Finite-temperature Density Functionals – Developments and Computational Consequences

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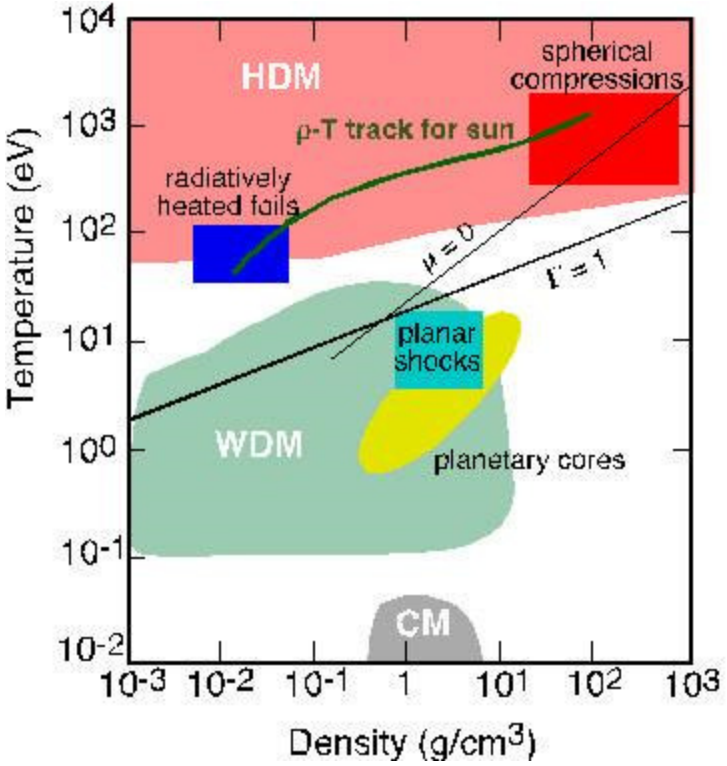
A motivating physical problem – Warm Dense Matter

Warm Dense Matter: 0.5 eV ≤ T ≤ 100 eV (≈ 1,000,000 K) –
HOT by standards of familiar condensed matter theory
Densities: from gas to ~ 100 × equilibrium density



Schematic diagram for hydrogen
(credit R.W. Lee presentation, LLNL)

$$\Gamma = e^2 / r_s k_B \mathrm{T} \approx 1 \qquad t = k_B \mathrm{T} / E_F \approx 1$$

- **Formation of molecules, clusters, and ions.**
- **High T & P for familiar quantum mechanical methods (quantum chem, cond. matt. Physics)**

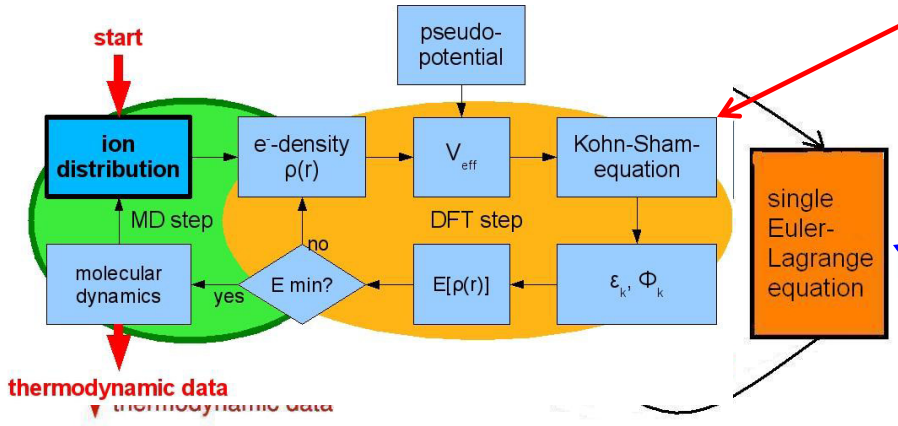
➔ **Almost prohibitively expensive**

- **But T is low for classical plasma physics methods**

➔ **QM is important.**

- **Happy but expensive medium: "ab initio molecular dynamics" (AIMD; also called "quantum MD")**

Motivating computational problem



KS calculational costs scale as cube of the number of occupied levels. Scaling worsens with increasing T (non-integer occupation).

Orbital-free Free Energy DFT – *No* explicit KS orbitals. Scales with system size.

Mermin, Hohenberg-Kohn DFT

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

$$F[n] = F_s[n] + F_H[n] + F_{xc}[n]$$

$F_s[n]$ = Non-interacting (KS) free energy, $F_H[n]$ = Hartree free energy

$F_{xc}[n]$ = eXchange-Correlation (XC) free energy

KS equation

Electrons Nuclei

$$\left\{-\tfrac{1}{2}\nabla_{r_1}^2 + v_H(\mathbf{r}_1;\{\mathbf{R}\}) + v_{xc}(\mathbf{r}_1;\{\mathbf{R}\}) + v_{ext}(\mathbf{r}_1;\{\mathbf{R}\})\right\}\varphi_j(\mathbf{r}_1;\{\mathbf{R}\}) = \varepsilon_j\,\varphi_j(\mathbf{r}_1;\{\mathbf{R}\})$$

$$n(\mathbf{r}_1;\{\mathbf{R}\}) = \sum_j f(\varepsilon_j;\beta)\left|\varphi_j(\mathbf{r}_1;\{\mathbf{R}\})\right|^2 \quad ; \quad v_{xc}[n] = \frac{\delta F_{xc}}{\delta n} \quad ; \quad \beta = 1/k_B T$$

Approaches to complexity, size, and extreme conditions

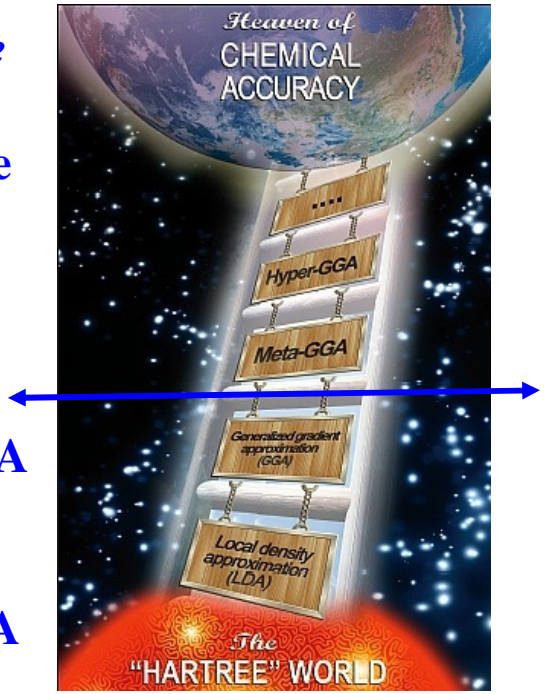
(0) Bring finite-T DFT up to date relative to much-more-developed T=0 K version.

