Finite-Temperature Orbital-Free Density Functional Calculations for Warm Dense Lithium

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I. Introduction

Warm dense matter (WDM) encompasses the region between condensed matter and plasmas. WDM occurs on the pathway to inertial confinement fusion and is thought to play a significant role in the structure of the interior of giant planets.

WDM is characterized by:
- Elevated temperature (from one to a few tens of eV).
- High pressure (up to thousands of GPa).

Motivation for development of orbital-free methods:
- Standard solid state physics methods become very expensive (due to high temperature).
- Standard approximations used in those methods cease to work (due to high material density).
- OF-DFT is a less expensive alternative to orbital-dependent methods.
- The high density and elevated temperature of WDM regime are favorable for use of OF-DFT.

Challenges of the OF-DFT approach:
- Development of accurate non-interacting free energy functionals.
- Development of accurate *local* pseudopotentials.

Purposes of present work:
- Provide Kohn-Sham reference data for *electronic degrees* of freedom which are accurate in WDM regime.
- Assess accuracy of orbital-free approximate functionals.
- Study the range of applicability (density and temperature) of *local* pseudopotentials based on simple models.

II. Finite-Temperature OF-DFT Formalism

In the finite-temperature version of DFT it is convenient to work in the grand canonical ensemble. The Grand canonical potential of a system of electrons in an external potential *v*(**r**) with electronic density *n*(**r**), chemical potential μ, and temperature T is given by:

$$\Omega[n] = F[n] + \int (v(\vec{r}) - \mu) n(\vec{r}) d\vec{r}$$

The universal functional *F*[n] has the following decomposition

$$F[n] = F_s[n] + F_H[n] + F_{xc}[n]$$

where F_s[n], F_H[n], and F_{xc}[n] are the non-interacting free energy, classical Coulomb repulsion energy, and exchange-correlation contribution to the free energy defined as:

$$F_s[n] = T_s[n] - \mathrm{T}S_s[n]$$

$$F_H[n] = \frac{1}{2} \int\int \frac{n(\vec{r}) n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r} d\vec{r}\,'$$

$$F_{xc}[n] = (T[n] - T_s[n]) - \mathrm{T}(S[n] - S_s[n]) + (U_{ee}[n] - F_H[n])$$

where *T*[n] and *S*[n] are the kinetic energy and entropy of the interacting system and U_{ee}[n] is the electron-electron potential interaction energy.

Thomas-Fermi approximation:

Evaluating the grand canonical potential for *non-interacting* uniform electron gas (UEG) of constant density *n* in a volume *V*, one obtains the non-interacting free-energy functional in the TF approximation

$$f_s^{\mathrm{TF}}(n(\vec{r}), \mathrm{T}) = \frac{\sqrt{2}}{\pi^2 \beta^{5/2}} \left[-\frac{2}{3} I_{3/2}(\beta\mu(\vec{r})) + \beta\mu(\vec{r}) I_{1/2}(\beta\mu(\vec{r})) \right],$$

$$n(\vec{r}) = \frac{\sqrt{2}}{\pi^2 \beta^{3/2}} I_{1/2}(\beta\mu(\vec{r})),$$

and

$$F_s^{\mathrm{TF}}[n] = \int f_s^{\mathrm{TF}}(n(\vec{r}), \mathrm{T}) d\vec{r}.$$

In 1979 Perrot developed the second-order temperature dependent gradient correction to the TF free-energy functional:

$$f_s^{\mathrm{SGA}}(n, \nabla n, \mathrm{T}) = f_s^{\mathrm{TF}}(n, \mathrm{T}) - \frac{1}{24} \frac{I_{1/2}(\beta\mu) I_{-3/2}(\beta\mu)}{I_{-1/2}^2(\beta\mu)} \frac{|\nabla n|^2}{n}.$$

III. Kohn-Sham Reference Calculations

Test of non-local pseudopotentials for WDM regime:

Pseudopotentials (PPs) are often used in KS calculations to reduce computational cost by excluding core electrons from self-consistent cycle. Pseudopotentials usually are intended to be used at "normal" external conditions of temperature and pressure. Transferability of PPs for conditions of high pressure and elevated temperature of WDM regime should be checked:

- Use small Li clusters of bcc symmetry with inter-atomic distances equal to the nearest-neighbor distance in bulk bcc-Li for densities in the range 0.5-150 g/cm^3
- Compare all-electron and PPs calculations to test transferability to high pressure
- Compare 1e- and 3e- PP results to test the transferability to temperature in range T=100K ... 100,000K.

