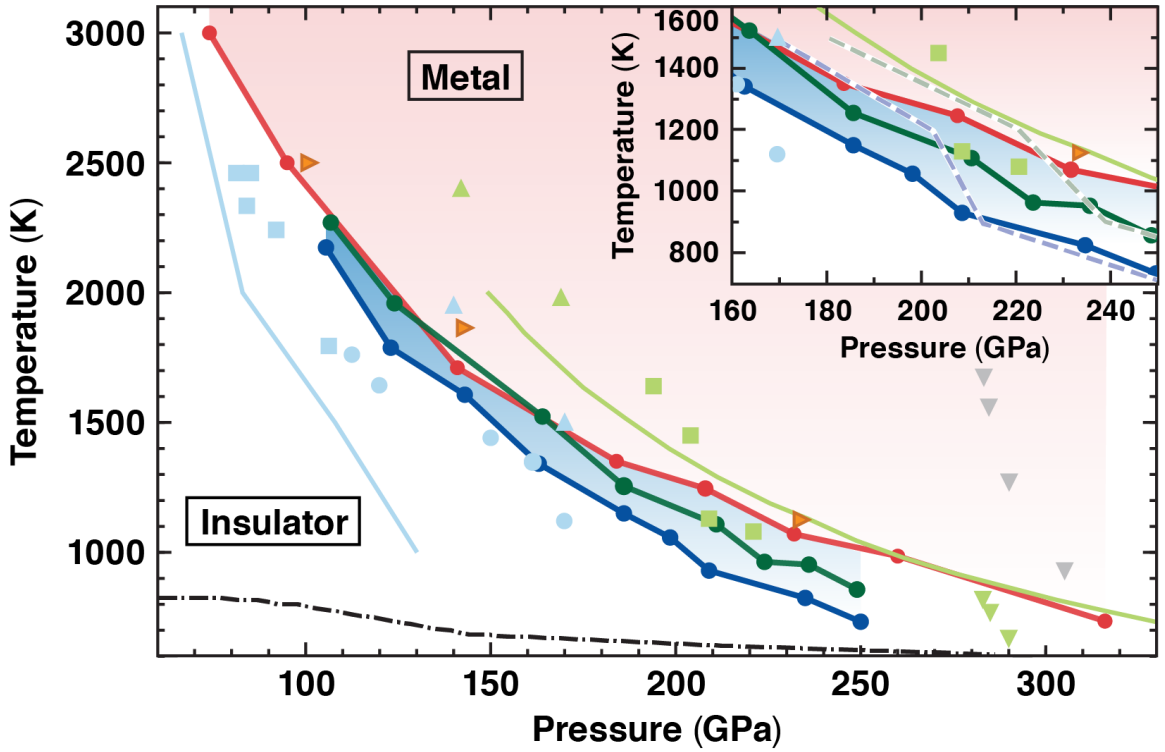
Accurate Density Functional Theory Simulations Across the Warm-Dense-Matter Regime: Thermal meta-GGA Exchange Correlation and Nuclear-Quantum Effects



NQE's affect the equation of state of H/D, lower the insulator-to-metal transition boundary, and introduce isotope effects (H versus D).

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62nd Annual Meeting of the American Physical Society
Division of Plasma Physics
9–13 November 2020

Summary

We developed a meta-GGA level XC functional with additive thermal corrections, T-SCAN-L, that is accurate across temperature regimes

- Exchange-correlation (XC) thermal effects and nuclear quantum effects (NQE's) play important roles in the structure and thermodynamic properties of warm dense H and D

- NQE's enhance the dissociation process in warm-dense molecular hydrogen, lower the insulator-to-metal transition boundary, and introduce isotope effects (H versus D)