(1) Push on orbital-free DFT for AIMD speed, despite conventional wisdom that OFDFT never has worked.

(2) Work on better functionals at the lower rungs of the Perdew-Schmidt Jacob's ladder of XC functionals *because orbital-independent functionals are faster.*
[Conventional wisdom – higher rung XC functionals are required.]

(3) Implement and distribute new functionals and capabilities

Remark: success for OFDFT, item (1), *requires* success with item (2)



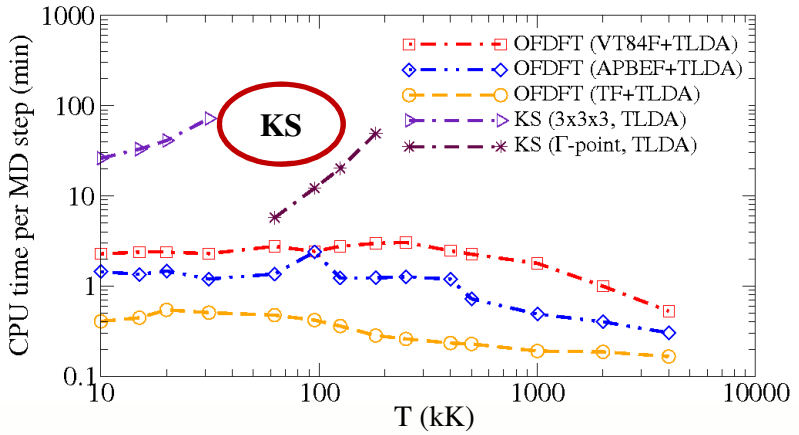
•GGA

•LDA

Credit: SCIDAC Review 17

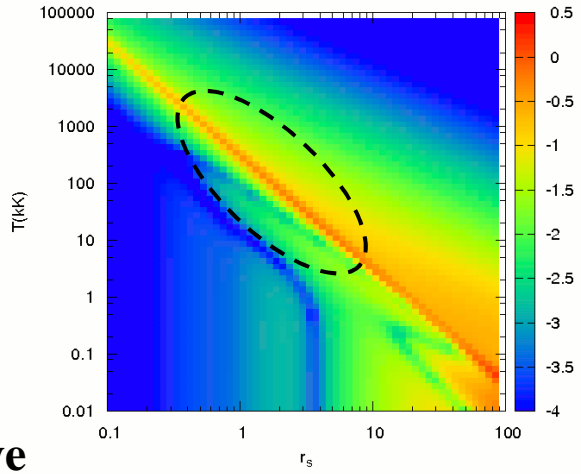
Challenges from T-dependence

1] Accurate orbital-free non-interacting free energy (KS KE & KS entropy). Why? Speed. OFDFT scales linearly with system size, independent of T.



2] XC free energy functional – needed in both conventional KS-AIMD & orbital-free AIMD. Why? Non-trivial T-dependence. At right (for HEG):

$$log_{10}\frac{\left|f_{xc}(r_s,\mathrm{T}) - \varepsilon_{xc}(r_s)\right|}{\left|f_s(r_s,\mathrm{T})\right|}$$



- DFT theorems provide no constructive routes to approximations.
- No mechanical recipe (e.g. pert. theory) for adding complexity (and, presumably, improvements).

Local spin density approximation (LSDA) $\square_{xc}[n]$

$$\mathrm{F}_{\mathrm{xc}}[n(T),T] \approx \int d\mathbf{r} n\left(\mathbf{r},T\right) f_{\mathrm{xc}}^{\ \mathrm{HEG}}\left(n\left(\mathbf{r},T\right),T\right)$$

- **Note: no gradient or higher derivative dependence.**
- **Determine $f_{xc}^{\ HEG}$ from fit to restricted path integral Monte Carlo (RPIMC) data [Brown et al., Phys. Rev. Lett. 110, 146405 (2013)]**
- **Fit must extrapolate smoothly to correct large-T, T=0, and small r_s limits.**
- **Fit must be augmented with T-dependent interpolation to intermediate spin polarization.**
- **Procedural issue: Four formally equivalent thermodynamic relationships between XC internal energy density ε_{xc} and XC free energy density f_{xc} are not computationally equivalent. Detailed study led to use of**

$$f_{\mathrm{xc}}(r_{\mathrm{s}},t) - t\frac{\partial f_{\mathrm{xc}}(r_{\mathrm{s}},t)}{\partial t}\Big|_{r_{\mathrm{s}}} = \varepsilon_{\mathrm{xc}}(r_{\mathrm{s}},t).$$

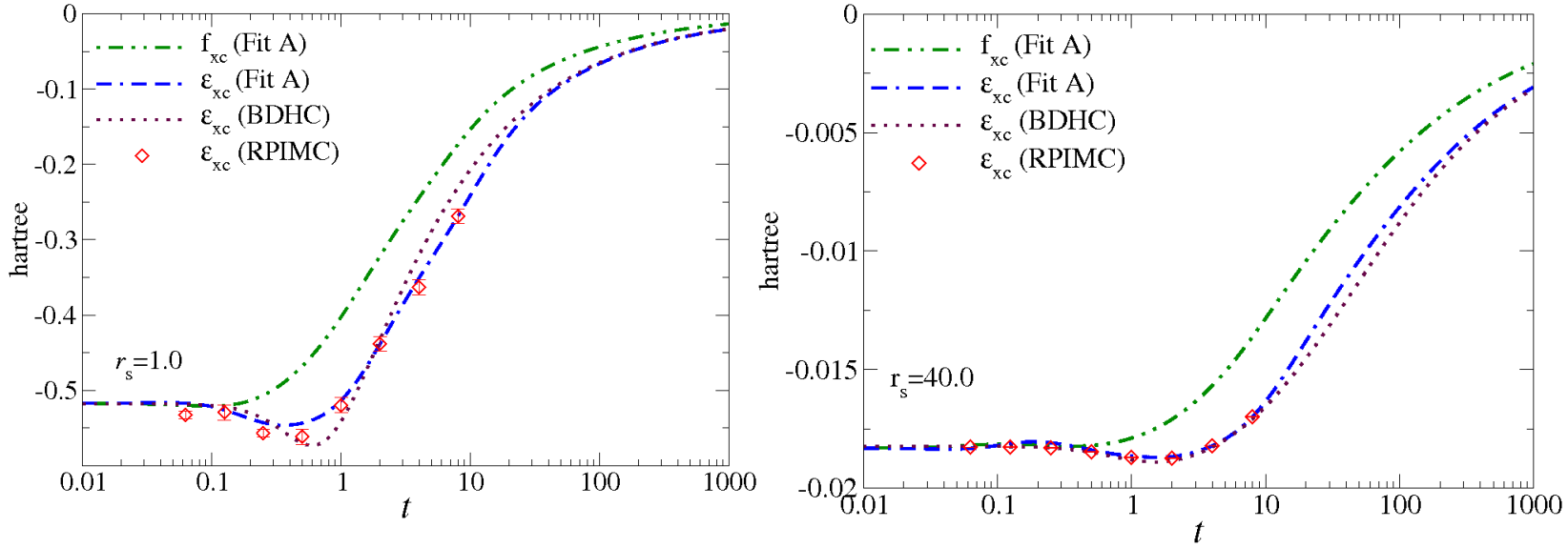
LSDA $\square_{xc}$ [n]

