Development of Free Energy Density Functional Theory: Predictive Power of First Principles Approximations for Warm Dense Matter

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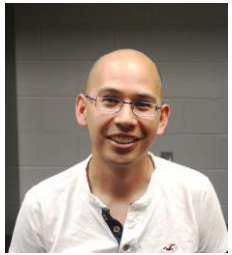

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Publications, preprints, & software at http://www.qtp.ufl.edu/ofdft

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Motivation

Physical problem: warm dense matter (WDM)

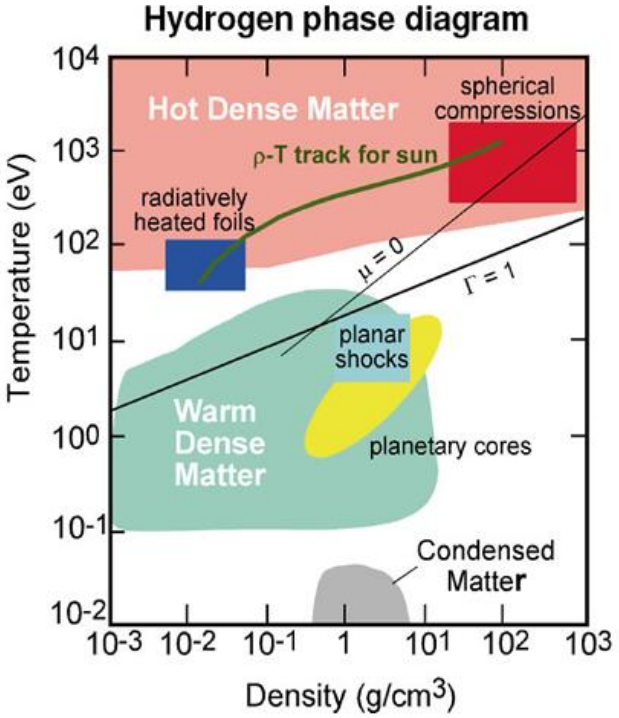
Challenging region between normal condensed matter and plasmas:

$$\Gamma := Q^2/(r_s k_B \mathrm{T}) \qquad \Theta := k_B \mathrm{T}/\epsilon_F$$

both parameters ≈ 1

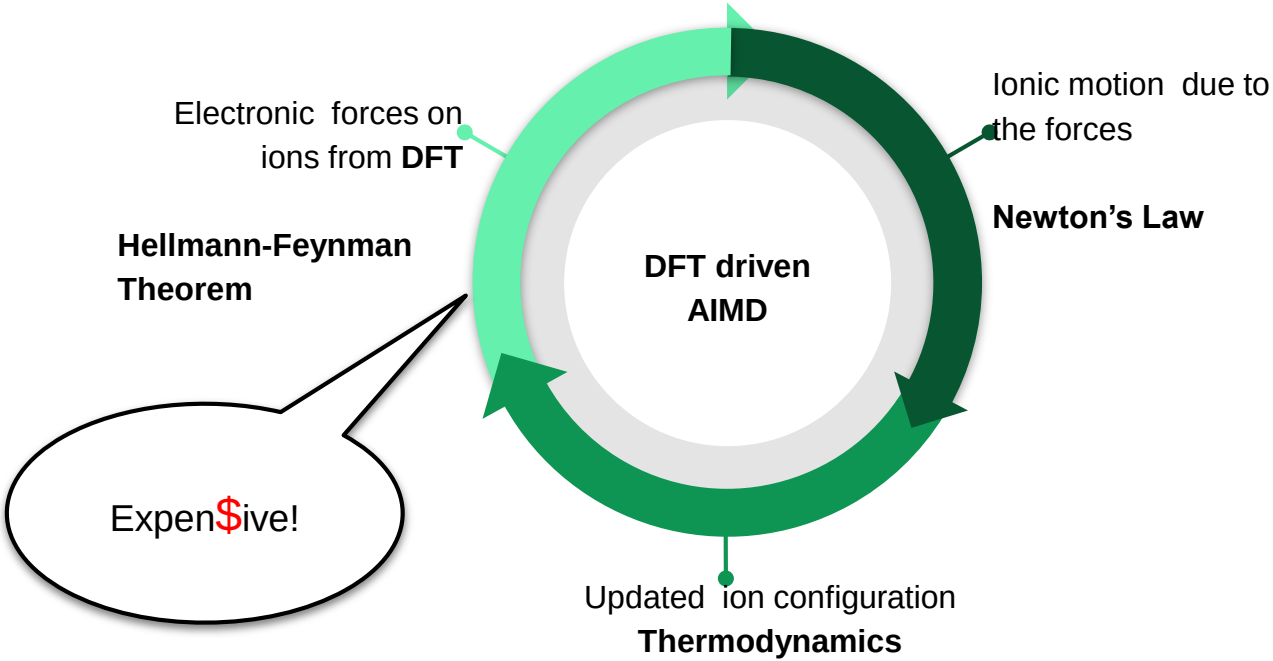
Mainly use non-perturbative method such as DFT for the electrons;