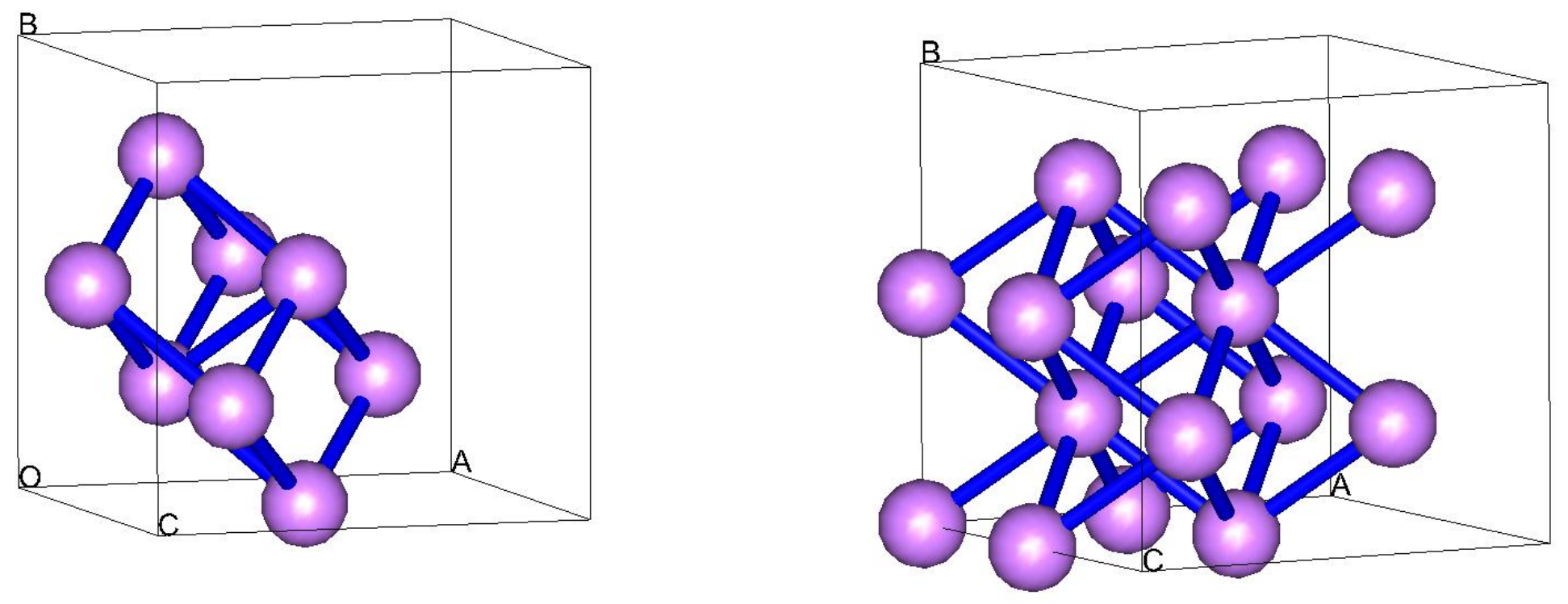

FIG. 1. Bcc Li_8 and Li_{16} clusters used to test pseudopotential KS calculations.