Fitted solution to thermodynamic differential relation

$$f_{\rm xc}^{\zeta}(r_{\rm s},t) = -\frac{1}{r_{\rm s}}\frac{\omega_\zeta a(t) + b_\zeta(t) r_{\rm s}^{1/2} + c_\zeta(t) r_{\rm s}}{1 + d_\zeta(t) r_{\rm s}^{1/2} + e_\zeta(t) r_{\rm s}}$$

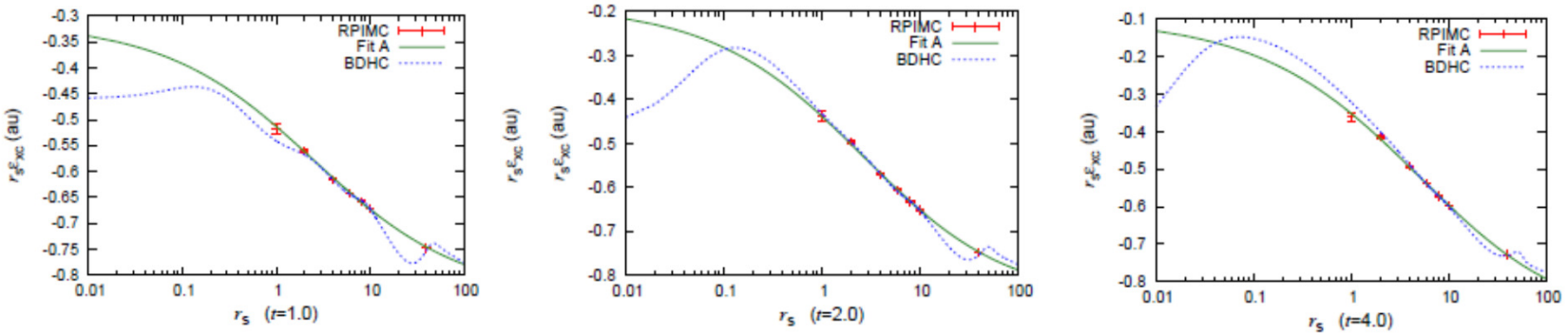
$$\zeta = \left(n_\uparrow - n_\downarrow\right)/n; \quad \omega_{\zeta=0} = 1; \quad \omega_{\zeta=1} = 2^{1/3}$$

***a(t), b(t), c(t), d(t), e(t)* are functions of $t=T/T_F$ with tabulated coefficients.**

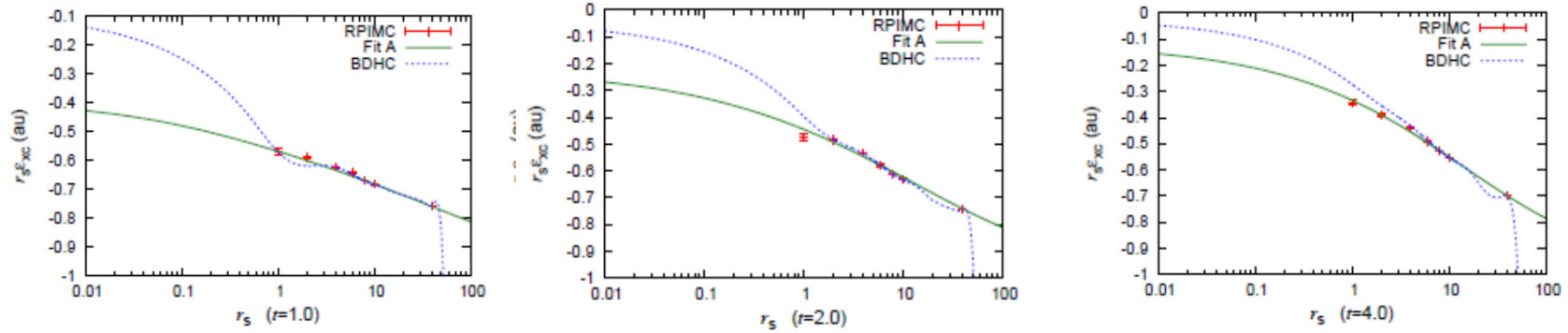


Comparison to RPIMC data (red dots) for ζ=0, r_s=1 (left) and 40 (right) for ε_{xc} and resulting f_{xc}.

