Applying an Explicit Temperature-dependent Generalized Gradient Approximation to Warm Dense Matter: Thermal PBE

11th Workshop on High Pressure, Planetary and Plasma Physics (HP4)

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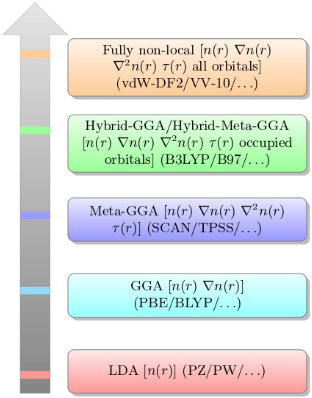
Exchange-Correlation functionals



- Local density approximation (LDA)

$$\boxed{E_{XC}^{LDA}[n(r)] = \int dr n(r) e_{XC}^{unif}[n(r)]}$$

- Generalized gradient approximation (GGA)

$$\boxed{E_{XC}^{GGA}[n(r)] = \int dr n(r) e_{XC}^{GGA}[n(r), \nabla n(r)]}$$

- Higher-rungs with increasing chemical accuracy but computationally expensive

Missing: thermal XC effects of explicitly including temperature which is important in the WDM regime

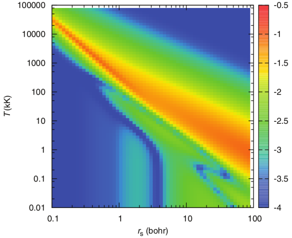
Thermal Exchange-Correlation functionals: LDA

- Replace the XC energy (per particle) $e_{XC}^{unif}(n)$ with the XC free energy $f_{XC}(r_s, \theta)$ for the UEG obtained from PIMC

$$\boxed{f_{XC}^{unif}(r_s,\theta) = -\frac{1}{r_s}\frac{a(\theta) + b(\theta) r_s^{1/2} + c(\theta) r_s}{1 + d(\theta) r_s^{1/2} + e(\theta) r_s}}$$

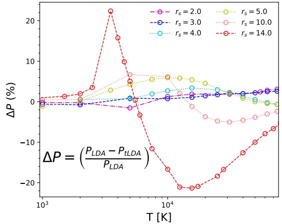
$$\boxed{r_s = \left(\frac{3}{4\pi n}\right)^{1/3}, \quad \theta = \frac{T}{T_F}}$$

$$\log_{10}\left[\frac{|f_{XC}(r_s,T) - e_{XC}(r_s,T)|}{|f_{XC}(r_s,T)| + |e_{XC}(r_s,T)|}\right]$$



Relative change in total pressure

[K. Ramakrishna *et al.* PRB 101, 195129 (2020)]

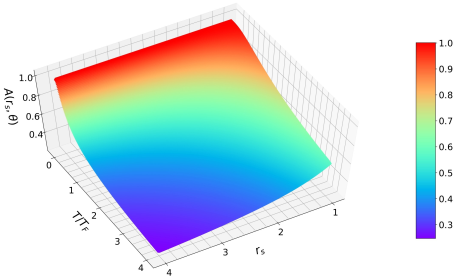


S. Groth *et al.* PRL 119, 135001 (2017); V. V. Karasiev *et al.* PRE 93, 063207 (2016)

Thermal Exchange-Correlation functionals: GGA

- The extension of XC free energy to finite temperature is through the enhancement factor

$$\boxed{A(r_s,\theta) = \frac{f_{XC}^{unif}(r_s,\theta)}{f_{XC}^{unif}(r_s)} \Rightarrow f_{XC}^{tPBE} = A(r_s,\theta) f_{XC}^{PBE}}$$



J. Kozlowski, D. Perchak, K. Burke, arXiv 2308.03319 (2023) ; V. V. Karasiev *et al.* PRL 120, 076401 (2018)

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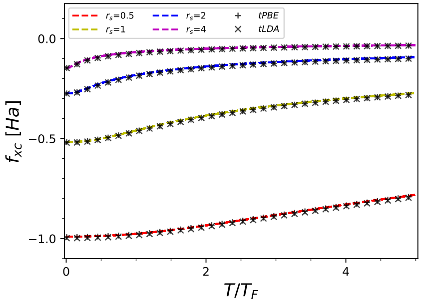
Testcase: Uniform electron gas