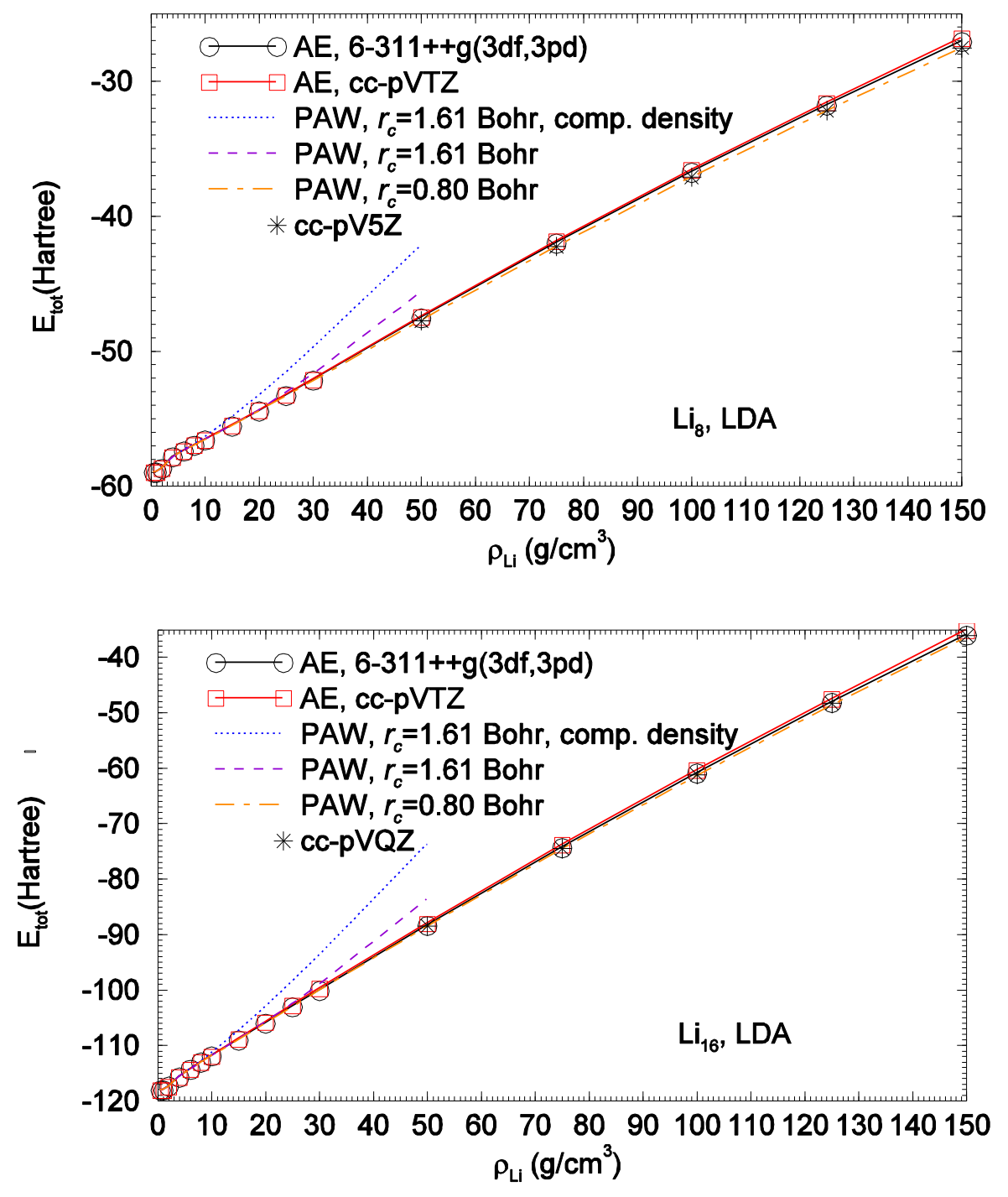

FIG. 2. All-electron and PAW LDA energies: Li_8 and Li_{16} clusters.

