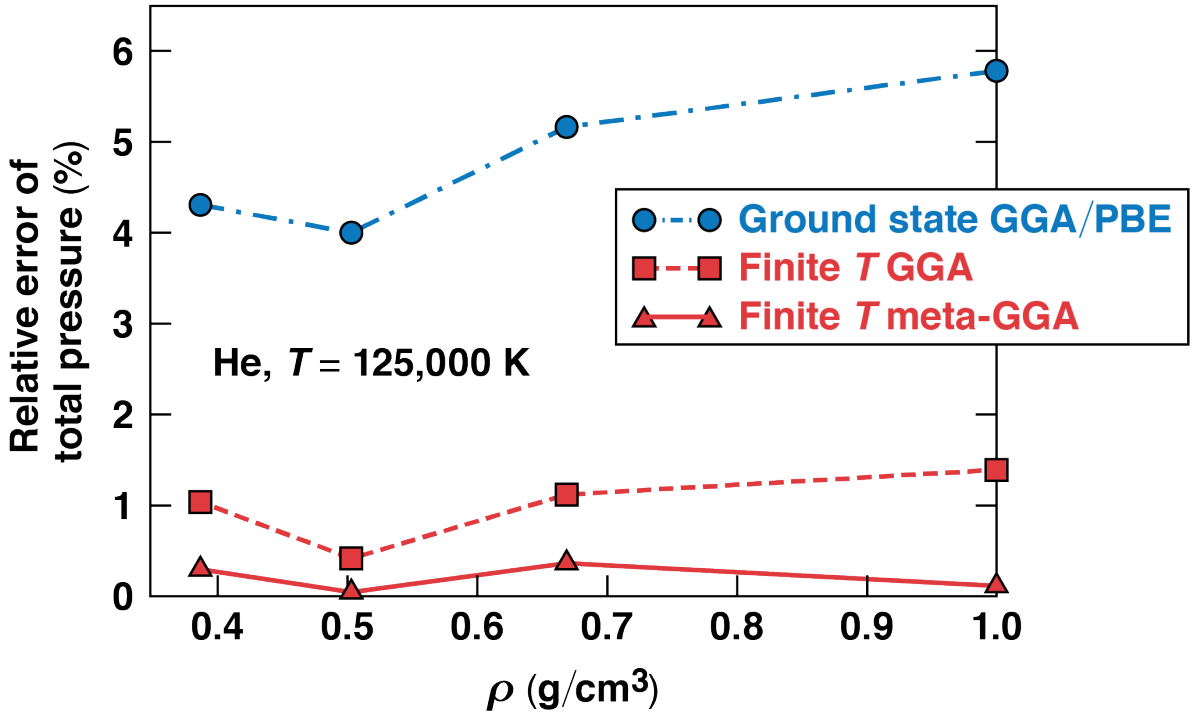
Advancing the Accuracy of DFT Simulations for High-Energy-Density Plasmas by Developing Temperature-Dependent Exchange-Correlation Functionals



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Summary

Exchange-correlation thermal effects are important in warm dense matter and dense plasma regimes and must be taken into account via a thermal XC functional for reliable DFT-based predictions

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- The first nonempirical thermal XC LDA functional is based on the parameterization of the accurate quantum Monte-Carlo (QMC) simulation data for homogeneous electron gas (HEG) at finite temperature
- Systematic development of thermal XC functionals at the LDA, GGA, and meta-GGA level of theory clearly demonstrate systematic improvements of the accuracy of DFT simulations in warm dense matter (WDM) and dense plasma regimes
- The new *T*-dependent meta-GGA XC T-SCAN-L, is the most reliable functional across the entire temperature range; T-SCAN-L provides accurate predictions of (as demonstrated so far)
  - (i) insulator-to-metal transition boundary of dense H
  - (ii) equation of state (EOS) of deuterium
  - (iii) EOS of dense helium
  - (iv) dc conductivity of low-density Al

XC: exchange correlation
DFT: density functional theory
LDA: local density approximation
GGA: generalized gradient approximation
SCAN-L: de-orbitalized strongly constrained appropriately normed

V. V. Karasiev et al., Phys. Rev. Lett. 112, 076403 (2014);
V. V. Karasiev, J. W. Dufty, and S. B. Trickey, Phys. Rev. Lett. 120, 076401 (2018);
D. I. Mihaylov, V. V. Karasiev, and S. X. Hu, Phys. Rev. B 101, 245141 (2020).
V. V. Karasiev, D. I. Mihaylov, and S. X. Hu, "Meta-GGA Exchange-Correlation Free Energy Density Functional to Achieve Unprecedented Accuracy for Warm-Dense-Matter Simulations," submitted to Physical Review Letters.); 78, 1396(E) (1997).

Collaborators

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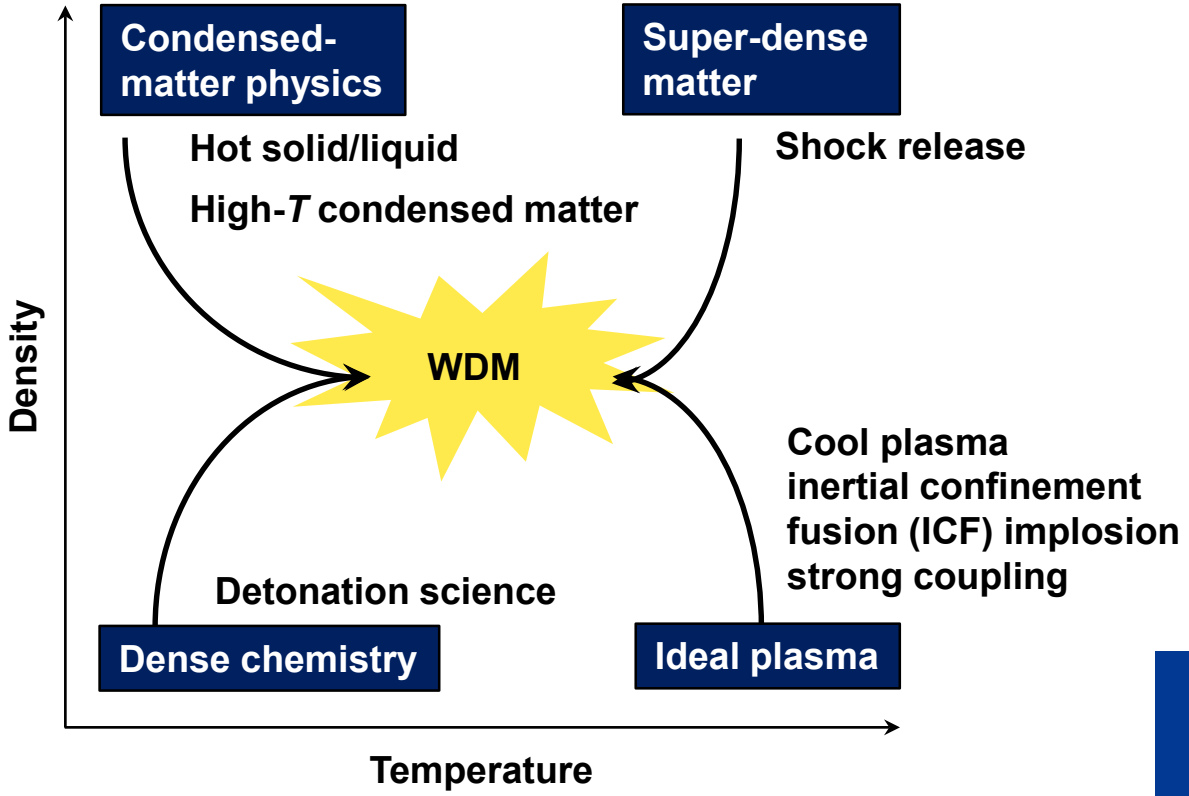
Motivation