Fast, accurate forces are required in the ab initio molecular dynamics (AIMD).

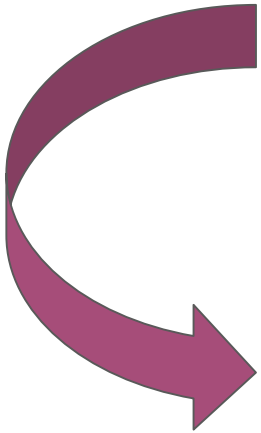


Schematic temperature-density diagram for Hydrogen (from R. Lee, LLNL)

Ab initio Molecular Dynamics(AIMD)



Finite-T DFT



Kohn-Sham DFT

Orbital-free DFT

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int dr^3\, v_{ext}(\mathbf{r}) n(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int dr'^3 \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})\right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n = \sum_i^{N_e} f_i |\varphi_i|^2, \quad v_{\text{xc}}[n] = \frac{\delta E_{\text{xc}}}{\delta n}$$

Number of thermally occupied bands is enormous

$$\frac{\delta E[n]}{\delta n} = \mu, \quad T_{\text{s}} = T_{\text{s}}[n]$$

Kinetic Energy Density Functional
KEDF

Not $T_s[\{\varphi_i\}]$

Progress Summary

We've made multiple contributions to **predictive accuracy** and **caculational speed**!

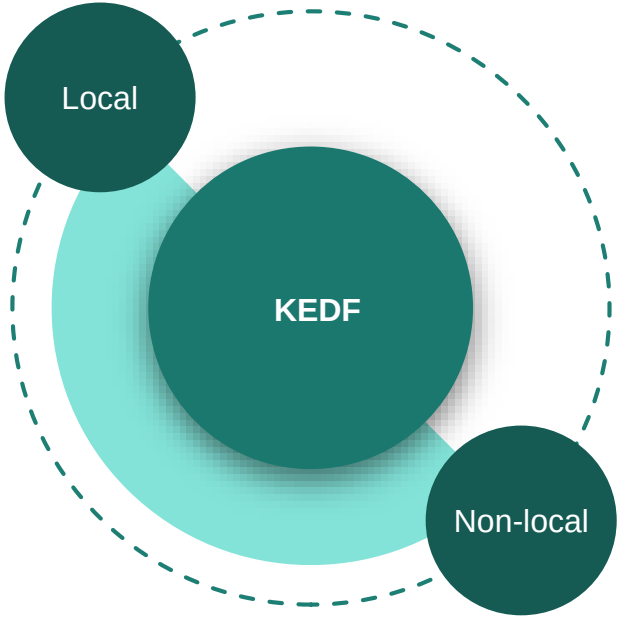
- Development of exchange-correlation (XC) free energy functionals
  Phys. Rev. Lett. **120**, 076401 (2018)
- Analysis of the theoretical underpinning of the Kubo-Greenwood approximation
  Comput. Phys. Commun. **221**, 118 (2017)
  Contrib. Plasma Phys. **58**, 150-154 (2018)
  Phys. Rev. E **97**, 012149 (2018)
  Phys. Rev. E, **98**, 033203 (2018)
- De-orbitalization of meta-GGA XC functionals for orbital-free calculations
  Phys. Rev. A **96**, 052512 (2017)
  Phys. Rev. B **98**, 115161 (2018)
- Pseudo-density adapted non-interacting free energy density functionals
  Phys. Rev. B **98**, 041111(R) (2018)

KEDF

$$T_s[n] = \int \mathrm{d}\mathbf{r}\, t_s[n(\mathbf{r}), \nabla n, \ldots]$$

One-point functionals

- Thomas-Fermi, von Weizsäcker
- GGA: LC94, TW02, E00, APBEK, VT84F
- meta-GGA: PC07, Pauli-Gaussian 2018
- ...