LSDA $\varepsilon_{xc}[n]$ – smooth extrapolation to proper limits

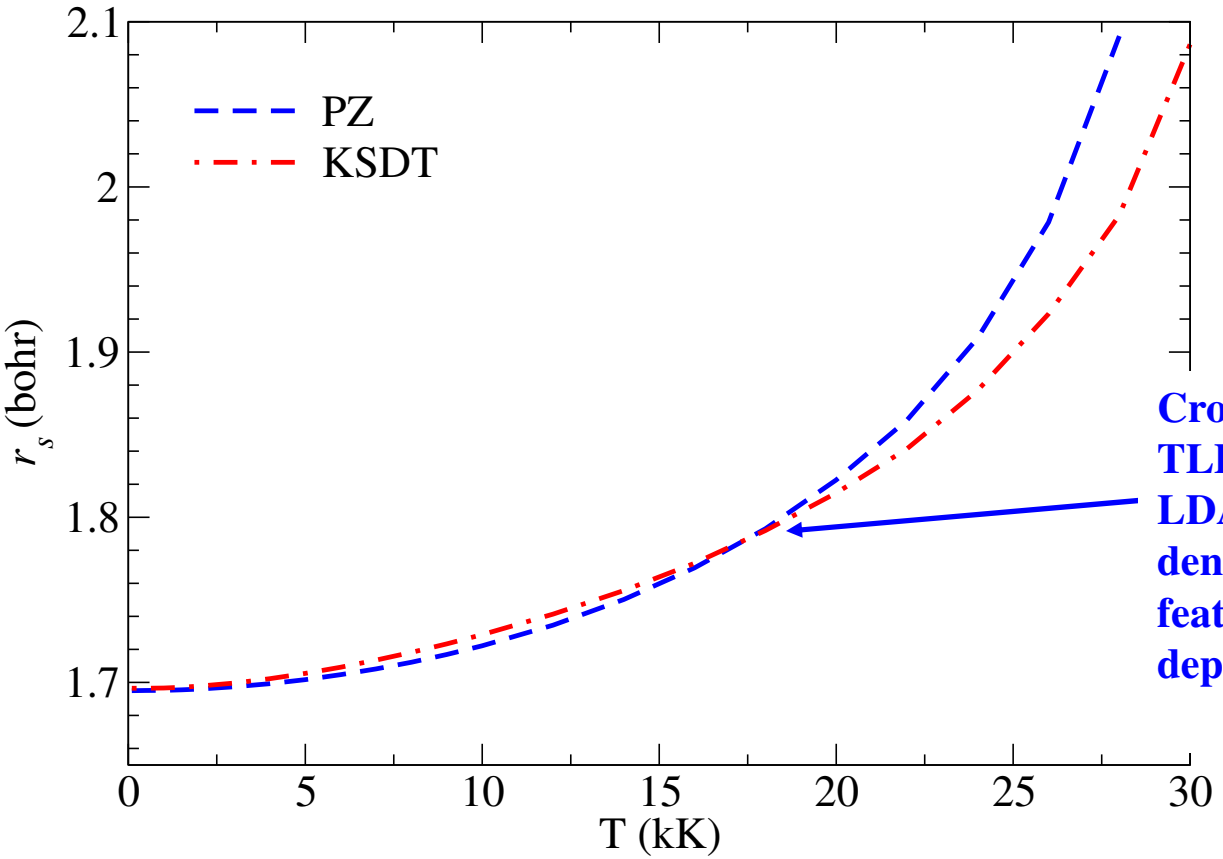


"Fit A" is Phys. Rev. Lett **Top: ς=0 ; bottom ς= 1**



Also fits rather well to subsequent configuration-PIMC data for $r_s \leq 1$ from Schoof, Groth, Vorberger, and Bonitz. See arXiv 1502.04616, Fig. 5.

Inhomogeneous Electron Gas (sc-Hydrogen) at finite-T:



Cross-over of TLDA & ordinary LDA (with T-dependent density) is a common feature of the T-dependence.

Equilibrium r_s for electron gas at temperature T in external field of H-nuclei fixed in simple-cubic positions (static, cold sc H ions with hot electrons).

Accurate orbital-free non-interacting free energy functional

Constraints from Pauli KE and Pauli potential. Start at T = 0 K.
An exact decomposition (at all T):

$$T_s[n] = T_W[n] + T_\theta[n], \quad T_\theta[n] \geq 0 \leftarrow$$ **Global positivity constraint**

$$E[n] = T_s[n] + E_{ee}[n] + E_{xc}[n] + E_{ne}[n]$$

$$T_W[n] := \frac{1}{8}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$T_s[n] = \int d\mathrm{r}\; t_S[n(\mathrm{r})] = \frac{1}{2}\sum f_i \int d\mathrm{r}\; |\nabla \varphi_i|^2$$

$$v_\theta(\mathrm{r}) = \delta T_\theta / \delta n \geq 0 \quad \forall\, \mathrm{r} \leftarrow$$ **Local (pointwise) positivity constraint**

$$T_s^{GGA}[n] = c_{TF}\int d\mathrm{r}\; n^{5/3}(\mathbf{r}) F_t\left(s(\mathbf{r})\right)$$

Generalized gradient approximation (GGA)

$$s(\mathbf{r}) := \frac{1}{2(3\pi^2)^{1/3}}\frac{|\nabla n|}{n^{4/3}}; \quad c_{TF} = \frac{3}{10}\left(3\pi^2\right)^{2/3}$$

M. Levy and H. Ou-Yang, Phys. Rev. B 38, 625 (1988); A. Holas and N.H. March, Phys. Rev. A 44, 5521 (1991); E.V. Ludeña, V.V. Karasiev, R. López-Boada, E. Valderama, and J. Maldonado, J. Comp. Chem. 20, 155 (1999) and references in these]

GGA Constraints for Non-empirical parameterization of T_s

1. Kato cusp condition gives density behavior near nucleus, charge *Z*,

$$n(\mathbf{r})\big|_{r\to 0} \propto e^{-2Z|r|}$$

For such a density, the GGA Pauli potential behaves as

$$v_\theta(\mathbf{r})\big|_{r\to 0} \equiv \left.\frac{\delta T_\theta}{\delta n}\right|_{r\to 0} = \frac{A}{r} + B + C\,r + \ldots$$

The constants *A*, *B*, *C* depend on detailed form of a specific T_θ approximation

Pauli potential positivity ⇒ GGA constraint: $A \geq 0$

2. Recover second-order gradient expansion (SGE) for *s<<1* :

$$F_t(s) = 1 + \left(5/27\right)s^2 + O(s^4)$$

3. Recover vW KE for *s* →∞ : $\lim_{s\to\infty} F_\theta(s) = 0$

4. Obey Lieb upper-bound: $T_s[n] \leq T_{TF}[n] + T_W[n]$

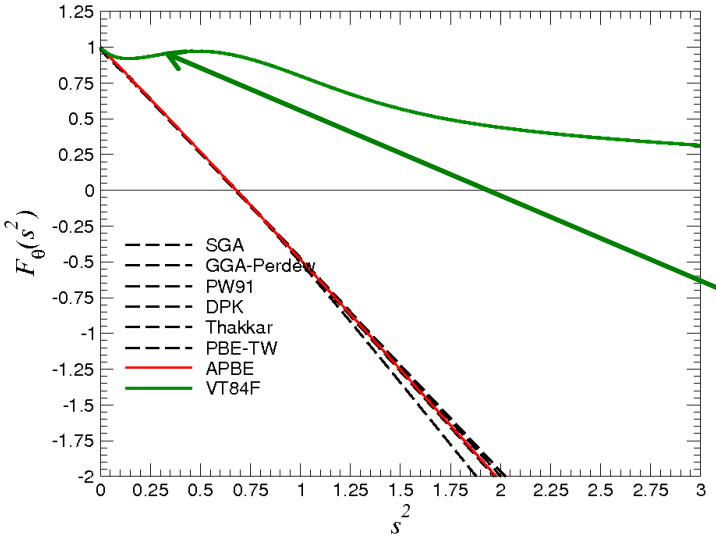
GGA for $\mathcal{T}_s$

"VT84F"

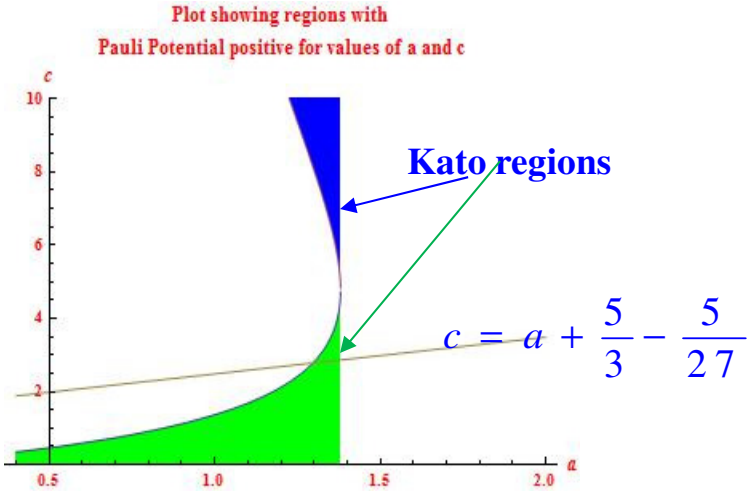
$$F_\theta[s(\mathbf{r})] = 1 - \frac{cs^2(\mathbf{r})\,e^{-as^2(\mathbf{r})}}{1+cs^2(\mathbf{r})} + (1-e^{-as^4(\mathbf{r})})\left(\frac{1}{s^2(\mathbf{r})} - 1\right)$$