Dense plasmas and WDM is a scientifically rich area of high-energy-density physics (HEDP) where several distinct physical regimes meet



$$\Gamma \equiv \frac{\langle \text{potential energy} \rangle}{\langle \text{kinetic energy} \rangle} \sim 1$$

$$\Theta_F \equiv \frac{kT}{E_F} \sim 1$$

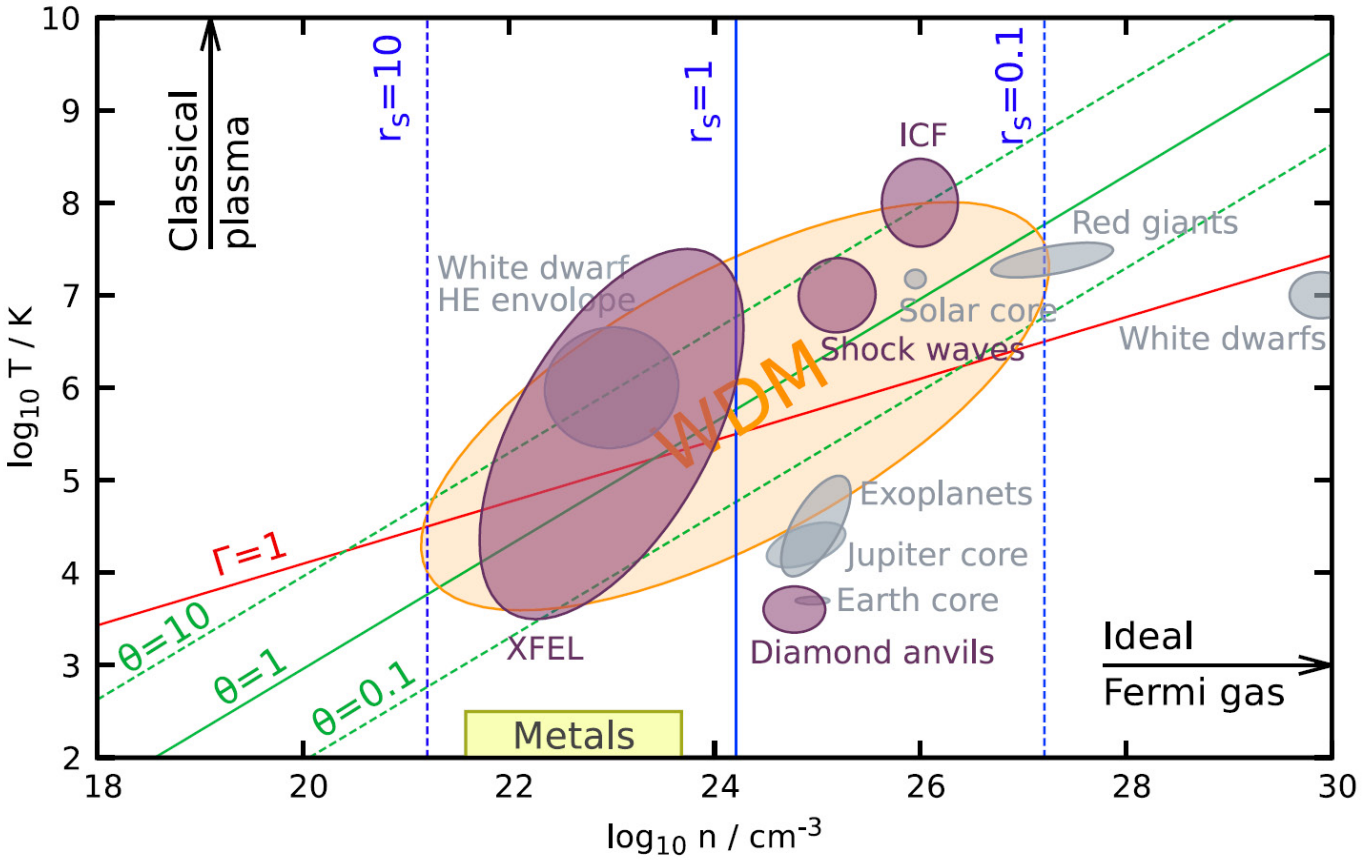
The WDM challenge:
- well-developed models used on WDM face severe problems
- Quantum treatment is required

ICF: inertial confinement fusion

S. B. Trickey, private communication (2021); R. More, private communication (2021).

Motivation

Our goal is to develop more accurate XC free-energy density functionals for a better description of warm dense matter and dense plasma properties



Schematic temp.-density diagram (T. Dornheim *et al.*, Phys. Rep 744, 1 (2018))

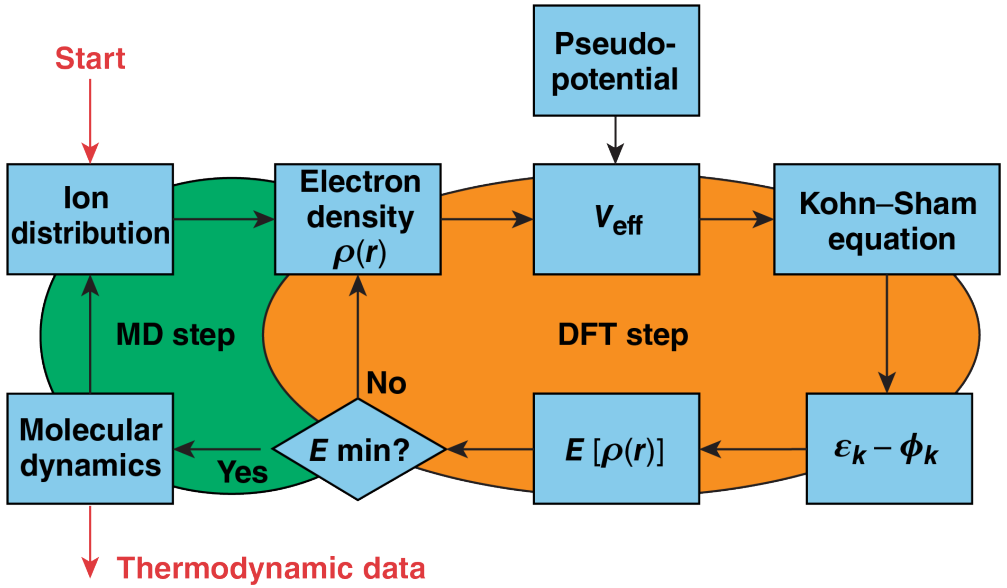
- **Classical plasma approaches work only for weakly coupled nondegenerate systems (Γ << 1: low density, very high temperature)**

All regions except left upper corner require quantum treatment of electronic degrees of freedom.