- A new thermal exchange-correlation functional, T-SCAN-L, changes the EOS of H up to 7% (energy) and 5% (pressure) in the range of conditions relevant to the principal Hugoniot

meta-GGA = meta-generalized gradient approximation
EOS = equation of state

Collaborators

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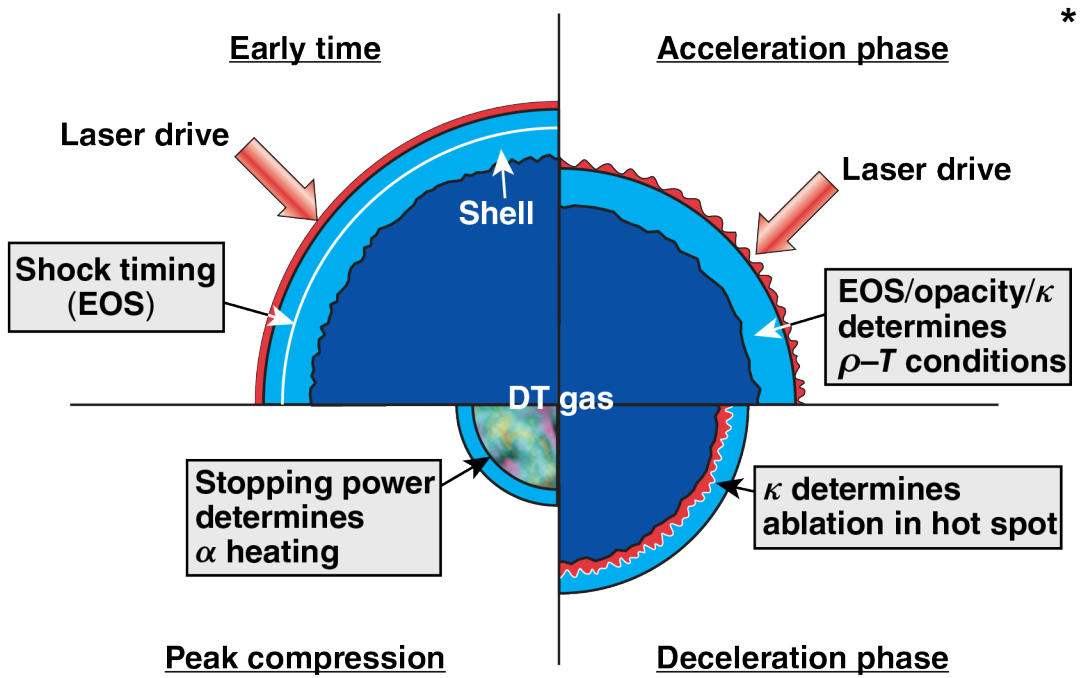
Funding Acknowledgments:

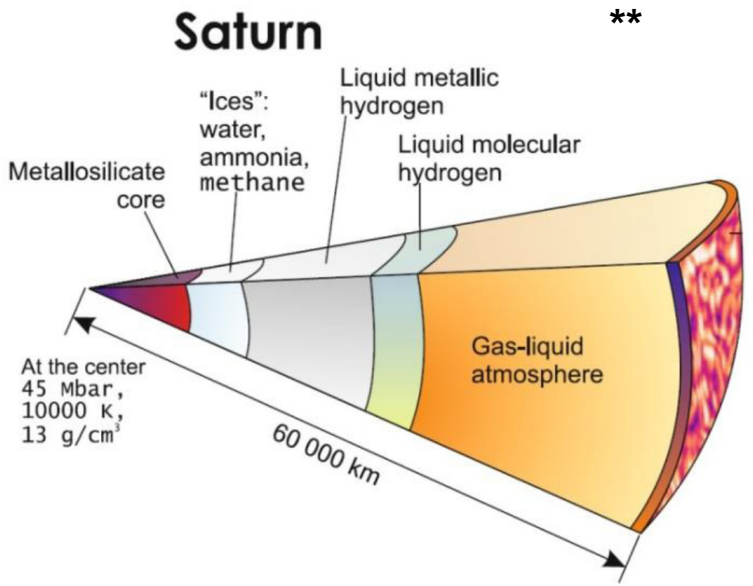
This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856, the University of Rochester, and the New York State Energy Research and Development Authority.

This work was partially supported by U.S. National Science Foundation PHY Grant No. 1802964

Motivation

H/D/T properties are important for inertial confinement fusion (ICF) target design and for modeling giant planetary interiors





- ICF target design and performance is sensitive to material-property models in warm-dense-matter (WDM) conditions
- The EOS and location of the insulator-to-metal transition boundary and its character (sharp versus smooth) are important for planetary models

Figures are adapted from:
*R. S. Craxton *et al.*, Phys. Plasmas 22, 110501 (2015).
**V. E. Fortov, *Extreme States of Matter: High Energy Density Physics*, 2nd ed., Springer Series in Materials Science, Vol. 216, edited by R. Hull *et al.* (Springer International Publishing, Switzerland, 2016).