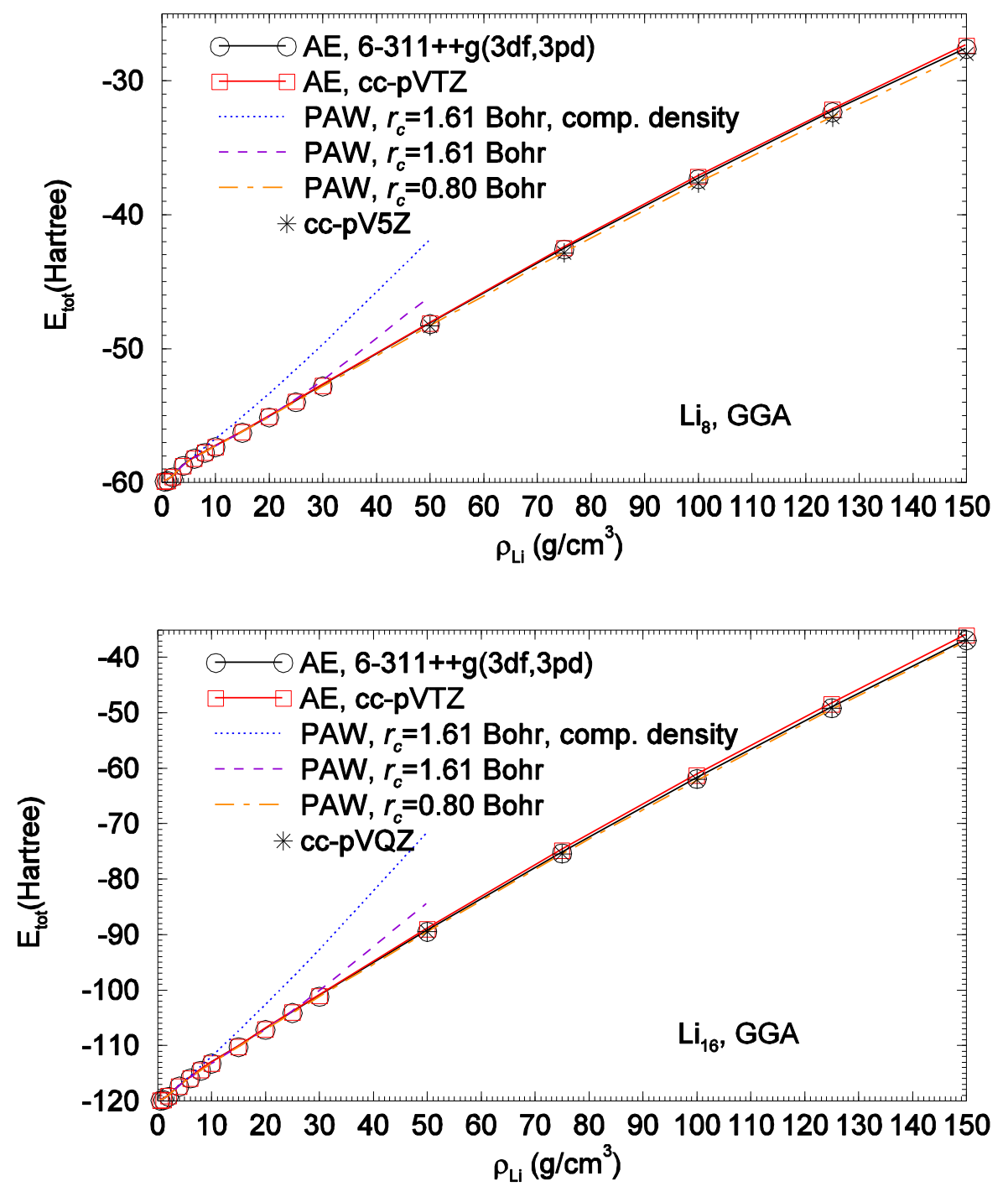

FIG. 3. All-electron and PAW GGA energies: Li_8 and Li_{16} clusters.