ICF: inertial confinement fusion

T. Dornheim, S. Groth, and M. Bonitz, Phys. Rep. 744, 1 (2018).

Thermal DFT coupled with *ab-initio* molecular dynamics (AIMD) has become a standard tool in HEDP



Molecular dynamics $m_I \ddot{\mathbf{R}}_I = -\vec{\nabla}_I V(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$

Born–Oppenheimer energy surface: $V(\{\mathbf{R}\}) = \Omega(\{\mathbf{R}\}) + E_{ion\text{-}ion}(\{\mathbf{R}\})$

$\Omega[n] = \mathcal{F}[n] + \int d\mathbf{r}\ (v_{ext}(\mathbf{r}) - \mu)\, n(\mathbf{r})$ -- Grand potential

$\mathcal{F}[n] = \mathcal{F}_s[n] + \mathcal{F}_H[n] + \mathcal{F}_{xc}[n]$ -- Free-energy functional

$\mathcal{F}_H[n]$ -- Hartree energy

$\mathcal{F}_{xc}[n]$ -- Exchange-Correlation (XC) free-energy

$\mathcal{F}_s[n]$ -- Non-interacting (Kohn-Sham) free-energy

Current best practice uses free-energy DFT with one-electron Kohn–Sham orbitals

Mermin-Kohn–Sham scheme replaces ($3N_e$)-dimensional problem by N_e coupled 3-D problems:

$$\left\{-\frac{1}{2}\nabla^2 + v_H(\mathbf{r};\{\mathbf{R}\}) + v_{\mathbf{xc}}(\mathbf{r};\{\mathbf{R}\}) + v_{\mathbf{ext}}(\mathbf{r};\{\mathbf{R}\})\right\}\varphi_j(\mathbf{r};\{\mathbf{R}\}) = \varepsilon_j \varphi_j(\mathbf{r};\{\mathbf{R}\})$$

$$n(\mathbf{r};\{\mathbf{R}\}) = \sum_j f(\varepsilon_j;\beta)\left|\varphi_j(\mathbf{r};\{\mathbf{R}\})\right|^2 \quad ; \quad v_{\mathbf{xc}}[n,T] = \frac{\delta \mathcal{F}_{\mathbf{xc}}[n,T]}{\delta n} \quad ; \quad \beta = 1/k_B T$$

Explicit *T*-dependence makes the difference

DFT-based AIMD allows for calculations of many material properties required for simulations of ICF implosions and provides predictions for HEDP experiments

Some of material properties accessible from DFT-based AIMD simulations

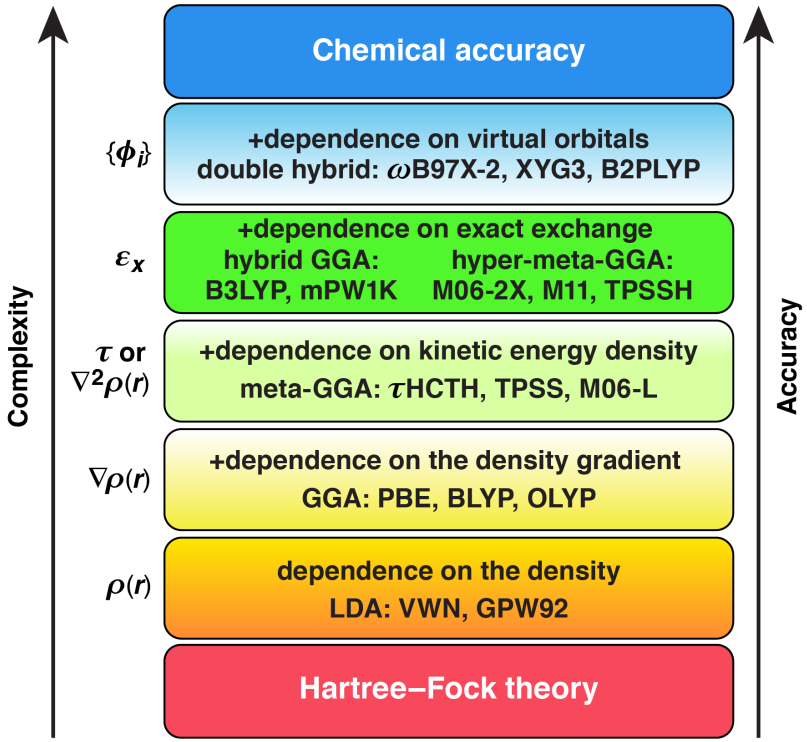
- **Equation of state**
- **Phase transitions**
- **Thermal conductivity**
- **Electrical conductivity**
- **Optic properties**
- **Absorption coefficients ➛ Rosseland and Planck mean opacities**

Accuracy of all DFT-predicted properties depends on the reliability of the XC density functional.

The great majority of DFT simulations use a zero-T XC functional.

We are developing advanced temperature-dependent XC functionals to improve density functional theory (DFT) predictions in warm-dense regime

Jacob's ladder* of the zero-*T* XC functional approximations:



Finite-*T* XC functional approximations:

← Finite-*T* Hybrids: KDT0: DIM, VVK, SXH, PRB 101, 245141 (2020)

← Finite-*T* meta-GGA: T-SCAN-L and T-r^{2}SCAN-L Phys. Rev. Lett. 2021 (submitted)

← Finite-*T* GGA (KDT16): Karasiev *et al.*, PRL 120, 076401 (2018)

← Finite-*T* LDA (KSDT): Karasiev *et al.*, PRL 112, 076403 (2014)

Development must start from the lowest rung because low-rung functionals are used as ingredients for higher rungs.

