials at the highest pressures, we finally compare our calculations with the results of a TF average atom model [43]. In this semiclassical model, widely used in the plasmas community, the medium is approximated by a neutral pseudoatom. The finite-temperature Thomas-Fermi approximation, where the kinetic contribution is expressed as an explicit functional of the density, is subsequently used to obtain the electronic ground state at a given density and temperature [30]. In the calculations shown here, we further use the Perrot temperature-dependent functional [44]. We also note that for the low-temperature situation investigated here, the introduction of a local approximation for exchange using such a functional corresponds, in effect, to the Thomas-Fermi-Dirac (TFD) approximation [45,46] and will be referred as such in the following.

The Thomas-Fermi approximation is the predecessor to present-day DFT calculations. While it is not reliable for electronic structure calculations at normal conditions, this limit must be recovered at high densities where the system becomes strongly degenerated and the electronic density tends to a free electron gas. Figure 2 shows that this is indeed the case for the *ab initio* calculations using the $5e$ pseudopotentials and for densities higher than about 10 times the normal density (i.e., $\rho > 50 \text{ g/cm}^3$). Figure 2 also shows that this comparison is improved by including exchange into the calculation. In the latter case, the pressures and energies obtained are in near perfect agreement with the calculations using the $5e$ pseudopotential at the highest densities.

As the density decreases, the two models diverge as quantum effects and the underlying ionic structure become important. This is best seen in Fig. 2(b) where we show the variation of energy as a function of density. For all the *ab initio* calculations shown in Fig. 2(b), we used the energy obtained at the lowest density as the reference energy. The TF and TFD results are normalized to the $5e$ pseudopotential calculation at the highest density. We see that the TF and *ab initio*

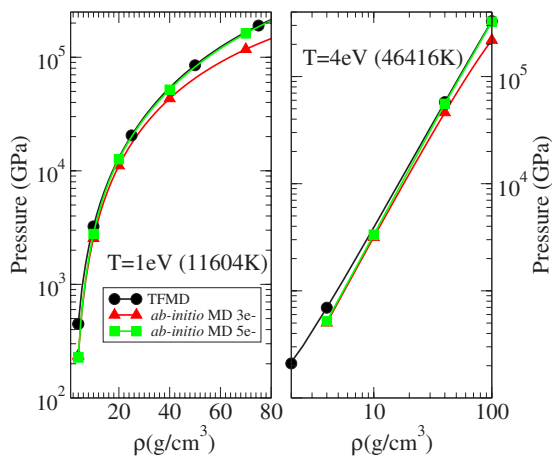


FIG. 3. (Color online) Variation of pressure as a function of density along the 1- and 4-eV isotherms.

calculations using the $5e$ pseudopotential exhibit a significantly different slope with respect to the energy variation. This, in turn, reflects directly onto different pressure variations as a function of density. We further point out that the Thomas-Fermi calculations overestimate the *ab initio* results by more than a factor of 2 at the lowest densities.

The good agreement between the result obtained with the $5e$ pseudopotential and the Thomas-Fermi-Dirac model at the highest densities demonstrates, in our view, that the pseudopotential built is accurate for high-pressure calculations. We further suggest that a comparison with a Thomas-Fermi atomic calculation could be used as a generic test to assess the transferability of pseudopotentials at high pressures. Having validated a pseudopotential where all the electrons are treated as valence electrons, we now turn to the molecular dynamics simulation results.

BORON SIMULATION RESULTS

We show, in Fig. 3, the pressure variation along the 1- and 4-eV isotherms as obtained by performing molecular dynamics simulations using the $5e$ pseudopotentials described above. The *ab initio* molecular dynamics simulations are performed using the recently developed version of the ABINIT structure code which takes full advantage of the parallelization over both the number of bands and the number of plane waves [47].

We recall that the $5e$ pseudopotential developed above requires a plane-wave cutoff of 180 hartrees to converge the various quantities of interest. While this is rather costly, even for *ab initio* simulations, we also note that the simulation time decreases as the density increases and fewer plane waves are needed in the calculations. In effect, the increase in computational time resulting from the small cutoff radius needed for high-pressure studies is mostly compensated for by the reduction in the number of plane waves. The additional computational cost comes directly from the increase in the number of active electrons and the number of bands used in the calculation, respectively 200 and 300, at, respectively, $T=1$ and 4 eV.