Method

We define a universal thermal XC additive correction at the GGA level of theory

- The new thermal SCAN-L (T-SCAN-L) is a meta-GGA XC with additive thermal correction

$$\Delta F_{\mathrm{xc}}^{\mathrm{GGA}}[n,T] = F_{\mathrm{xc}}^{\mathrm{KDT16}}[n,T] - E_{\mathrm{xc}}^{\mathrm{PBE}}[n]$$

$$F_{\mathrm{xc}}^{\mathrm{T-SCAN-L}}[n,T] = E_{\mathrm{xc}}^{\mathrm{SCAN-L}}[n] + \Delta F_{\mathrm{xc}}^{\mathrm{GGA}}[n,T]$$

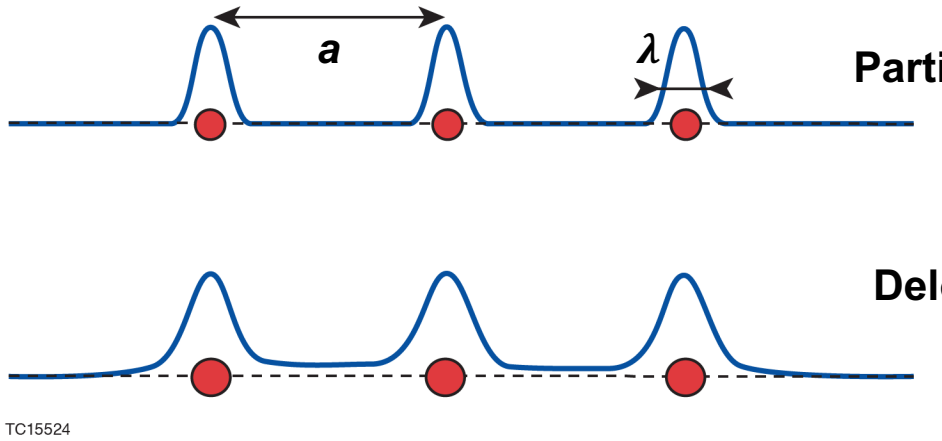
- T-SCAN-L by construction reduces to the ground-state meta-GGA SCAN-L in the zero-*T* limit
- T-SCAN-L has improved meta-GGA level accuracy at low *T*
- T-SCAN-L takes into account XC thermal effects at elevated *T*

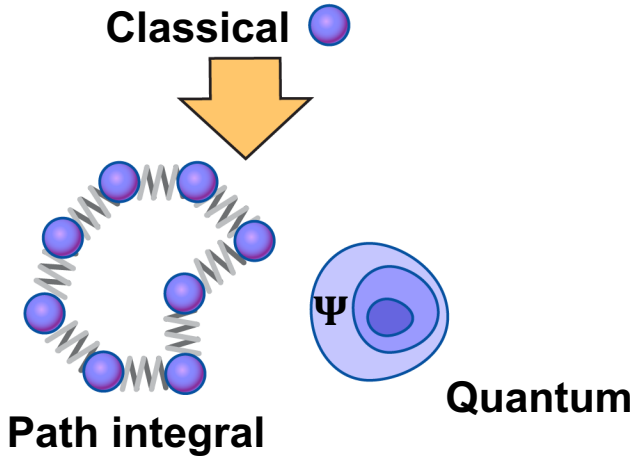
V. V. Karasiev, J. W. Dufty, and S. B. Trickey, Phys. Rev. Lett. 120, 076401 (2018);
J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996); 78, 1396(E) (1997);
D. Mejia-Rodriguez and S. B. Trickey, Phys. Rev. A 96, 052512 (2017).