PBE/GGA: Perdew, Burke, Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
PZ/LDA: Perdew and Zunger, Phys. Rev. B 23, 5048 (1982)
*Perdew and Schmidt, AIP Conf. Proc. 577, 1 (2001)

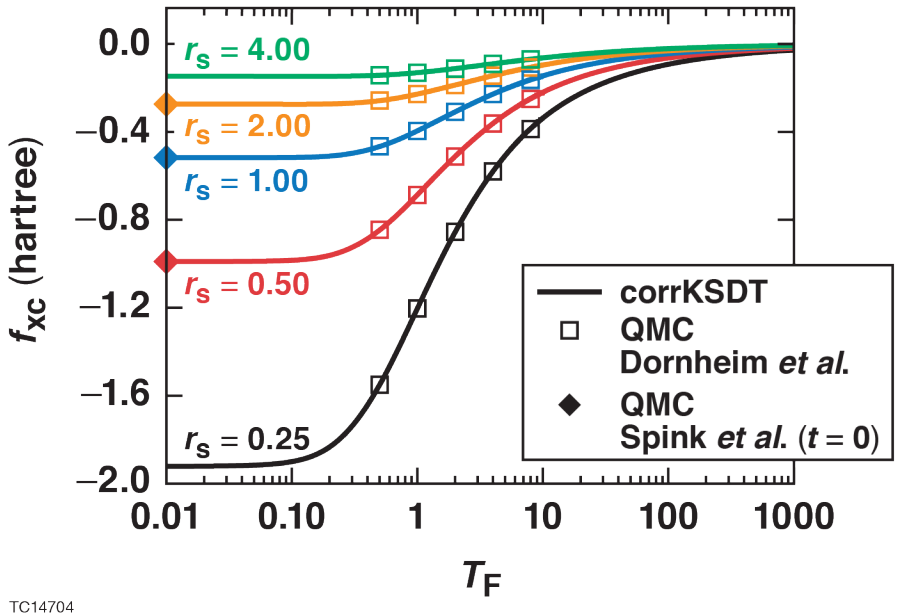
Finite-*T* LDA exchange-correlation is based on parameterization of accurate quantum Monte-Carlo data

- KSDT: Karasiev–Sjostrom–Dufty–Trickey finite-*T* LDA XC functional*
  - parametrization based on restricted path-integral Monte Carlo data (RPIMC)
- corrKSDT**
  - based on improved QMC data set at $T/T_F \geq 0.5$
- GDB: Growth-Dornheim-Bonitz†
  - duplicates the original KSDT parametrization method
  - based on improved QMC data set at $T/T_F \geq 0.5$

Comparison shows that corrKSDT and GDB fits are virtually identical.

* V. V. Karasiev *et al.*, Phys. Rev. Lett. 112, 076403 (2014).
** V. V. Karasiev, J. W. Dufty, and S. B. Trickey, Phys. Rev. Lett. 120, 076401 (2018).
† S. Groth *et al.*, Phys. Rev. Lett. 119, 135001 (2017).

QMC simulation data for the homogeneous electron gas (HEG) show strong *T*-dependence of XC free energy for temperatures above a few tenths of Fermi temperature



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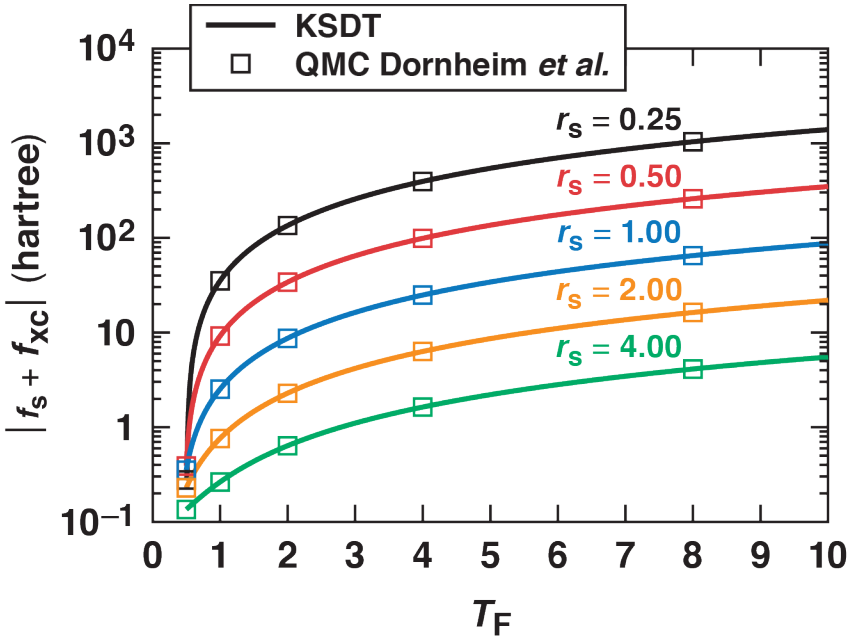
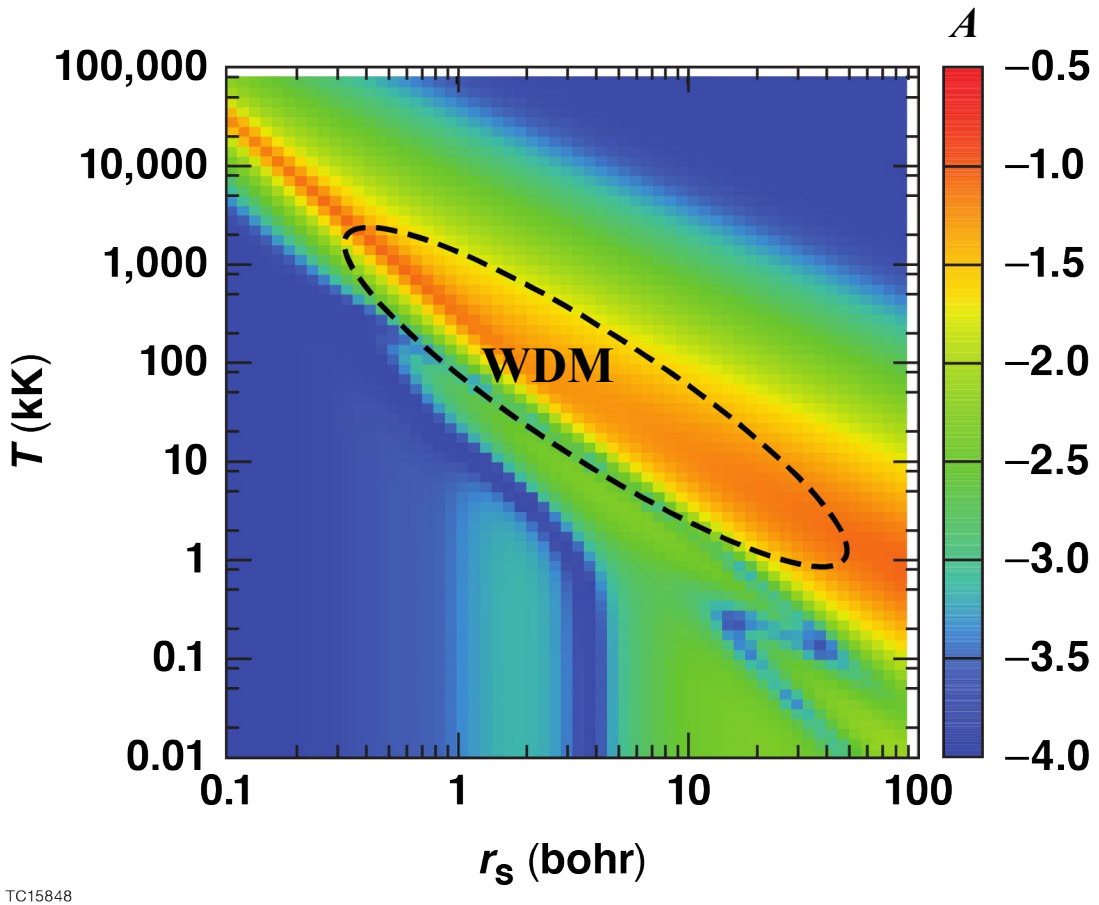