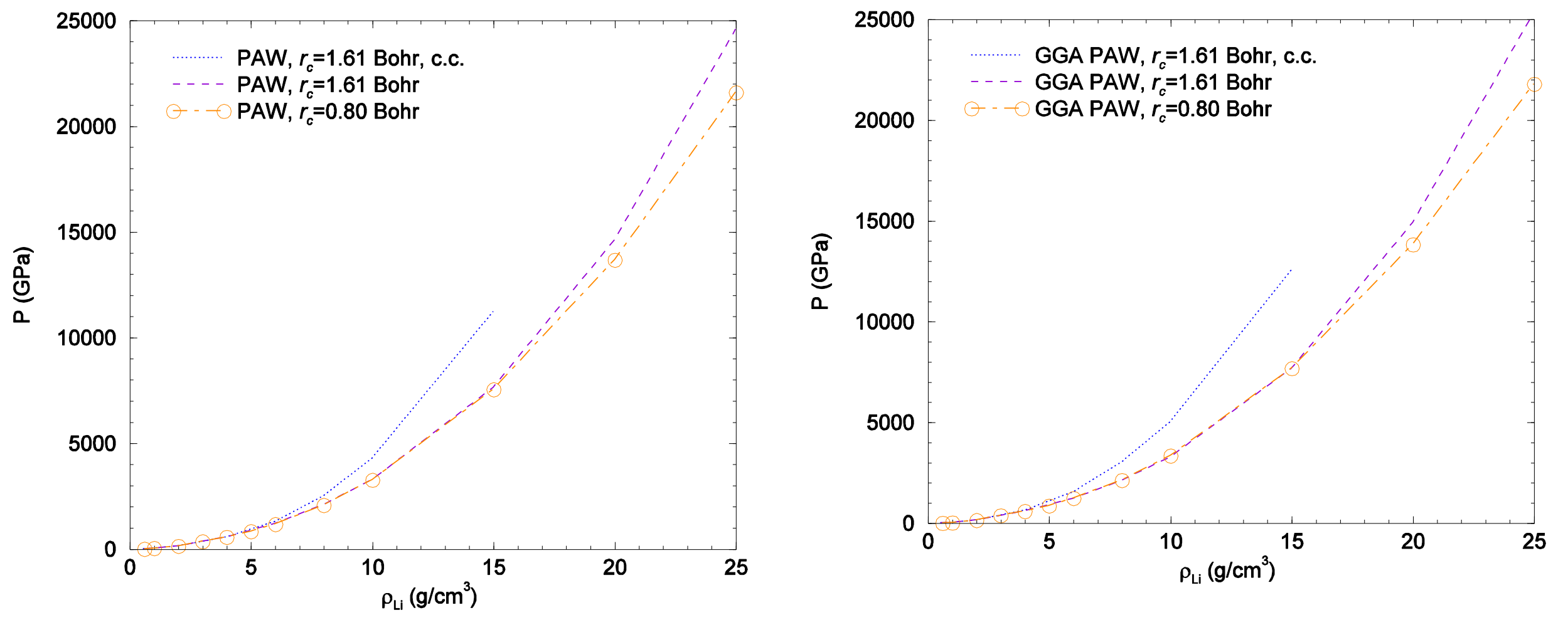

FIG. 4. Bulk bcc Li pressure vs. material density from PAW LDA (PW correlation) (left panel) and from PAW GGA (PBE XC) (right panel).

