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

- 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

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**Abbreviations**

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

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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);
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Dense plasmas and WDM is a scientifically rich area of high-energy-density physics (HEDP) where several distinct physical regimes meet. The WDM challenge:
- well-developed models used on WDM face severe problems
- Quantum treatment is required

\[ \Gamma \equiv \frac{\langle \text{potential energy} \rangle}{\langle \text{kinetic energy} \rangle} \sim 1 \]
\[ \Theta_F \equiv \frac{kT}{E_F} \sim 1 \]

ICF: inertial confinement fusion

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.

- Classical plasma approaches work only for weakly coupled nondegenerate systems ($\Gamma \ll 1$: low density, very high temperature).

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

ICF: inertial confinement fusion

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

\[ \Omega [n] = \mathcal{F}[n] + \int dr \left( v_{\text{xc}}(r) - \mu \right) n(r) \quad \text{Grand potential} \]

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

\[ \mathcal{F}_H[n] \quad \text{Hartree energy} \]

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

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

**Molecular dynamics**

\[ m_j \ddot{R}_j = -\vec{\nabla}_j V(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) \]

**Born–Oppenheimer energy surface:**

\[ V(\{\mathbf{R}\}) = \Omega(\{\mathbf{R}\}) + E_{\text{ion-ion}}(\{\mathbf{R}\}) \]

**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:

\[ \begin{align*}
-\frac{1}{2} \nabla^2 + v_H(\mathbf{r}; \{\mathbf{R}\}) + v_{\text{xc}}(\mathbf{r}; \{\mathbf{R}\}) + v_{\text{ext}}(\mathbf{r}; \{\mathbf{R}\}) \varphi_j(\mathbf{r}; \{\mathbf{R}\}) = \varepsilon_j \varphi_j(\mathbf{r}; \{\mathbf{R}\}) \\
n(\mathbf{r}; \{\mathbf{R}\}) = \sum_j f(\varepsilon_j; \beta) |\varphi_j(\mathbf{r}; \{\mathbf{R}\})|^2 \\
v_{\text{xc}}[\beta, T] = \frac{\delta F_{\text{xc}}[n, T]}{\delta n} \\
\beta = \frac{1}{k_B T}
\end{align*} \]
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 GGA (KDT16): Karasiev et al., PRL 120, 076401 (2018)

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

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.

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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.

- 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 $T$

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.

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

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

$$f_s(r_s, T) - \text{non-interacting free-energy per particle;}$$

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

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:**

$$F_{x}^{\text{GGA}}[n,T] = \int n f_{x}^{\text{LDA}}(n,T) F_{x}(s_{2x}(T)) \, dr$$

$$F_{x}(s_{2x}) = 1 + \frac{\nu_{x} s_{2x}}{1 + \alpha |s_{2x}|}$$

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

$$f_{x}^{\text{LDA}}(n,T) = \epsilon_{x}^{\text{LDA}}(n) \tilde{A}_{x}(t) \quad ; \quad t = T / T_{f}$$

**Correlation:**

$$F_{c}^{\text{GGA}}[n,T] = \int n f_{c}^{\text{GGA}}(n,\nabla n, T) \, dr$$

GGA correlation energy per particle:

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

$$q_{c}(n,\nabla n, T) \equiv q(n,\nabla n) \sqrt{B_{c}(n,t)}$$

**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

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Next meta-GGA rung depends on $n$, $\nabla n$ and $\Delta n$

- Strongly constrained and appropriately normed (SCAN)$^\dagger$ and de-orbitalized SCAN-L$^\ddagger$ ground-state XC provide the best overall performance at $T=0K$.

- Original ground-state SCAN XC depends on electron density ($n$), density gradient ($\nabla n$), and the chemical region detector $\alpha$, which depends on Kohn–Sham orbitals via kinetic energy density ($t_s$):

$$
\varepsilon_{\text{SCAN}}(n, \nabla n, \alpha) \quad \alpha = \frac{t_s - t_W}{t_{\text{unif}}} \quad t_s = \frac{1}{2} \sum |\nabla \phi_i|^2 \quad t_W = \frac{\nabla n}{n} \quad t_{\text{unif}} = c_0 n^\frac{5}{3}
$$

- $\alpha$ recognizes covalent ($\alpha = 0$), 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, $t_{s}^{\text{OF}}$:

$$
t_s(\{\phi_i\}) \rightarrow t_{s}^{\text{OF}}(n, \nabla n, \Delta n) \quad \varepsilon_{\text{SCAN-L}}^{\text{SC-}}(n, \nabla n, \Delta n)
$$

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

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

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:

\[ \Delta F^{\text{GGA}}_{\text{xc}}[n, T] = F^{\text{KDT16}}_{\text{xc}}[n, T] - E^{\text{PBE}}_{\text{xc}}[n]; \lim_{T \to 0} \Delta F^{\text{GGA}}_{\text{xc}}[n, T] \approx 0 \]

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

\[ F^{\text{metaGGA}}_{\text{xc}}[n, T] = E^{\text{metaGGA}}_{\text{xc}}[n] + \Delta F^{\text{GGA}}_{\text{xc}}[n, T]; \lim_{T \to 0} F^{\text{metaGGA}}_{\text{xc}}[n, T] \approx E^{\text{metaGGA}}_{\text{xc}}[n] \]

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, \( \rho = 0.6 \text{ g/cm}^3 \)
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

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

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

![Graphs showing relative difference between total pressure from DFT simulations with SCAN-L, KDT16, T-SCAN-L, and PBE XC for different densities and temperatures.](image)

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

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

\[ \sigma_{dc} (\Omega \text{cm})^{-1} \]

\[ \rho_{A1} (\text{g/cm}^3) \]

\[ \text{Al dc conductivity as a function of density along } T = 10,000 \text{ K isotherm} \]

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