- XC free energy, f_{xc}, vanishes at very high *T*
- Noninteracting free energy, f_s, increases with increase of *T* and becomes the dominating contribution at high *T*
- We should expect that
  - XC thermal effects are important at intermediate temperatures (*T* between a few tenths and Fermi temperature)
  - the DFT results will not depend on XC functional used at very high *T*

V. V. Karasiev *et al.*, Phys. Rev. Lett. 112, 076403 (2014).

Most quantum MD simulations use $T = 0$ XC functionals, which do not take into account XC thermal effects; Our calculations show the importance of these effects for HEG in the warm dense regime



$f_{xc}(r_s, T)$ - XC LDA free-energy per particle, KSDT parameterization;

$\varepsilon_{xc}(r_s)$ - XC zero-T LDA energy per particle, Perdew-Zunger (1981) parameterization;

$f_s(r_s, T)$ - non-interacting free-energy per particle;

$$A = \log\left(\frac{|f_{xc}(r_s,T) - \varepsilon_{xc}(r_s)|}{|f_s(r_s,T) + \varepsilon_{xc}(r_s)|}\right)$$ - measure of importance of the explicit T-dependence in XC free-energy.

V. V. Karasiev, L. Calderín, and S. B. Trickey, Phys. Rev. E 93, 063207 (2016).

GGA rung: We developed a framework for *T*-dependent XC GGA functional to address the issue of combined thermal and non homogeneity effects

Generalized gradient approximation (GGA)

eXchange:

$$F_{\mathrm{x}}^{\mathrm{GGA}}[n,T]=\int n\, f_{\mathrm{x}}^{\mathrm{LDA}}(n,T)\,\mathrm{F}_{\mathrm{x}}(s_{2\mathrm{x}},T)\,\mathrm{d}\mathbf{r}$$

$$\mathrm{F}_{\mathrm{x}}(s_{2\mathrm{x}})=1+\frac{\nu_{\mathrm{x}} s_{2\mathrm{x}}}{1+\alpha\left|s_{2\mathrm{x}}\right|}$$

$$s_{2\mathrm{x}}(n,\nabla n,T)\equiv s^{2}(n,\nabla n)\tilde{B}_{\mathrm{x}}(t);\quad s=\frac{1}{2(3\pi^{2})^{1/3}}\frac{\nabla n}{n^{4/3}}$$

$$f_{\mathrm{x}}^{\mathrm{LDA}}(n,T)=\varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(n)\tilde{A}_{\mathrm{x}}(t)\quad;\quad t=T/T_{\mathrm{F}}$$

Correlation:

$$F_{\mathrm{c}}^{\mathrm{GGA}}[n,T]=\int n\, f_{\mathrm{c}}^{\mathrm{GGA}}(n,\nabla n,T)\,\mathrm{d}\mathbf{r}$$

GGA correlation energy per particle:

$$f_{\mathrm{c}}^{\mathrm{GGA}}(n,\nabla n,T)=f_{\mathrm{c}}^{\mathrm{LDA}}(n,T)+H(f_{\mathrm{c}}^{\mathrm{LDA}},q_{c}(T))$$

$$q_{c}(n,\nabla n,T)\equiv q(n,\nabla n)\sqrt{\tilde{B}_{\mathrm{c}}(n,t)}$$

XC thermal effects

XC nonhomogeneity effects

Imposed constraints on exchange and correlation:

- **Reproduce finite-*T* small-*s* gradient expansion**
- **Satisfy Lieb–Oxford bound at *T* = 0**
- **Reduce to correct *T* = 0 limit**
- **Reduce to correct high-*T* limit**

V. V. Karasiev, J. W. Dufty, and S. B. Trickey, Phys. Rev. Lett. 120, 076401 (2018).

Next meta-GGA rung depends on n, ∇n and Δn

- **Strongly constrained and appropriately normed (SCAN)† and de-orbitalized SCAN-L‡ ground-state XC provide the best overall performance at T=0K**
- **Original ground-state SCAN XC depends on electron density (n), density gradient (∇n), and the chemical region detector α, which depends on Kohn–Sham orbitals via kinetic energy density (t_s):**

$$\varepsilon_{xc}^{SCAN}(n, \nabla n, \alpha); \quad \alpha = \frac{(t_s - t^W)}{t^{unif}}; \quad t_s = \left(\frac{1}{2}\right)\Sigma|\nabla\phi_i|^2 \; ; \; t^W = \frac{1}{8}\frac{\nabla n}{n}; \quad t^{unif} = c_0 n^{\frac{5}{3}}$$

- **α recognizes covalent (α = 0), metallic ($\alpha \approx 1$), and weak ($\alpha \gg 1$) bonds in local chemical environment**
- **Deorbitilized SCAN-L: the orbital-dependent kinetic energy density, t_s, is replaced with an orbital-free Laplacian-dependent KE density, t_s^{OF}:**

$$t_s(\{\phi_i\}) \rightarrow t_s^{OF}(n, \nabla n, \Delta n); \quad \varepsilon_{xc}^{SCAN-L}(n, \nabla n, \Delta n)$$

$$E_{xc}^{SCAN-L}[n] = \int d^3r \, n(r) \varepsilon_{xc}^{SCAN-L}(n, \nabla n, \Delta n)$$

* J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. 115, 036402 (2015).
** D. Mejia-Rodriguez and S. B. Trickey, Phys. Rev. A 96, 052512 (2017).