Method

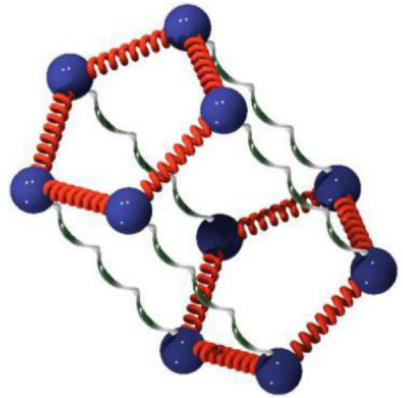
NQE's are taken into account via path-integral molecular dynamics (PIMD)

- PIMD exploits the isomorphism between a quantum system and a classical system of ring polymers



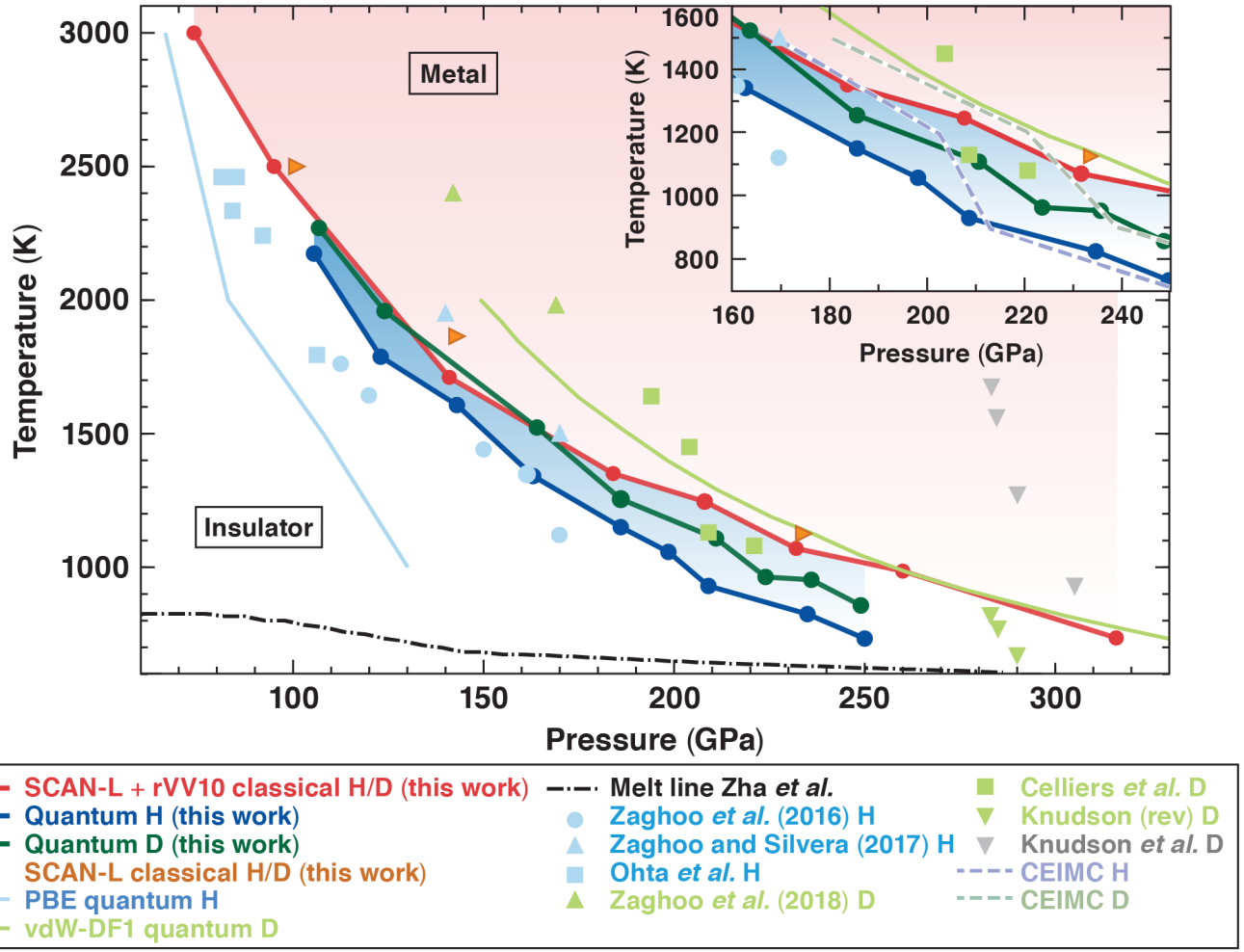


- An *N*-particle quantum system can be made approximately isomorphic to a classical system consisting of *N* ring polymers, and each polymer has *P* beads
  - interaction between interpolymer beads is described within density functional theory framework