Two-point functionals

- Wang-Teter 92
- Wang-Govind-Carter 98, 99
- Huang-Carter 10
- Sjostrom-Daligault 14
- ...

$$T_{NL}[n] = c_{\mathrm{TF}} \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, n^{\alpha}(\mathbf{r}) K[n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'] n^{\beta}(\mathbf{r}')$$

Generalized Gradient Approximation (GGA) for $T_S[n]$

$$T_s^{\mathrm{GGA}}[n] = \int \mathrm{d}\mathbf{r}\, t_{\mathrm{TF}}(\mathbf{r}) F_t(s(\mathbf{r})) \qquad t_{\mathrm{TF}}(\mathbf{r}) := c_{\mathrm{TF}} n^{5/3}(\mathbf{r}) \qquad s := \frac{|\nabla n|}{2nk_f} \equiv \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n|}{n^{4/3}}$$

Thomas-Fermi $F_t(s) = 1$ and von Weizsäcker $F_t(s) = 5s^2/3$;

★ Uniform scaling for T_S is automatically satisfied.

Previously, the most successful GGA was VT84F (Phys. Rev. B **88**, 161108(R) (2013)), constrained according to densities obeying Kato cusp condition.

$$F_\tau^{\mathrm{VT84F}}(s) = 1 - \frac{\mu s^2 e^{-\alpha s^2}}{1+\mu s^2} + (1 - e^{-\alpha s^{m/2}})(s^{-n/2} - 1) + \frac{5s^2}{3}$$

$$m = 8, n = 4. \ \alpha = 1.2965 \ \mu = 2.778$$

Constraints

- Pseudo potentials are used ubiquitously in AIMD, so an approximate KEDF must be adapted accordingly;
- Lieb-conjectured bound: $T_s \leq T_{\mathrm{TF}} + T_{\mathrm{W}}$;
- Exact constraints from Pauli decomposition:
  (see Levy-Ou-yang, Phys. Rev. A 38, 625 (1988)).

$$T_s[n] = T_{\mathrm{W}}[n] + T_\theta[n]\,, \quad v_\theta(\mathbf{r}) := \frac{\delta T_\theta}{\delta n(r)}$$

$$t_s^{orb} := \frac{1}{2}\sum_i^{N_e} |\nabla \varphi_i|^2\,, \quad t_\theta := t_s^{orb} - t_{\mathrm{W}},$$

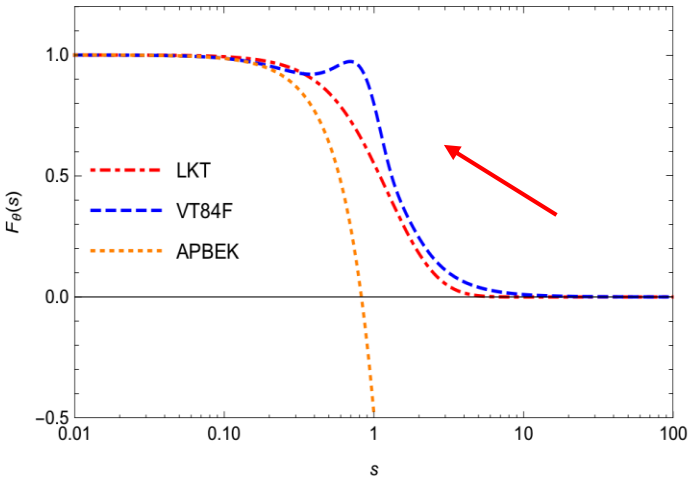
Non-universality of KEDF is necessary.