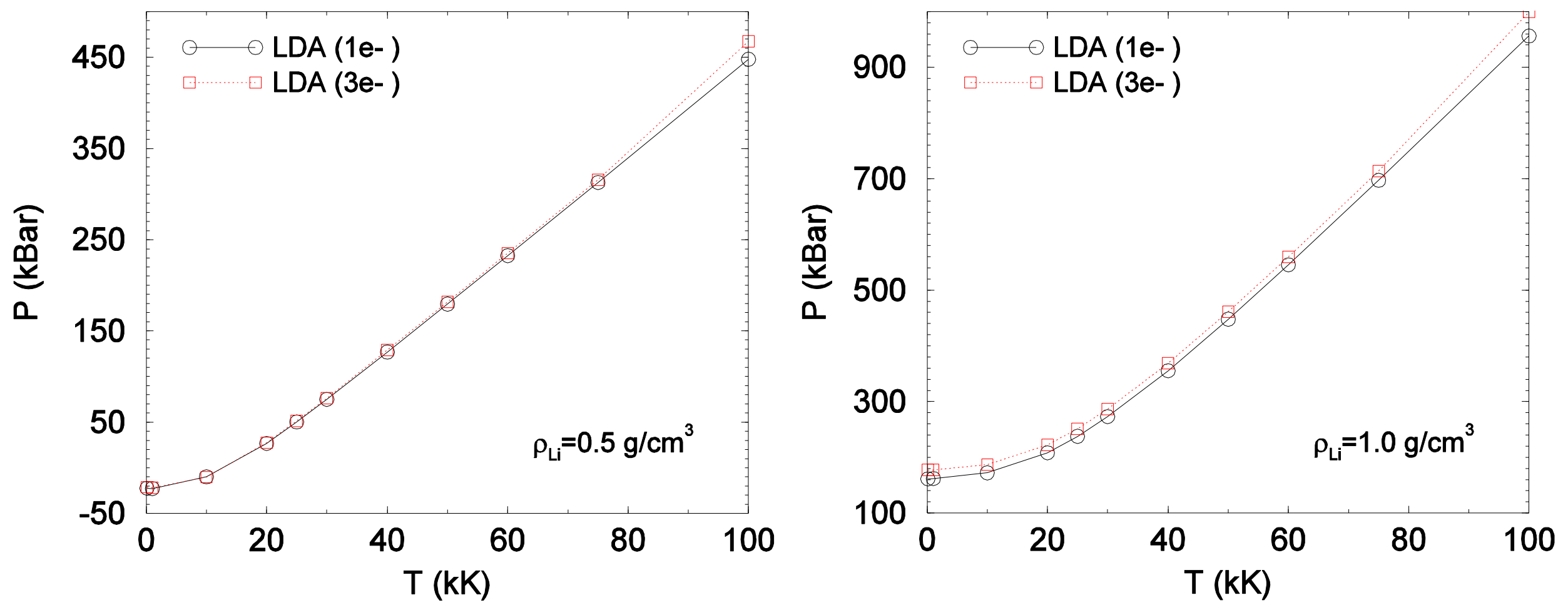

FIG. 5. Bulk bcc Li pressure vs. temperature obtained with 3e- and 1e- norm-conserving PPs for the Perdew-Zunger LDA XC functional as implemented in QUANTUM-ESPRESSO (2-atom unit cell, 9x9x9 k-mesh, 128 bands). Left panel: ρ=0.5 g/cm^3. Right panel: ρ=1.0 g/cm^3.

IV. Local pseudopotentials

We used the model potential proposed by Heine and Abarenkov. In real space, it is:

$$v_{\mathrm{mod}}(r) = \begin{cases} -A, r < r_c \\ -Z/r, r \geq r_c \end{cases}$$

Here A is a constant, r_c is the core radius, *Z* is the core charge. The model potential in reciprocal space is given by

$$v_{\mathrm{mod}}(q) = \frac{-4\pi}{\Omega q^2} [(Z - Ar_c)\cos(qr_c) + (A/q)\sin(qr_c)] f(q),$$

where

$$f(q) = \exp[(-q/q_c)^6]$$

yields a smoothed step function used to reduce spurious oscillations and to ensure rapid decay of $v_{mod}(q)$ at large wave-vectors.

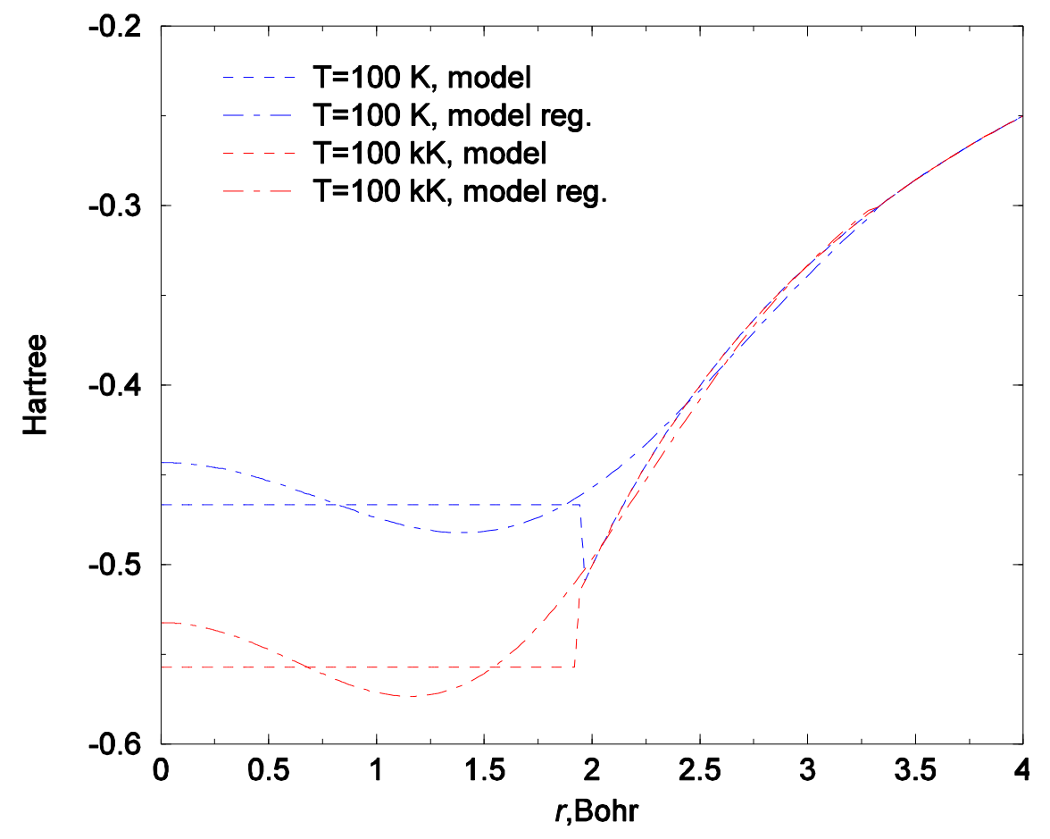

FIG. 6. Local PPs for Li with parameters fitted to reproduce pressure in bcc-Li in the range of densities between 0.5 and 2.0 g/cm3 for two temperatures, T=100K and T=100 000K.