Results

NQE's lower the insulator-to-metal (IMT) transition boundary and introduce isotope effects (H versus D)



TC14950a

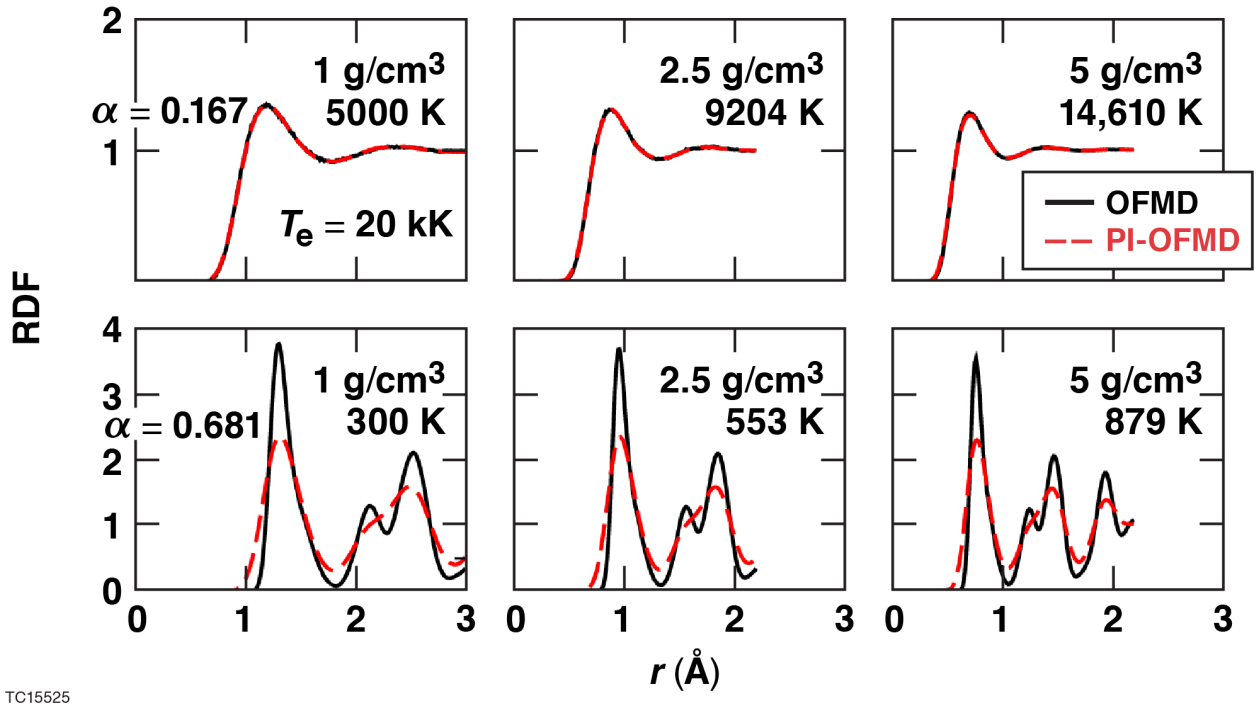
Insulator-to-metal transition boundary in dense fluid H/D

- classical ions (H and D): solid red curve
- quantum ions, H: solid blue curve
- quantum ions, D: solid green curve