Parameters from constraints, *not fitting*
See Phys. Rev. B 88, 161108R (2013)

$$c = 2.778; \quad a = 1.296518$$



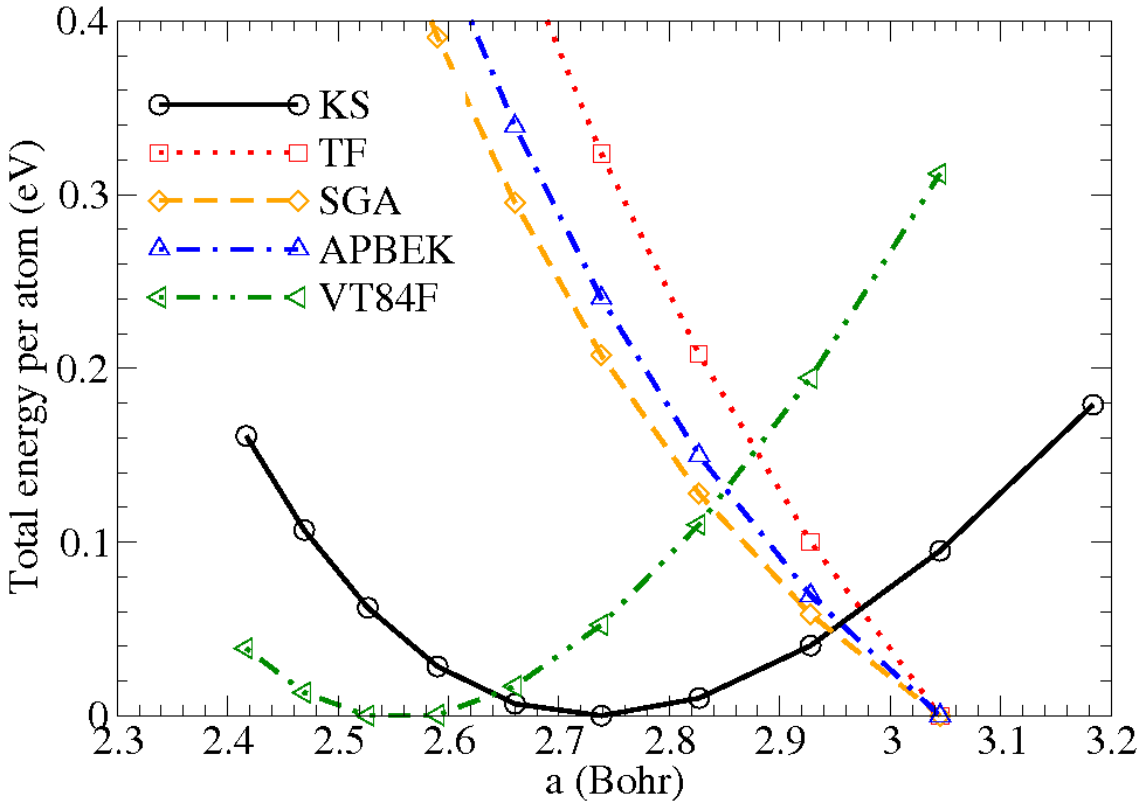
Above: Pauli part of enhancement factors.



Positive slope of VT84F for $s^2 > s^2(0) \approx 0.375$ guarantees $v_\theta > 0$ near nucleus; all others fail.

Non-empirical T_s GGA "VT84F"

VT84F gives binding. Other GGAs do not.
At right: Total E (relative to min.) vs. lattice constant, for simple-cubic H. "APBEK" is L. Constantin et al. non-empirical GGA.
[Phys. Rev. Lett. 106, 186406 (2011)].



Phys. Rev. B 88, 161108R (2013)

Extension to Finite-T GGA for $\mathcal{T}_s$[n] and S_s [n]

Finite-*T* GGA via generalized reduced density variables.

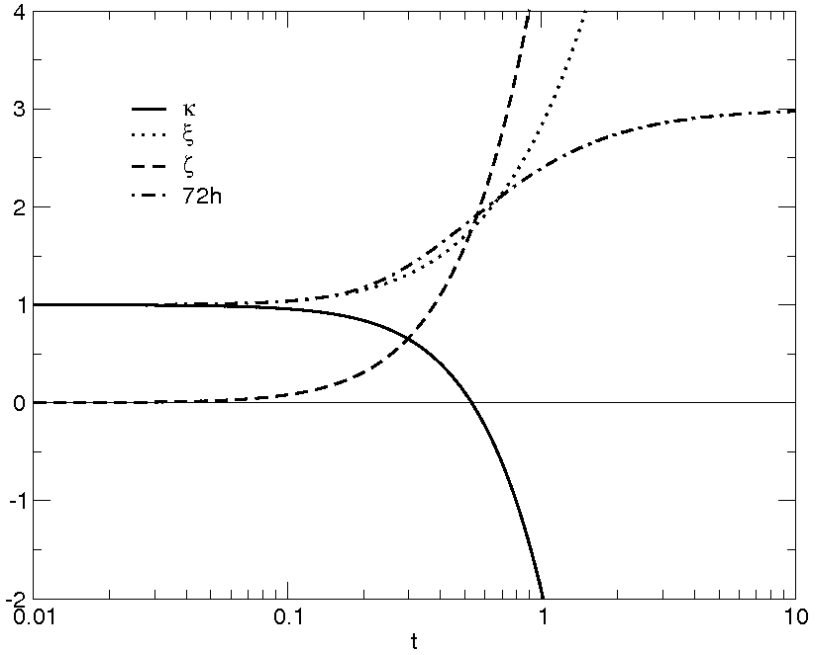
$$F_s^{ftGGA}[n] = \int d\mathbf{r}\left[\tau_0^{TF}(n)\xi(t)F_\tau(s_\tau)\right] - \int d\mathbf{r}\left[\tau_0^{TF}(n)\zeta(t)F_\sigma(s_\sigma)\right]$$

$$s_\tau(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{\tilde{h}(t) - t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\xi(t)}}$$

$$s_\sigma(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\zeta(t)}}$$

$$t = T/T_F$$

Form of T-dependent reduced density derivative variables motivated by 2nd order gradient expansion.