A simple thermalization scheme using perturbative-like approach via universal thermal additive correction treated self-consistently has been developed

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Taking into account the following considerations:

- The leading T-dependent LDA and GGA XC terms account for most of thermal effects
- Thermal corrections beyond the GGA level are expected to be small

We define the following additive thermal XC correction:

$$\Delta F_{\mathrm{xc}}^{\mathrm{GGA}}[n,T] = F_{\mathrm{xc}}^{\mathrm{KDT16}}[n,T] - E_{\mathrm{xc}}^{\mathrm{PBE}}[n]; \quad \lim_{T\to 0} \Delta F_{\mathrm{xc}}^{\mathrm{GGA}}[n,T] \approx 0$$

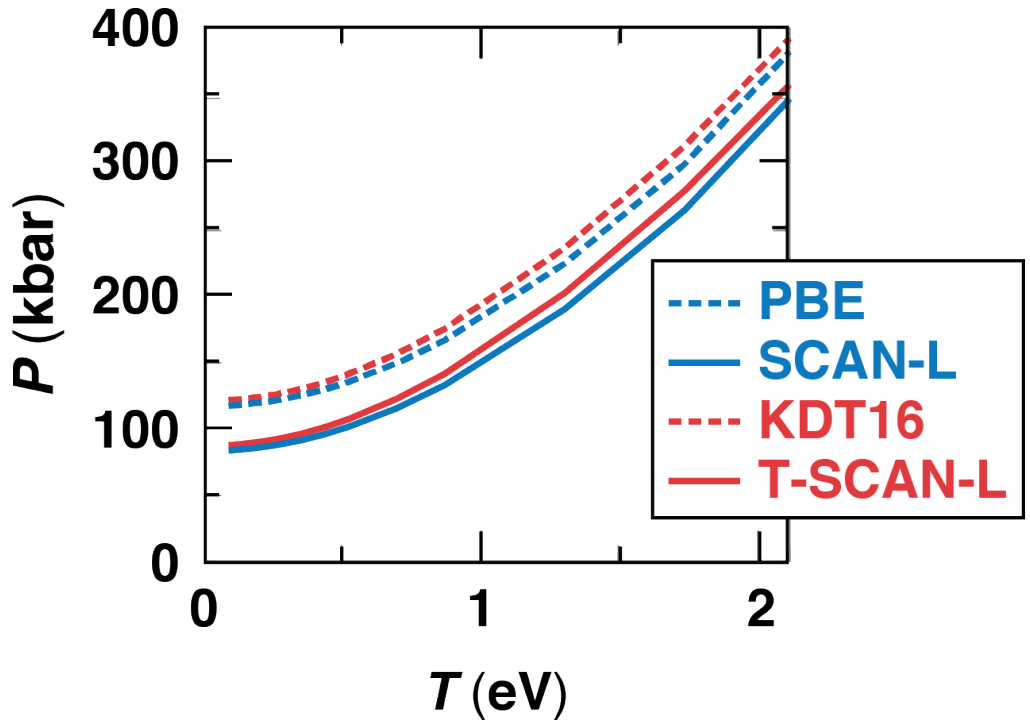
The new thermal SCAN-L (T-SCAN-L) is a meta-GGA XC with additive thermal correction:

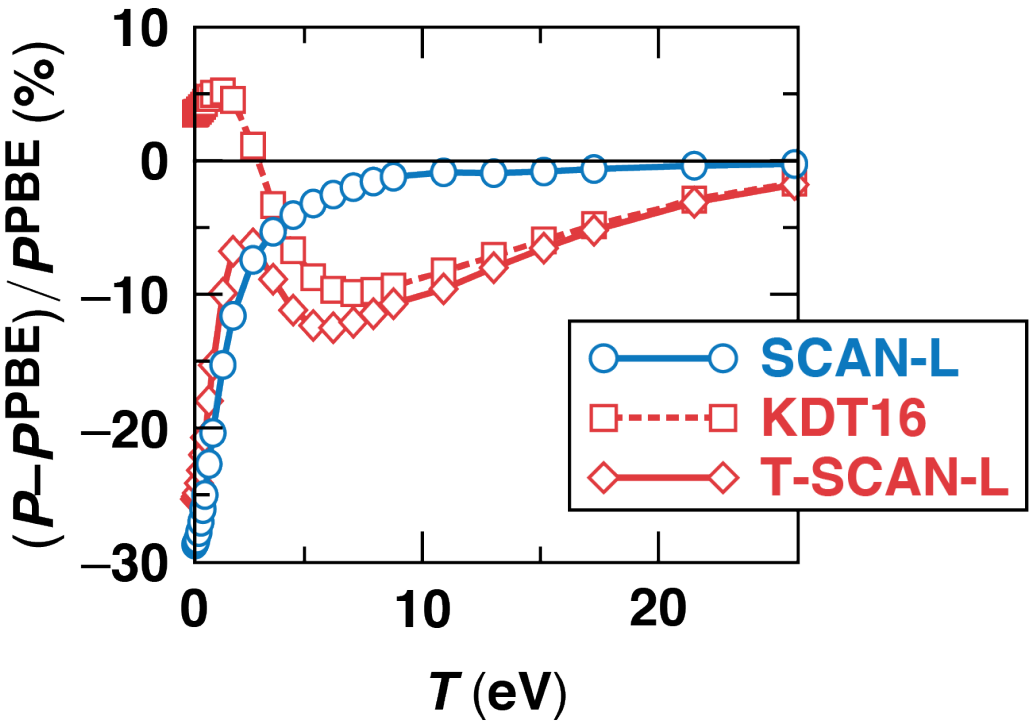
$$F_{\mathrm{xc}}^{\mathrm{metaGGA}}[n,T] = E_{\mathrm{xc}}^{\mathrm{metaGGA}}[n] + \Delta F_{\mathrm{xc}}^{\mathrm{GGA}}[n,T]; \quad \lim_{T\to 0} F_{\mathrm{xc}}^{\mathrm{metaGGA}}[n,T] \approx E_{\mathrm{xc}}^{\mathrm{metaGGA}}[n]$$

Properties:

- T-SCAN-L by construction reduces to the ground-state meta-GGA SCAN-L in the zero-*T* limit, preserving its accuracy
- T-SCAN-L reduced to the thermal KDT16 in the high-*T* limit
- T-SCAN-L smoothly interpolates between these two limits taking into account combined XC thermal and non-homogeneity effects

T-SCAN-L preserves the accuracy of SCAN-L at low-*T*, including combined XC thermal and inhomogeneity effects: model system sc-H, ρ = 0.6 g/cm^3