J. Hinz *et al.*, Phys. Rev. Research 2, 032065(R) (2020).

Results

NQE's facilitate dissociation in molecular fluid H_2



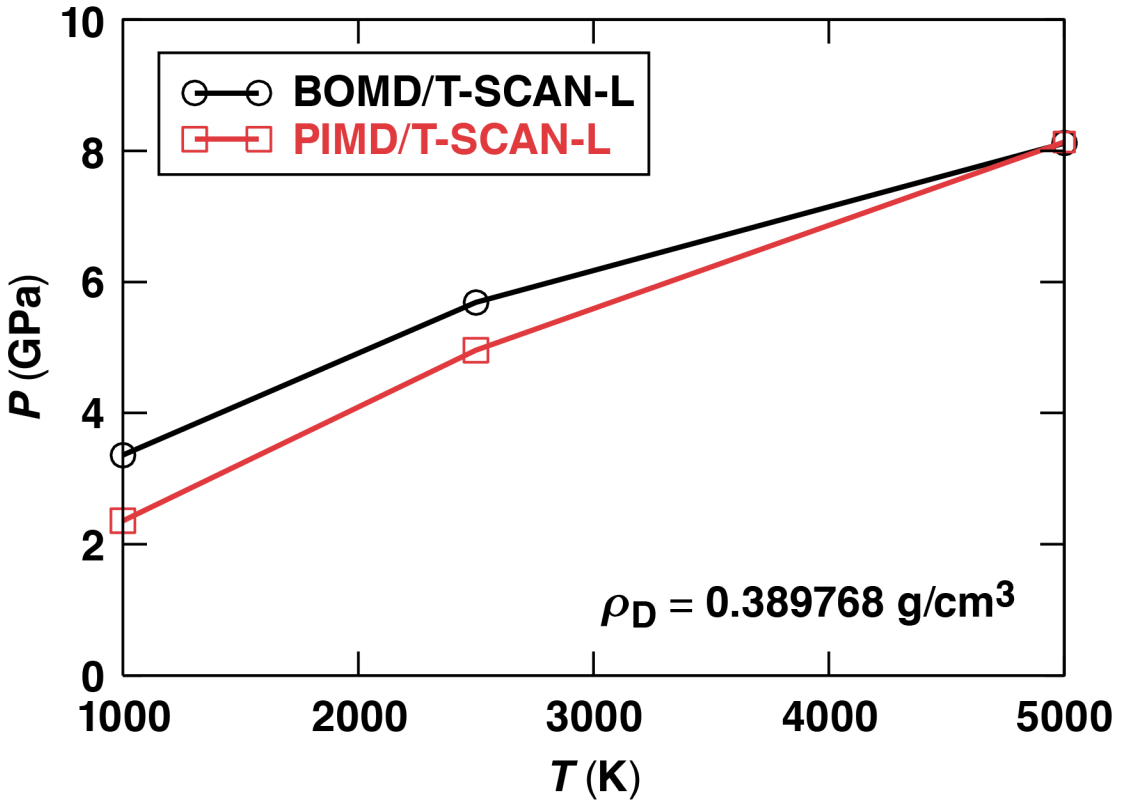
- When the ratio of the ionic thermal de Broglie wavelength, $\lambda = h/(2\pi m k_B T_i)^{1/2}$, to the mean distance between ions ($\alpha = \lambda/2r_s$) is larger than about 0.30, the ionic radial distribution function (RDF) is affected perceptibly by NQE's