$$T_\theta[n] \geq 0;$$

$$v_\theta(\mathbf{r}) \geq \frac{t_\theta(\mathbf{r})}{n(\mathbf{r})} \geq 0, \quad \forall \mathbf{r}.$$

New Functional LKT

$$F_t^{\mathrm{LKT}}(s) = \frac{1}{\cosh(a\,s)} + \frac{5}{3}s^2$$



1. A set of Kohn-Sham atomic pseudo densities from H to Ne is used.

1. Post-SCF calculations of Pauli potential v_θ. Vary the value of parameter a, and check if $v_\theta > 0$. This requires parameter

   $a < 1.4$,

   which ensures all atoms have $v_\theta > 0$.

1. We performed some tests beyond the training set at both SCF and post-SCF levels. Bulk derived local pseudopotentials(BLPS) are used for the tests.

a=1.3

Performance of LKT at T=0 K

Two-point functionals: WGC, HC, KGAP

$$T_{NL}[n] = c_{\mathrm{TF}} \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, n^{\alpha}(\mathbf{r}) K[n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'] n^{\beta}(\mathbf{r}')$$

LKT takes **less iterations** to converge and each iteration takes about ⅕ CPU time of HC.

TABLE I. KEDF performance on solid metals and semiconductors: MARE of equilibrium volumes V_0, energies E_0, and bulk moduli B_0, as percentages. See text for notation.

	Metals			Semiconductors		
KEDF	V_0	E_0	B_0	V_0	E_0	B_0
WGC	0.7	0.0	2.7			
HC	5.5	0.6	12.3	1.5	0.5	4.9
KGAP[a]	4.0		5.1	3.0		16.2
VT84F	6.0	0.1	11.6	10.5	3.6	56.4
SOF-CFD[a]	5.2	0.6	8.5	3.4	0.9	10.0
LKT	4.0	0.2	7.7	2.1	2.8	4.3

[a]Note: only metals with cubic symmetry were included and PBE XC was used.

See details in Phys. Rev. B **98**, 041111(R) (2018)

Thomas-Fermi free-energy functional

$$\mathcal{F}_s^{\mathrm{UEG}}(n,T) = \Omega_s^{\mathrm{UEG}}(n) - \mu\left(\frac{\partial\Omega_s^{\mathrm{UEG}}(n)}{\partial\mu}\right)_{T,V}$$

$$= V\frac{\sqrt{2}}{\pi^2\beta^{5/2}}\left[-\frac{2}{3}I_{3/2}(\beta\mu) + \beta\mu I_{1/2}(\beta\mu)\right]$$

$$t = T/T_F = \frac{2}{\beta[3\pi^2 n]^{2/3}}$$

$$\tau_0^{\mathrm{TF}}(n) = \frac{3}{10}(3\pi^2)^{2/3}n^{5/3} = \frac{2}{5}\frac{\sqrt{2}}{\pi^2\beta^{5/2}t^{5/2}}$$

$$f_s^{\mathrm{TF}}(n,T) = \tau_0^{\mathrm{TF}}(n)\kappa(t)$$

$$\kappa(t) = \frac{5}{2}t^{5/2}\left[-\frac{2}{3}I_{3/2}(\beta\mu) + \beta\mu I_{1/2}(\beta\mu)\right]$$

$$\mathcal{F}_s^{\mathrm{TF}}[n] = \int f_s^{\mathrm{TF}}(n(\mathbf{r}),T)d\mathbf{r}$$

See details in Phys. Rev. B **86**, 115101 (2012)

GGA free-energy functional

$$\mathcal{F}_{\rm s}^{\rm ftGGA}[n,T] = \int \tau_0^{\rm TF} \left[\xi(t) F_\tau(s_\tau) - \zeta(t) F_\sigma(s_\sigma)\right] d\mathbf{r}$$

kinetic entropic

$$\xi(t) = \kappa(t) - t\kappa'(t)\,,$$
$$\zeta(t) = -t\kappa'(t)\,.$$

$$h(t) = -\frac{1}{24}\frac{I_{1/2}(\beta\mu) I_{-3/2}(\beta\mu)}{I^2_{-1/2}(\beta\mu)}$$

$$s_\tau(n,\nabla n,T) = s(n,\nabla n)\sqrt{\frac{\tilde{h}(t) - t\tilde{h}'(t)}{\xi(t)}}$$