V. Results

OF-DFT calculations were performed for a bcc-Li 128-atom supercell with LPPs shown in FIG.6 for temperatures T=100K and T=100,000K, and material densities in the range 0.5-10 g/cm^3.

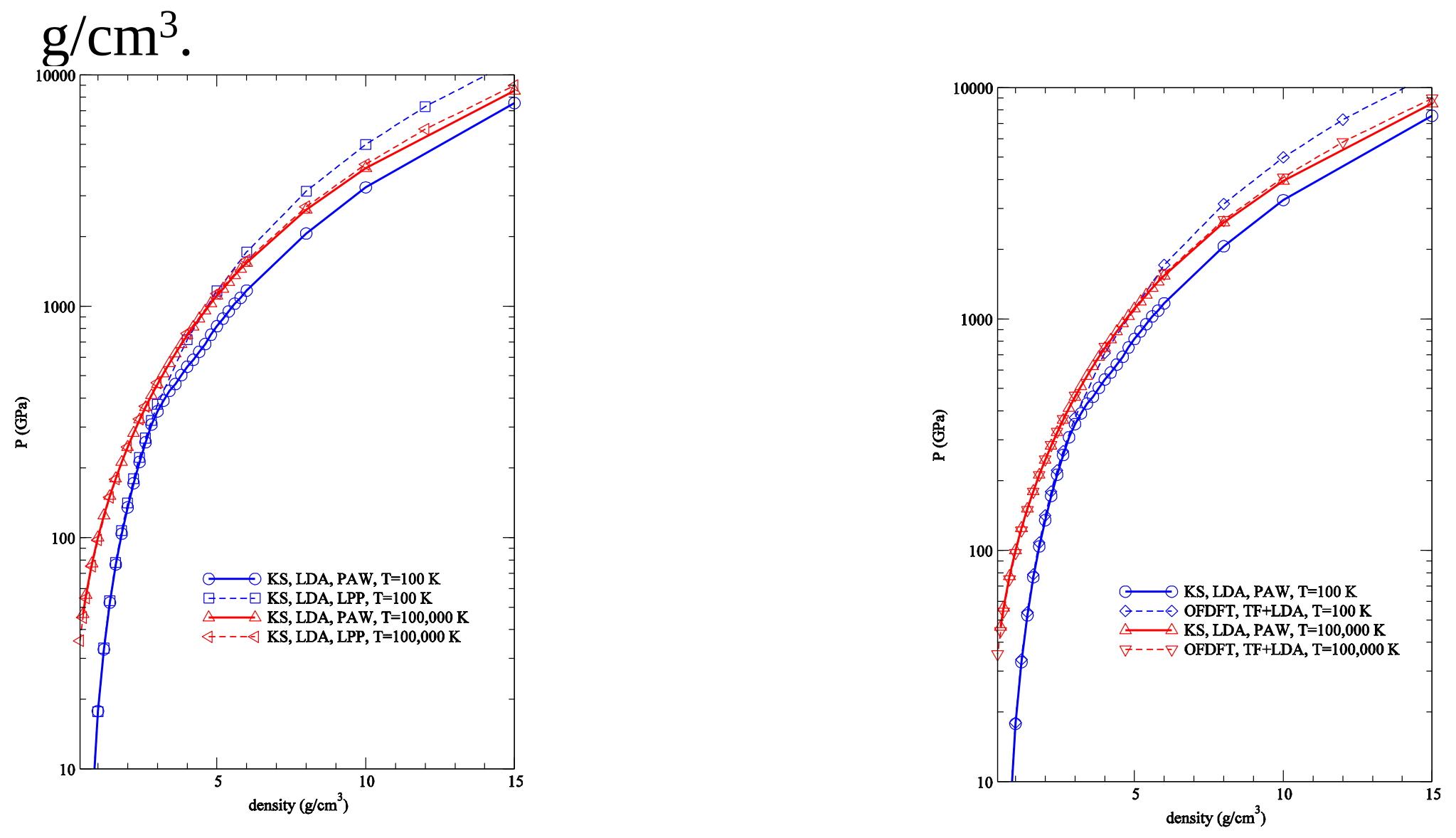

FIG. 7. Pressure as a function of material density for bcc-Li Left panel: validation of local pseudopotential. Right panel: comparison between OF-DFT (local PP) and PAW Kohn-Sham results for T=100K and T=100 000K.