$\tilde{h}$ **, ζ, ξ are combinations of Fermi-Dirac integrals.**

$\tilde{h}$ **from Perrot's (1979) analytic fit;** Beware one obviously wrong coefficient (exponent) in that fit.

Phys. Rev. B 86, 115101 (2012)

Non-Empirical finite-T GGA for $\mathcal{T}_s$[n] and S_s[n]

Express finite-T KE with non-empirical VT84F written with the finite-T reduced density variable for KE. Get entropy functional from an approximate thermodynamic symmetry.

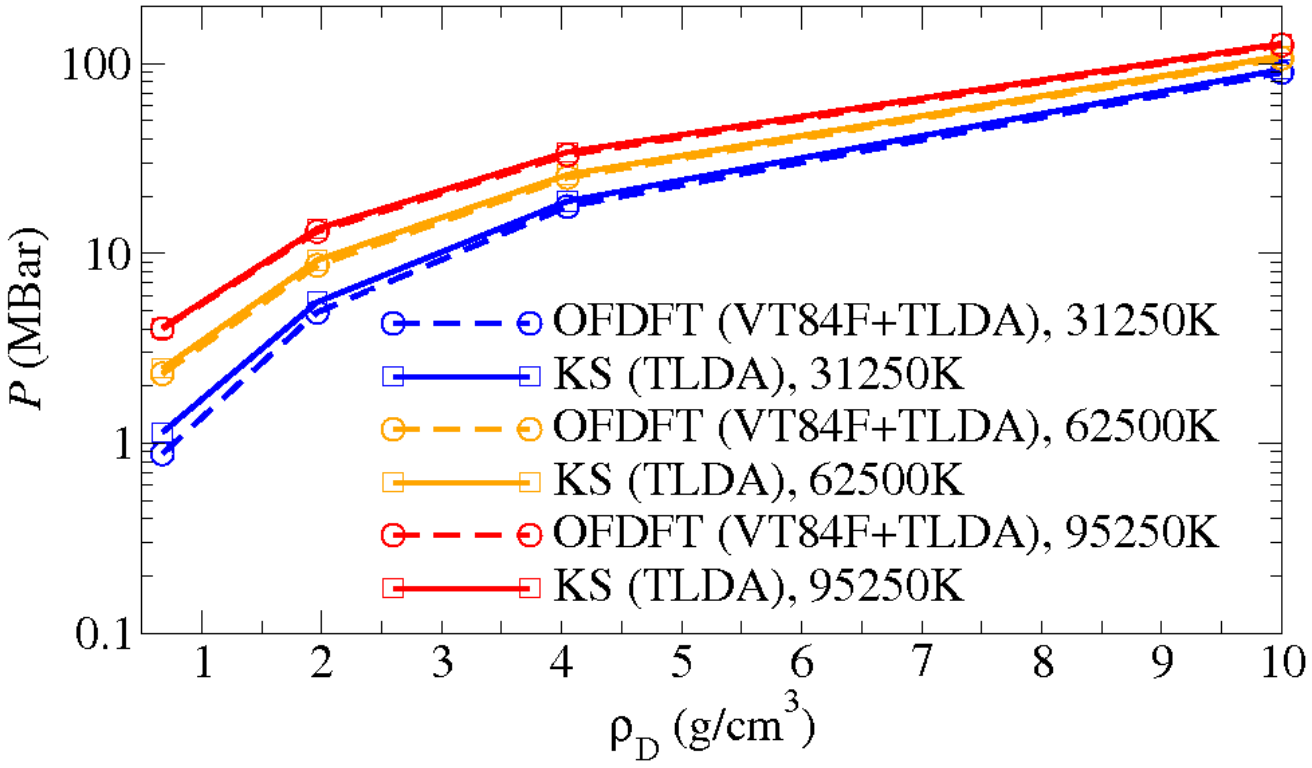
$$F_\tau^{VT84F}(s_\tau) := 1 - \frac{c s_\tau^2 \, e^{-a s_\tau^2}}{1 + c s_\tau^2} + (1 - e^{-a s_\tau^4}) \left(\frac{1}{s_\tau^2} - 1 \right)$$

$$F_\sigma^{VT84F}(s_\sigma) := 2 - F_\tau^{VT84F}(s_\sigma)$$

Non-empirical GGA "VT84F" with finite-T gradient variables.

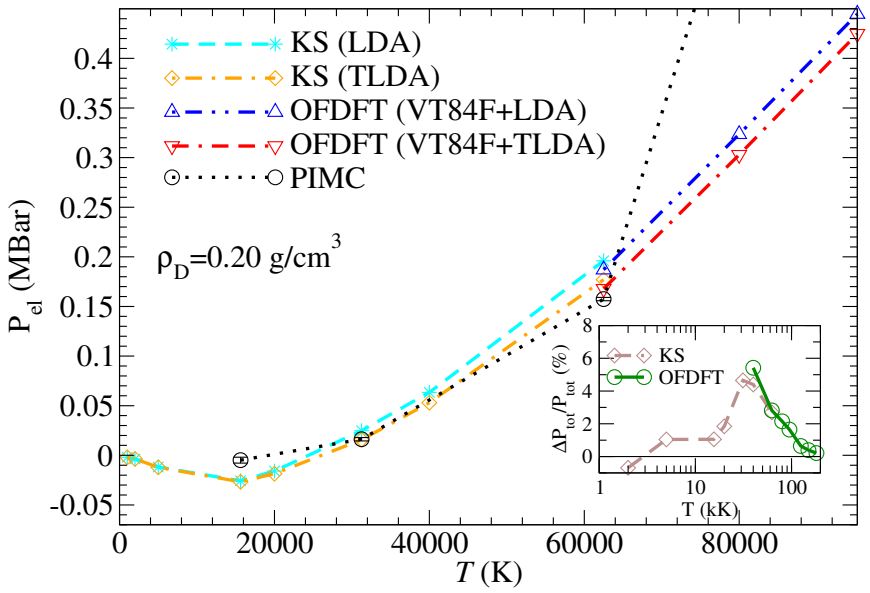
Phys. Rev. B 88, 161108R (2013)