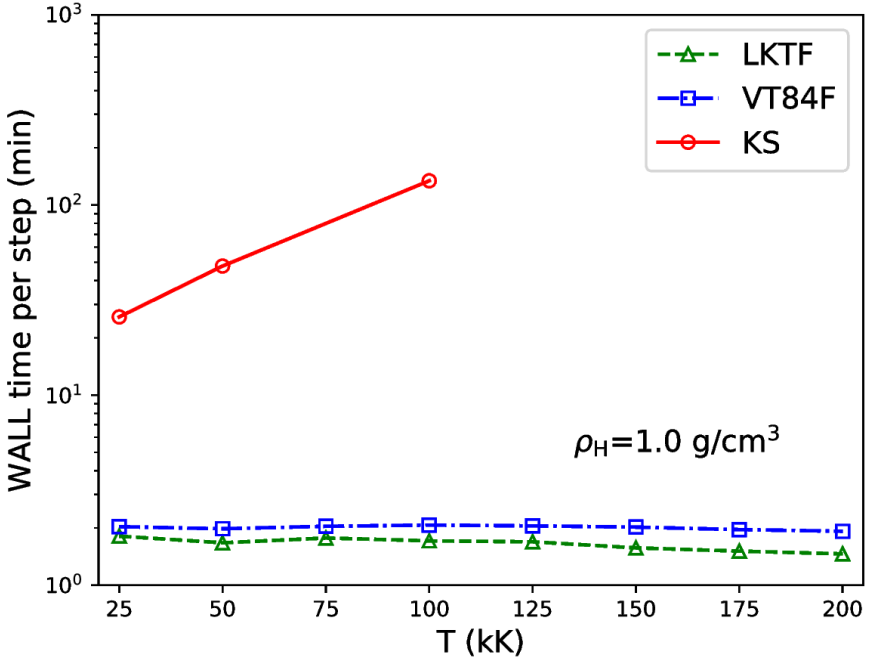
$$s_\sigma(n,\nabla n,T) = s(n,\nabla n)\sqrt{\frac{t\tilde{h}'(t)}{\zeta(t)}}$$

$$F_\tau^{\rm SGA}(s_\tau) = \left(1 + \tfrac{5}{27}s_\tau^2\right)$$
$$F_\sigma^{\rm SGA}(s_\sigma) = \left(1 - \tfrac{5}{27}s_\sigma^2\right)$$

$$F_\sigma(x) = 2 - F_\tau(x)$$

See details in Phys. Rev. B **86**, 115101 (2012)

Computational Cost



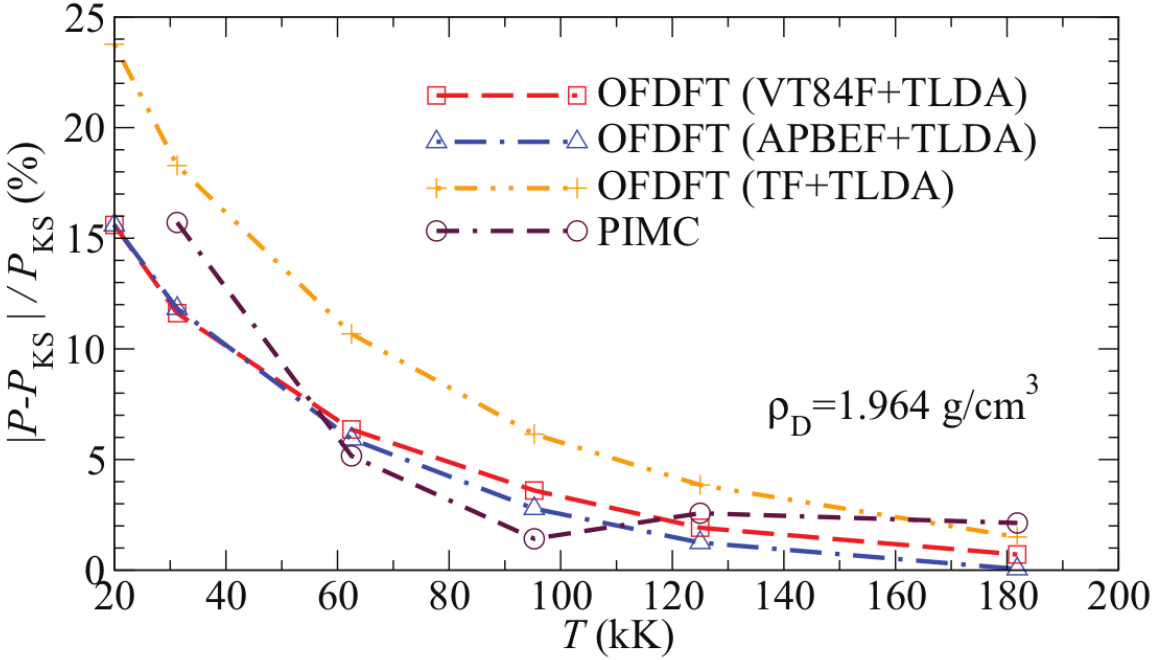
The AIMD simulation was performed with PROFESS@QuantumEspresso for both Kohn-Sham and orbital-free DFT on the equal footing.