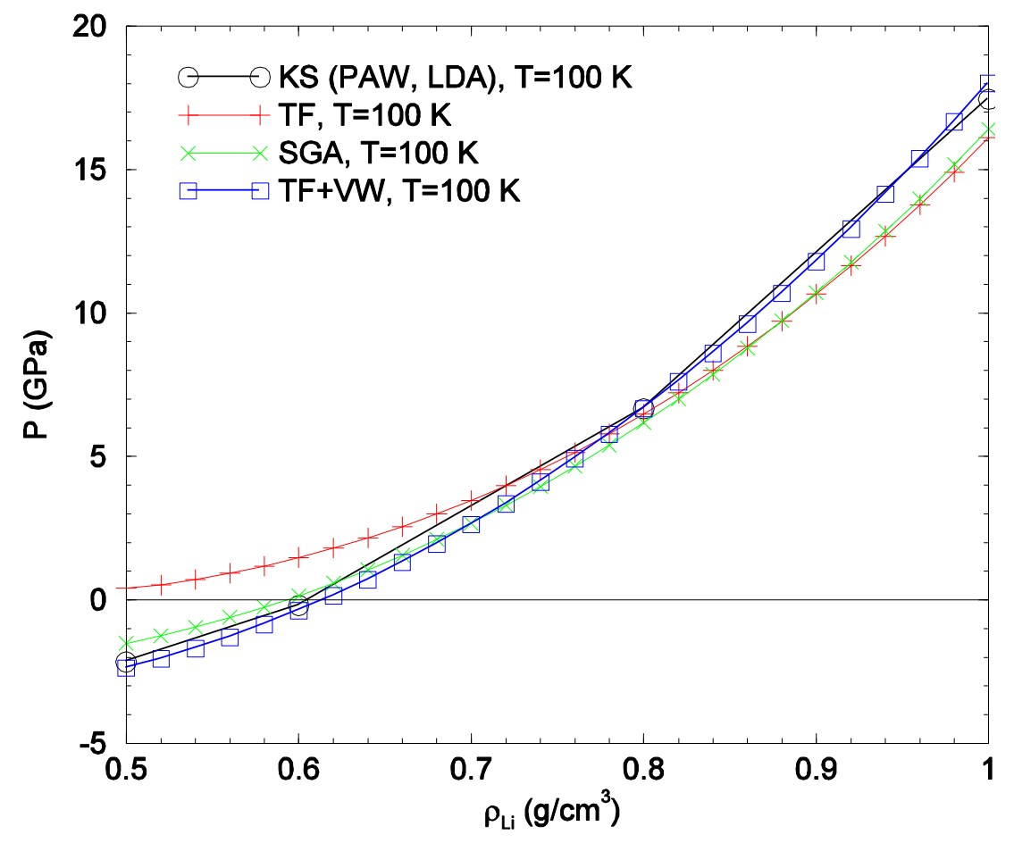

FIG. 8. Pressure as a function of material density for bcc-Li Comparison between OF-DFT (local PP) and PAW Kohn-Sham results for T=100K near equilibrium (ambient) density).

VI. Conclusions

- Pseudopotentials used in standard Kohn-Sham calculations are not generally transferable to high pressure conditions.
- We constructed LDA and GGA PAW data sets for Li with a small cut-off radius which are reliable for the density range up to ~80 g/cm^3.
- Simple local model potentials are reliable for densities in the range 0.5-3.0 g/cm^3 for T=100 K and in the range 0.5-8 g/cm^3 for T=100 000K.
- OF-DFT results obtained with non-interacting free energy functional in Thomas-Fermi approximation provides good agreement with reference KS data for high material density.
- At materials density close to the equilibrium value, gradient corrections to the TF approximation should be taken into account.

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