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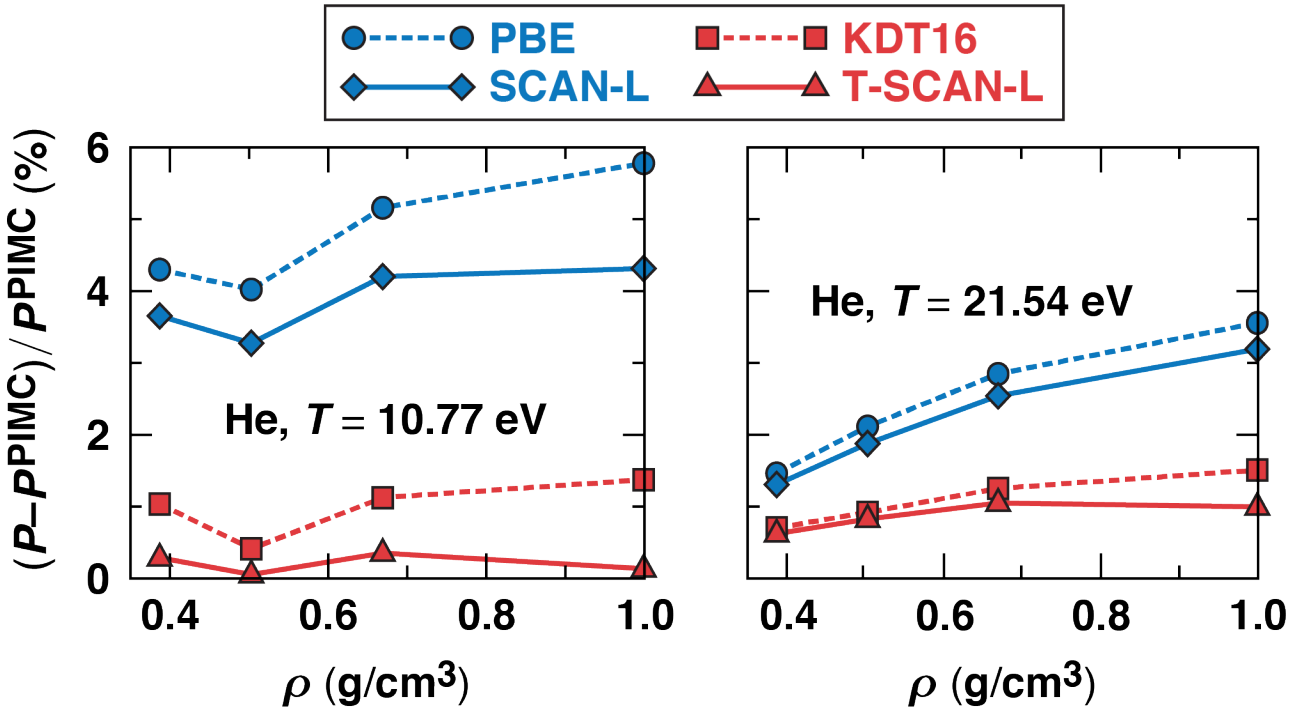
Relative error of pressure is reduced by a factor of 3 to 10 when T-SCAN-L is applied to EOS of warm-dense He

- Path-integral Monte Carlo (PIMC) data at high-*T* are used as a reference
- T-SCAN-L (meta-GGA + thermal) provides excellent agreement with regard to the PIMC reference



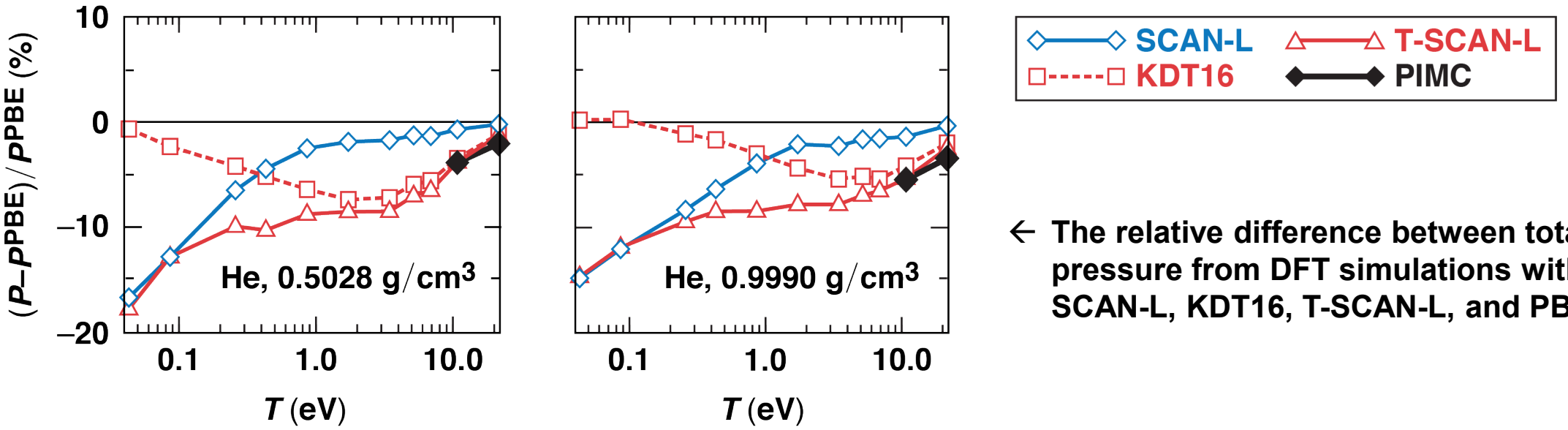
TC15736

← The relative error of total pressure from DFT simulations with respect to the reference PIMC results

B. Militzer, Phys. Rev. B 79, 155105 (2009).

Application to warm dense He: Quantifying non homogeneity and thermal XC effects

- The magnitude of these effects (missed by standard PBE XC) on total pressure ≈ 5% to 10% for *T* between 0.1 and 10 eV
- T-SCAN-L smoothly interpolates between low-*T* and high-*T* limits (SCANL and KDT16 respectively)
- The EOS table combined from the PBE/DFT + PIMC data is thermodynamically inconsistent, as opposite to the *T*-SCAN-L/DFT + PIMC combined EOS table



← The relative difference between total pressure from DFT simulations with SCAN-L, KDT16, T-SCAN-L, and PBE XC