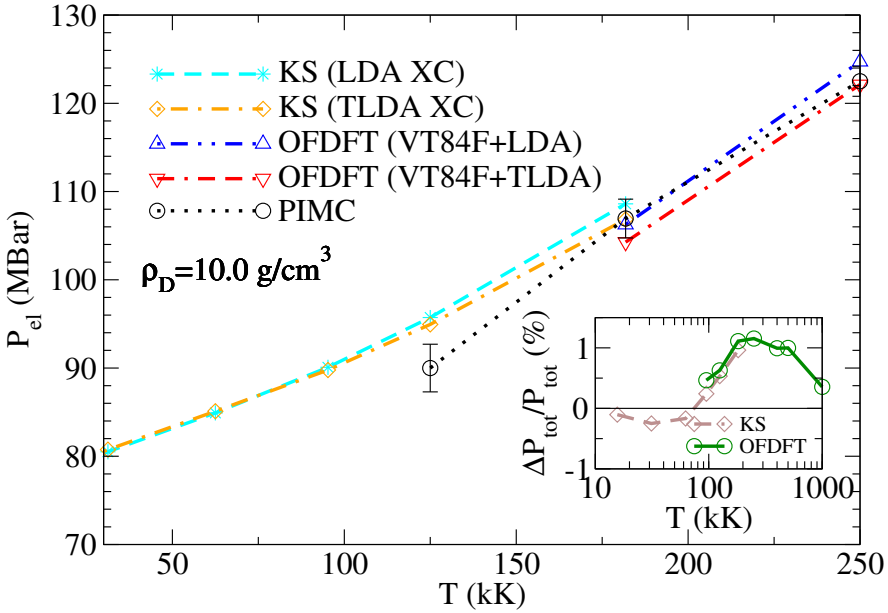
All together - Warm Dense Deuterium Eq. of State AIMD (VT84F & TLDA)



Deuterium AIMD pressure vs. material density. New VT84F OFDFT functional compared to KS, both with same T-dependent LDA XC ("TLDA"). OFDFT had 128 atoms in simulation cell, KS 3x3x3 BZ or Gamma point. APBEF is built analogously from APBEK, which does not give a bound ground state. [Phys. Rev. B 88, 161108R (2013)]

Warm Dense Deuterium Equation of State





FIGS: Electronic pressure as a function of temperature T.

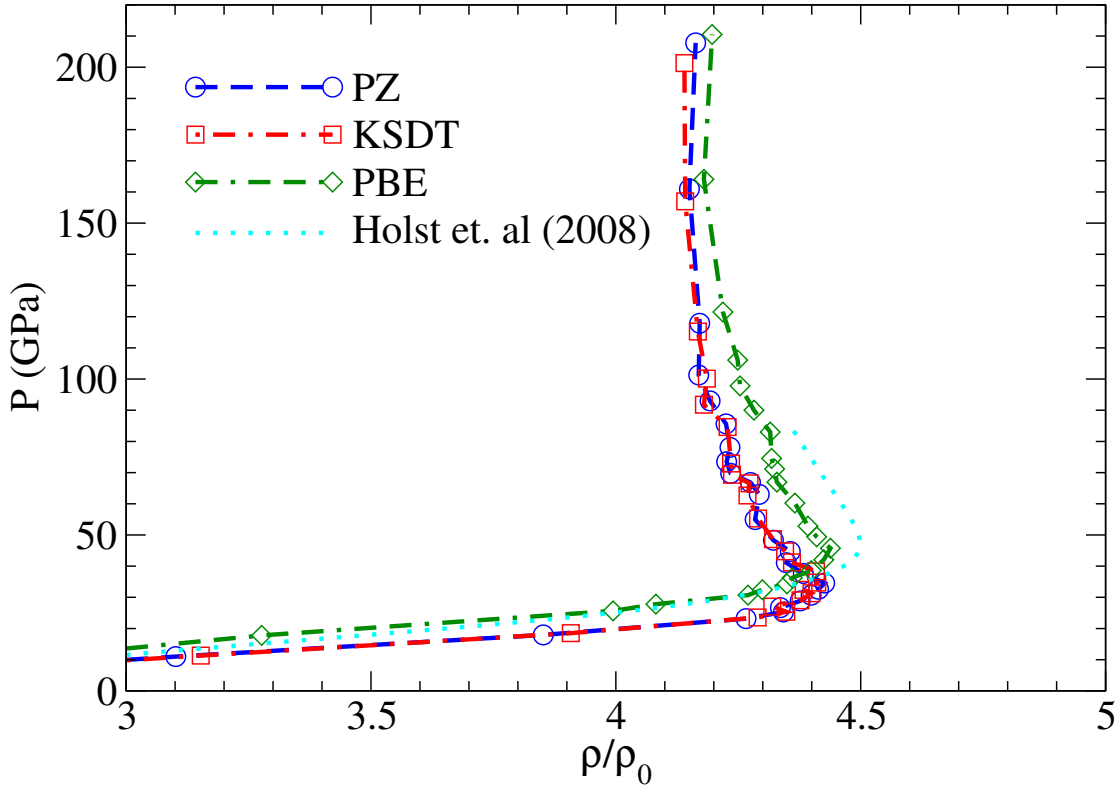
INSET: $$\frac{\Delta P_{tot}}{P_{tot}} \equiv \frac{P_{tot}^{LDA} - P_{tot}^{TLDA}}{P_{tot}^{TLDA}} \times 100\%$$

METHOD: Kohn-Sham MD at low-T (Quantum-Espresso)
Orbital-free DFT MD at high-T (Profess@Quantum-Espresso)

PIMC: Hu, Militzer, Goncharov, and Skupsky, Phys. Rev. B 84, 224109 (2011)

Hugoniots are Insensitive

Hydrogen principal Hugoniot; Initial density ρ_0=0.0855 g/cm^3



$$E - E_0 = \frac{1}{2}(P + P_0)\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)$$

Two issues: (1) Huge error bars on experiment (not shown). (2) Cancellation between internal energy difference and PV work difference terms in Rankine–Hugoniot equation.