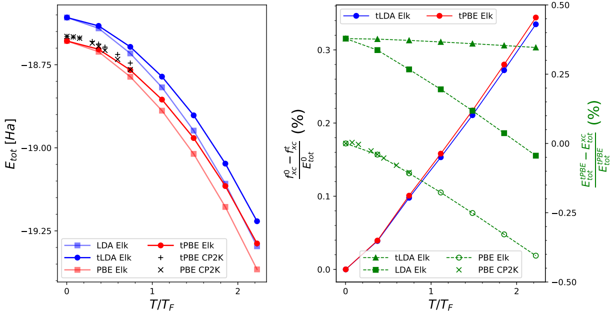
- Evaluate XC free energy (per particle) for uniform electron gas as a function of reduced temperature ($\theta = T/T_F$) at various densities (r_s) using FP-LAPW code (Elk).
- Comparison with Groth *et al.* parametrization.



S. Groth *et al.* PRL 119, 135001 (2017)

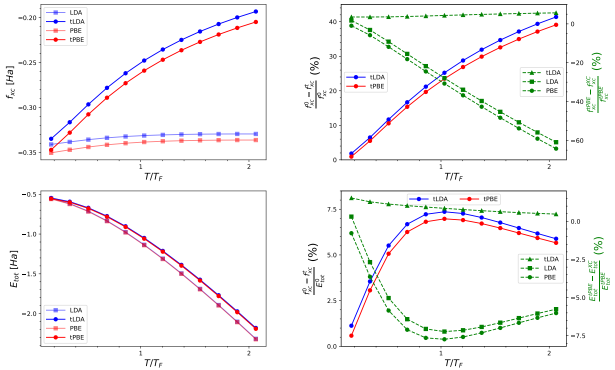
Testcase: Aluminum

- Static fcc lattice at ambient density. Ionic temperature (cold) and electronic temperature varied.
- Comparison using FP-LAPW (Elk) and basis-set (CP2K) results.



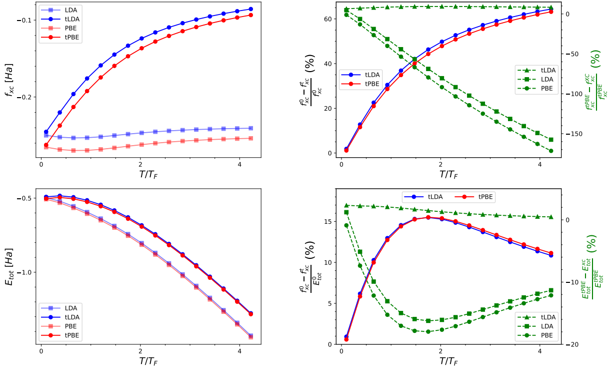
Warm dense hydrogen: $r_s = 2\ (0.337\ g/cm^3)$

- Comparison of the ground state (LDA/PBE) and thermal XC functionals (tLDA/tPBE).
- Considerable changes in total energy between ground state PBE and thermal PBE (up to 7.5 % around T/T_F).



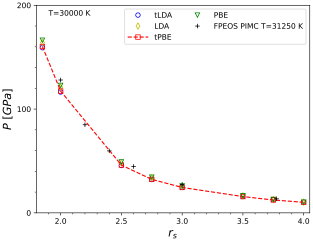
Warm dense (slightly) hydrogen: $r_s = 4\ (0.04\ g/cm^3)$

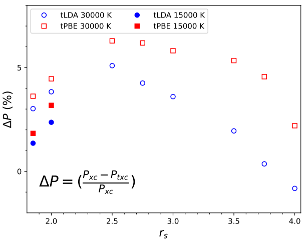
- Comparison of the ground state (LDA/PBE) and thermal XC functionals (tLDA/tPBE).
- Considerable changes in total energy between ground state PBE and thermal PBE (up to 18 % around $2T/T_F$).



Pressure effects

- Equation of state at a constant isotherm (T=30000 K).
- Deviations between ground state and thermal PBE at lower densities (larger r_s) even at relatively lower temperatures.





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Summary

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- A systematic implementation of a finite-temperature GGA XC functional into a plane wave code.
- The approach is straightforward and considers the temperature dependence explicitly demonstrated in the evaluation of static properties of warm dense hydrogen.
- Little additional cost compared to ground state PBE and importantly thermal XC effects are considered.
- Future work to compute properties relevant for experiments.

Thank You!!!

Collaborators

- Attila Cangi (CASUS/HZDR)
- Mani Lokamani (HZDR)
- Jan Vorberger (HZDR)
- Kieron Burke (UC Irvine)
- John Kozlowski (UC Irvine)

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