KDT16 free energy XC functional

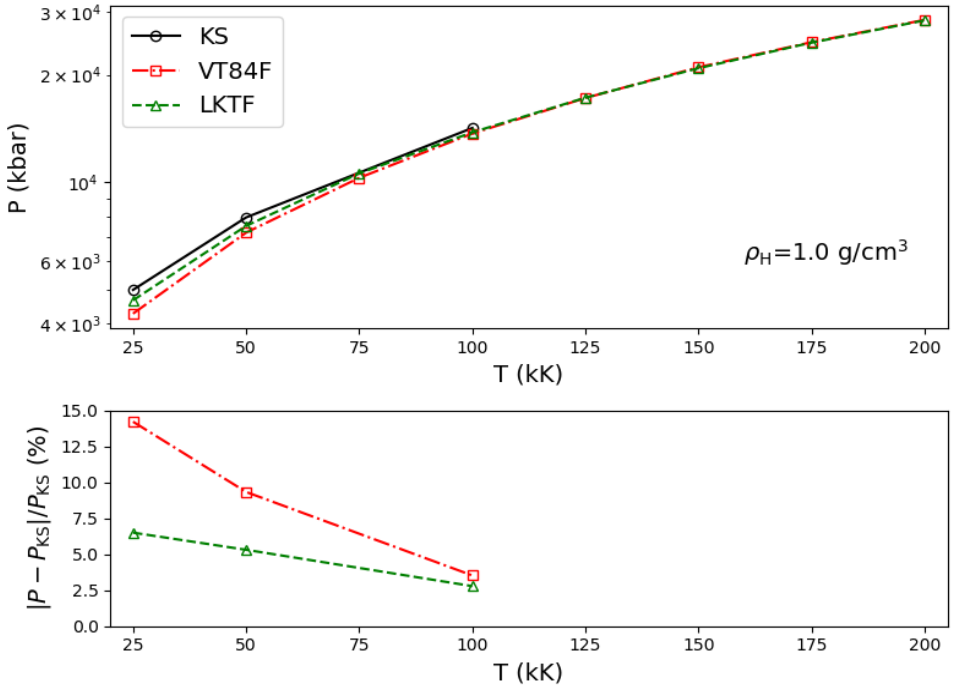
Andersen thermostat, ρ=1.0 g/cm^3

Hard local pseudo-potential for H with core radius 0.25 au.