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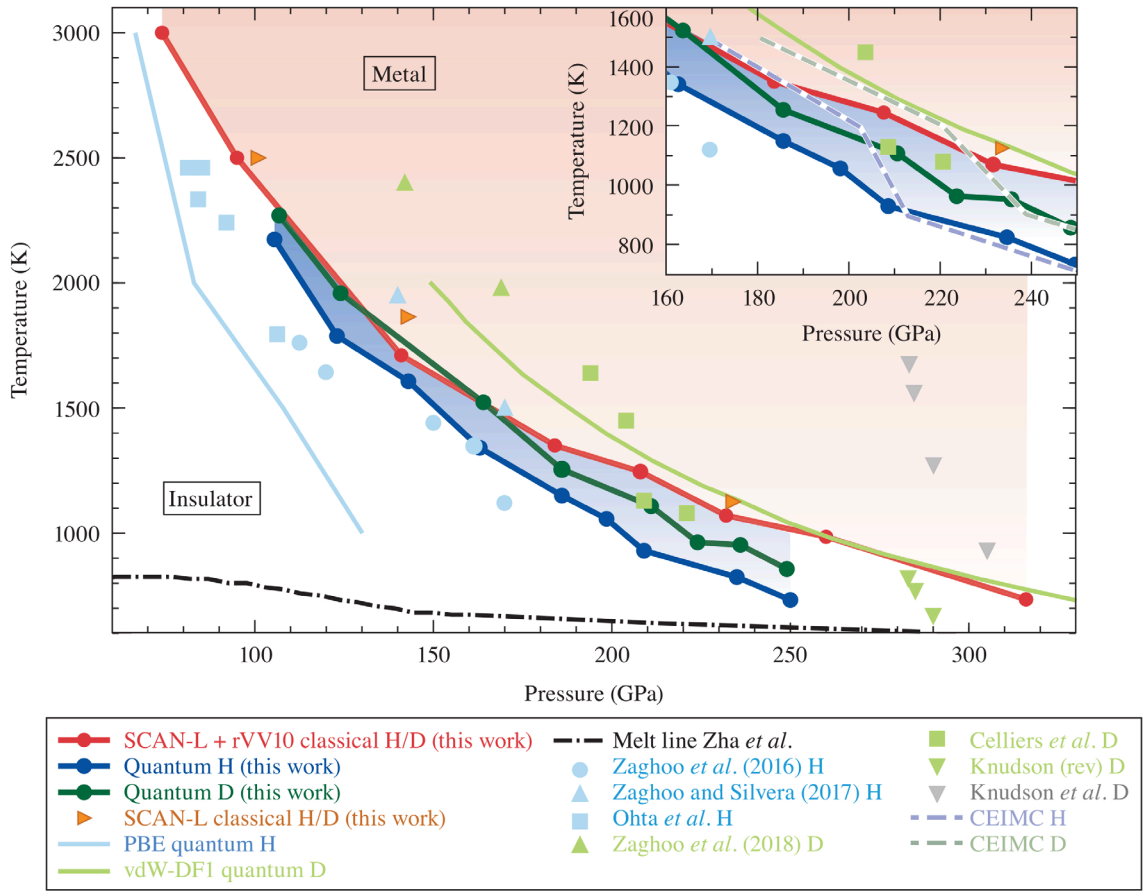
With SCAN-L/T-SCAN-L we have closed the decade-long discrepancy between experiments and DFT calculations in metallization of hydrogen/deuterium *

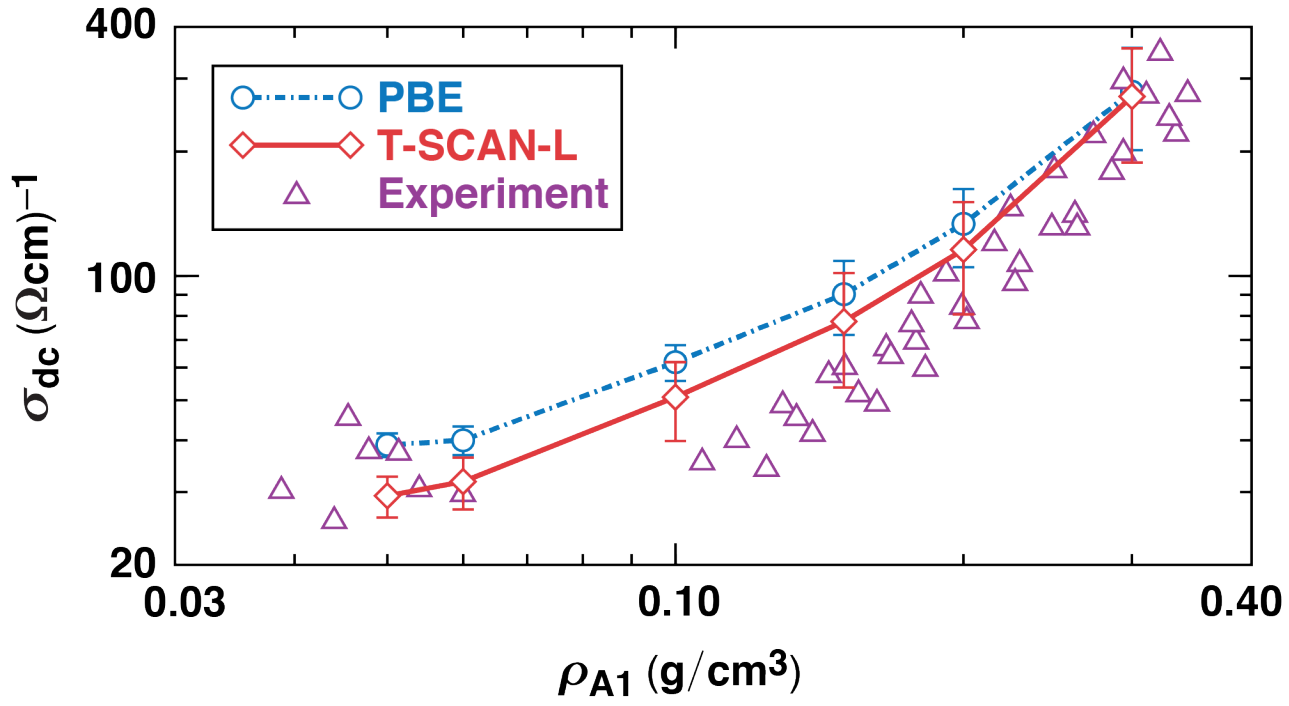


DFT-predicted insulator-to-metal transition boundary is now in good agreement with experimental measurements across a wide range of pressure and temperatures

* J. Hinz, V. V. Karasiev, S. X. Hu, M. Zaghoo, D. Mejia-Rodriguez, S. B. Trickey, L. Calderin, Phys. Rev. Res. 2, 032065(R) (2020); D. I. Mihaylov, V. V. Karasiev, S. X. Hu, J. R. Rygg, V. N. Goncharov, G. W. Collins, Phys. Rev. B 104, 144104 (2021).

Application of T-SCAN-L to dc conductivity of warm-dense Al shows better agreement w/r to experimental measurements

- The new T-SCAN-L functional improves the accuracy of transport property predictions as compared to standard ground-state functionals



TC15738

← Al dc conductivity as a function of density along T = 10,000 K isotherm

* A. W. DeSilva and J. D. Katsouros, Phys. Rev. E 57, 5945 (1998).

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V. V. Karasiev, D. I. Mihaylov, and S. X. Hu, "Meta-GGA Exchange-Correlation Free Energy Density Functional to Achieve Unprecedented Accuracy for Warm-Dense-Matter Simulations," submitted to Physical Review Letters.); 78, 1396(E) (1997).