The *ab initio* simulations presented here are performed at the γ point and using 54 atoms in the simulation cell. A time step varying between 1 and 0.1 fs was used. We compare our results with simulations using the $3e$ pseudopotential described above and the results obtained with TFD molecular dynamics (TFMD) simulations. These simulations include exchange using the Perrot functional as described above. In this approach, the ions are also propagated in time, but in this case, the forces are calculated from the electronic density obtained using the Thomas-Fermi-Dirac approximation. These simulations are performed using 32 atoms in the simulation cell and a time step of 1 fs. Further details of this approach can be found in [30,48,49].

The variations in pressure along the 1- and 4-eV isotherms are rather similar, and we displayed the results with the density on a logarithmic and linear scales to facilitate the comparison between the different calculations. Figure 3 shows that for both isotherms, the calculations using the $3e$ and $5e$ pseudopotentials are in good agreement at the lowest

density. As the density increases, the two calculations depart with the calculation using the $3e$ pseudopotential and a cutoff radius $r_c=1.6a_B$ gradually giving lower pressures. It is also interesting to note that the pressure obtained with the $3e$ pseudopotential only slowly degrades as the density increases. At $\rho=10$ g/cm³, the pressures obtained only depart by 10%. We further recall that for this potential, there is an overlap of the “pseudoization” spheres for densities higher than 7 g/cm³.

Figure 3 shows that the $5e$ pseudopotential simulations tend to the TFMD results as the density increases. Furthermore, we note that the small cutoff radius and the inclusion of the $1s$ orbital allows us to push the *ab initio* simulations well into the semiclassical regime. Figure 3 also shows that there is a significant density region where the two methods overlap. For these two boron isotherms, we find that the TFMD simulation results can be considered as accurate for densities higher than 20 g/cm³. Above this density, the difference in pressure between the two models is less than 10%. We also point out that for densities higher than 20 g/cm³, TF average atom calculations such as presented in the preceding section indicate that the ionization fraction varies from 3 to 4. This further indicates that the $1s$ orbital can not be treated as frozen in this density region. The good agreement between the *ab initio* and TFMD simulations at these densities further suggests that the effect of the $1s$ orbital is properly accounted for with the $5e$ pseudopotential developed in this study.

Finally, we point out that the system is strongly coupled in this regime and the electrons fully degenerated. As shown in [30], at these conditions the structure is very close to the one obtained using the one-component plasma (OCP) model [31] which is known to freeze at a coupling parameter $\Gamma=172$. Considering that the $2s$ and $2p$ orbitals are ionized, $Z^*=3$, the ion-ion coupling constant is estimated to be around $\Gamma=200$ at a density of 20 g/cm³ and $T=1$ eV. Indeed, we find that both the *ab initio* and TFMD simulations indicate that the system is no longer liquid and crystallizes for densities above 20 g/cm³. We further note that, in contrast, the system stays in a liquid state along the 4-eV isotherm and for the density range explored here. Using an ionization fraction of $Z^*=3.5$, the coupling constant is estimated at around 144 for a density of 100 g/cm³ and a temperature of 4 eV. Finally, the good agreement between the *ab initio* and TFMD calculations further suggests that the semiclassical approximation can be considered as valid for density beyond 20 g/cm³ and this whether the system crystallizes or stays in a liquid state.

SUMMARY

In summary, we developed a Troullier-Martins norm-conserving pseudopotential for boron where all the electrons are treated as active. We first find that the angular components of the pseudopotential cannot be limited to occupied atomic orbitals to be valid at high densities. Despite the very large plane-wave cutoff needed to perform the calculations, we further show that *ab initio* molecular dynamics simulations using such a potential are practical well into the semiclassical regime where simpler methods such as the

Thomas-Fermi MD approach can be used. This allows us to establish, for the case of boron plasmas, that the TFMD approach leads to satisfactory dynamical properties for densities higher than about 10 times the normal densities.

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