ft Thomas-Fermi



LKTF for H at fixed bulk density

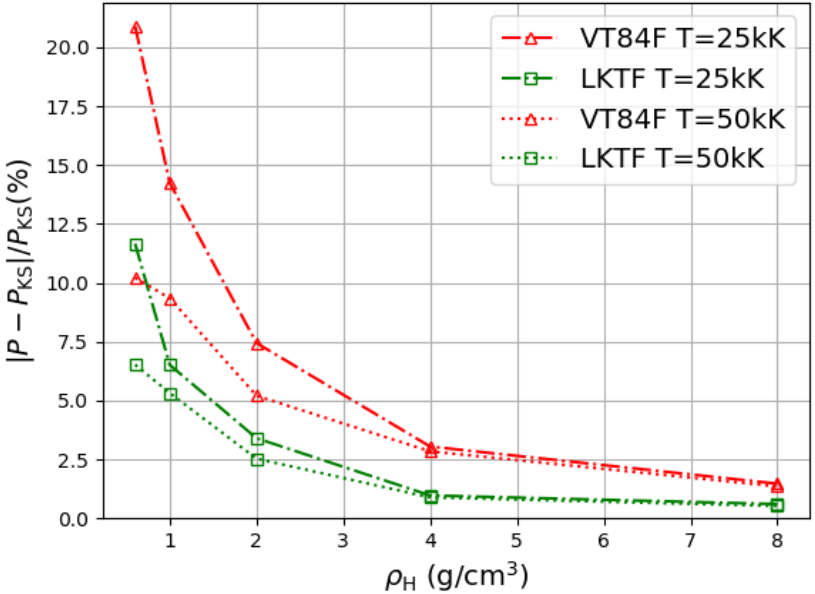


Kohn-Sham

VT84F

LKTF

LKTF for H at various densities



T=25 kK dash-dot line

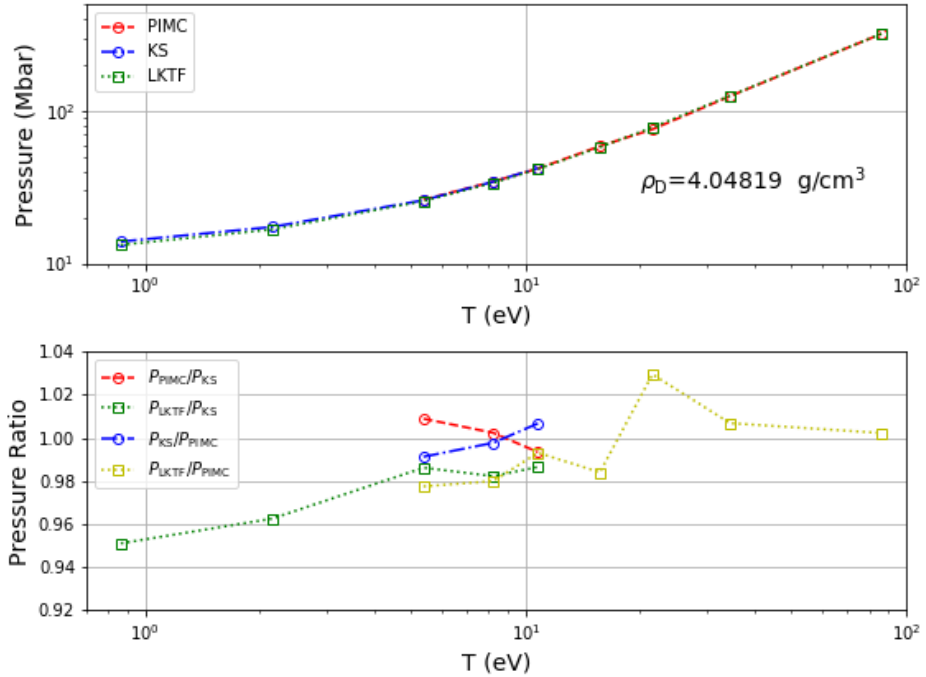
T=50 kK dotted line

△ VT84F

□ LKTF

ρ_H = 0.6, 1.0, 2.0, 4.0, 8.0 g/cm^3

Deuterium: r_S=1.10 bohr



PZ LDA XC functional

Andersen Thermostat,
density 4.04819 g/cm^3,
Same hard local pseudo-potential as H

Conclusions

- We have built a new **constraint-based** GGA non-interacting KEDF adapted to pseudo density, instead of Kato density;

- The free energy functional has reduced the pressure error by a factor of two. It enables fast determination of equation of state.

- More tests on other elements are underway.