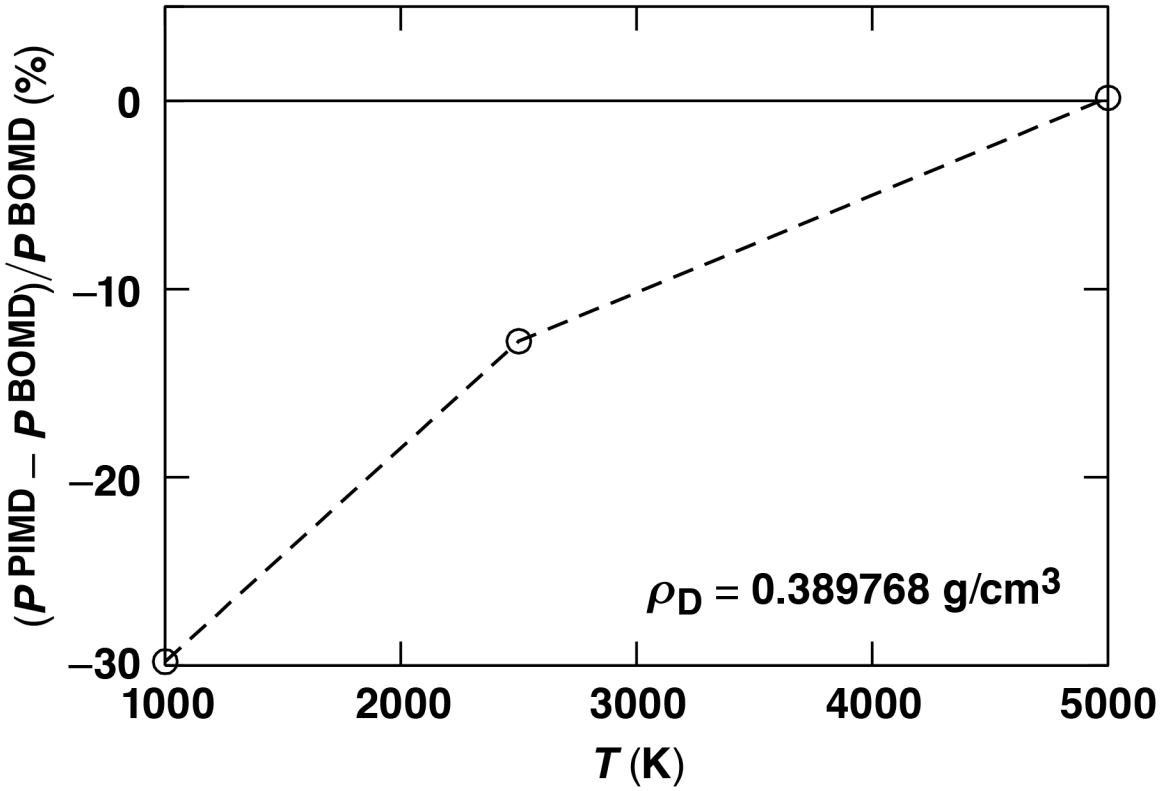
OFMD = orbital-free molecular dynamics
PI-OFMD = path integral orbital-free molecular dynamics

D. Kang *et al.*, "Two-Temperature Warm Dense Hydrogen as a Test of Quantum Protons Driven by Orbital-Free Density Functional Theory Electronic Forces," to be published in Matter and Radiation at Extremes.

Results

NQE's on the EOS of liquid D at low-density $\rho_D = 0.389768$ g/cm^3 lower pressure up to 30%



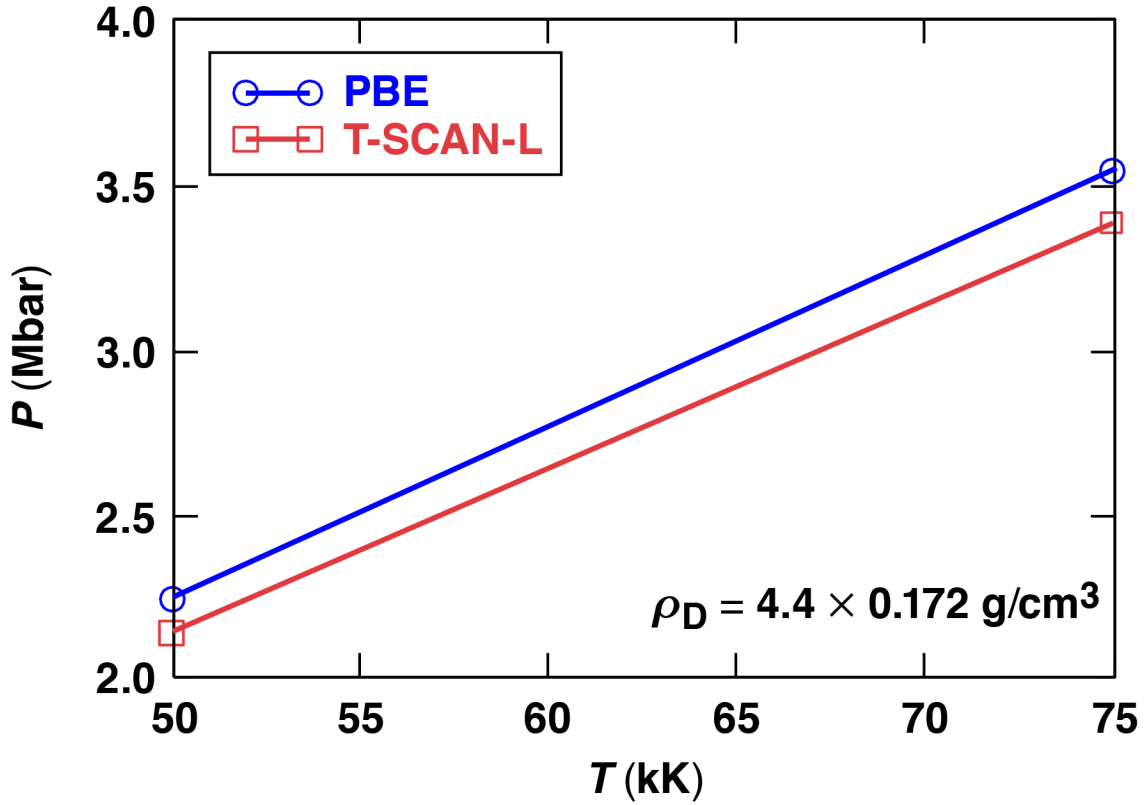


TC15526

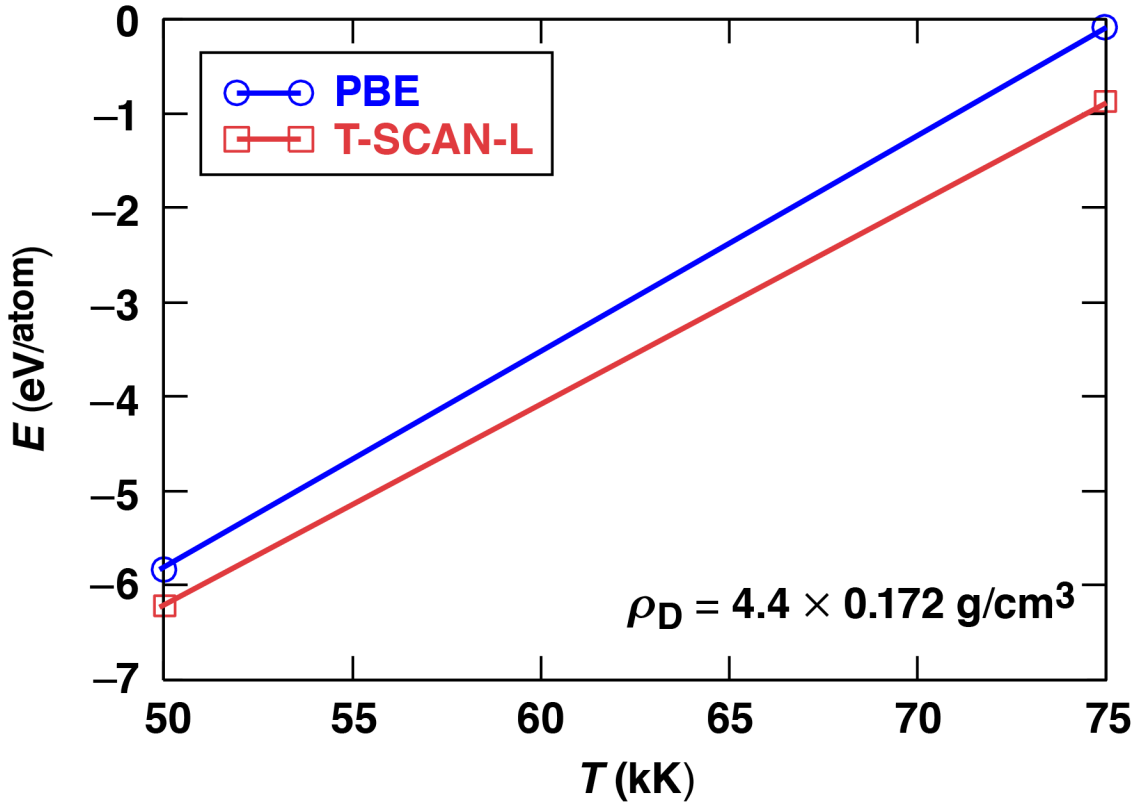
- Classical ions: Born–Oppenheimer molecular dynamics (BOMD);
- Quantum ions: path integral molecular dynamics
- DFT treatment of electrons via thermal meta-GGA T-SCAN-L exchange-correlation functional

Results

The new T-SCAN-L functional lowers pressure and energy by 5% and 7%, respectively, with respect to commonly used ground-state PBE XC at conditions along the principal Hugoniot of hydrogen



TC15588



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