Better GGA X enhancement factors

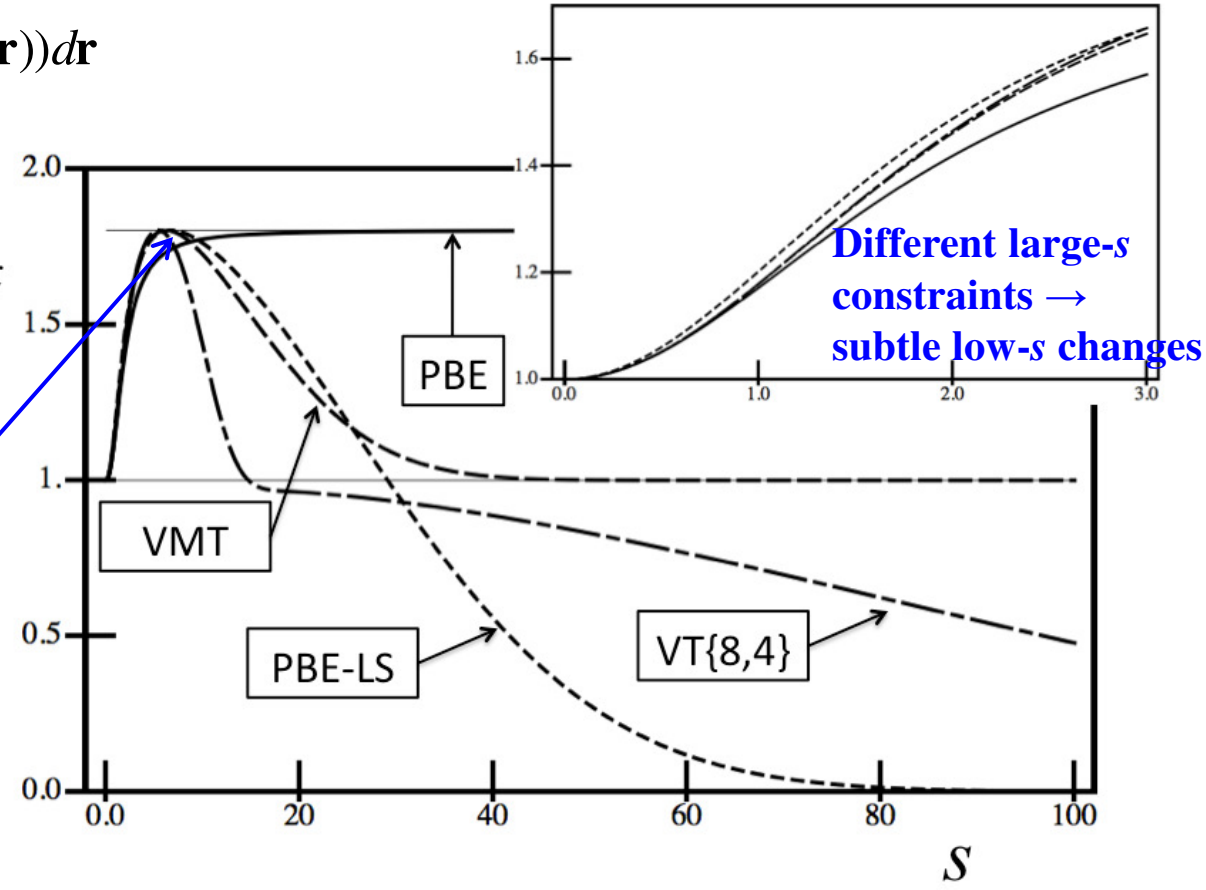
Oddity: All the rather different GGAs we (Mexican collaboration) have constructed (VMT, VT{8,4}, PBEmol, PBE-LS) have roughly the same MAE report card. *All* obey the Lieb-Oxford bound *locally*.

$$E_x^{GGA}[n] = c_x \int n^{4/3}(\mathbf{r}) F_x\,(s(\mathbf{r}))d\mathbf{r}$$

$$s(\mathbf{r}) := \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n|}{n^{4/3}};$$

$$c_x := -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Differing *local* Lieb-Oxford bound enforcement



Try the other large-s limit

$$v_x := \delta E_x / \delta n$$

$$v_x[\mathrm{n};\mathbf{r}] \xrightarrow[r\to\infty]{} -\frac{1}{r}$$

Exact limiting behavior of X potential for finite systems

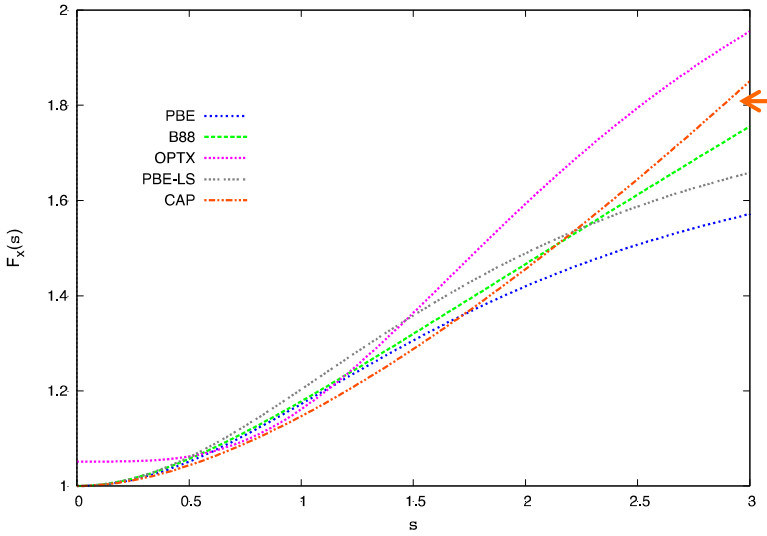
$$\Rightarrow F_x(s) \xrightarrow[s\to\infty]{} -\frac{(3\pi^2)^{1/3}}{c_x} s$$

Remarks – (i) This constraint contradicts the one used in VT{84) and PBE-LS (a GGA X functional can't do everything); (ii) It surely is possible to construct a density for which this kind of F_x will yield a global LO bound violation. (iii) If such densities are essentially unphysical, this form may correspond to a very effective X functional (example of "design choice").

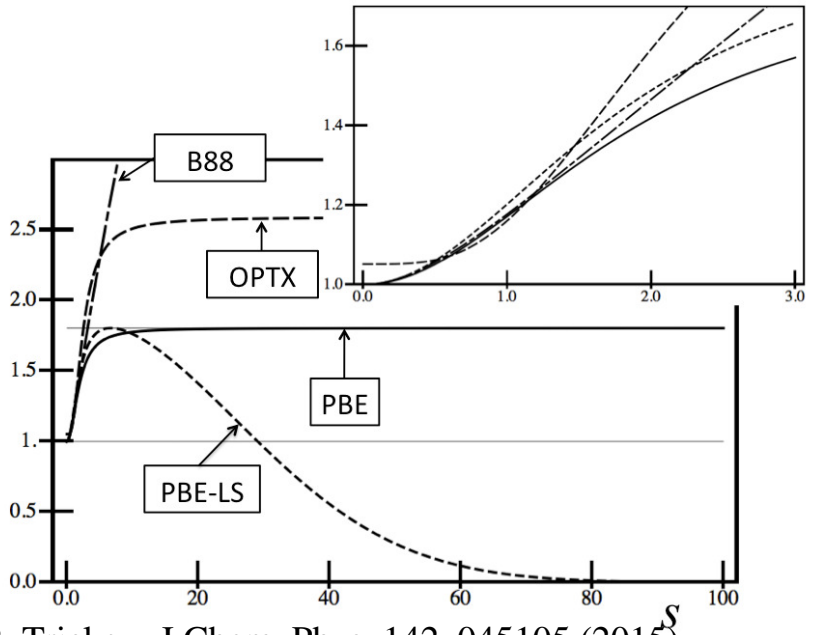
"Generalized gradient approximation exchange energy functional with correct asymptotic behavior of the corresponding potential", Javier Carmona-Espíndola, José L. Gázquez, Alberto Vela, and S. B. Trickey, J.Chem. Phys. 142, 054105 (2015)

GGA X enhancement factor oddity

Oddity is confirmed : All the rather different GGAs we have constructed (VMT, VT{8,4}, PBEmol, PBE-LS, CAP) have roughly the same MAE report card *on the standard test sets*.



CAP



MAJOR ADVANTAGE of CAP: correct long-range behavior gives substantially better TDDFT polarizabilities & hyper-polarizabilities.

J. Carmona-Espíndola, J.L. Gázquez, A. Vela, and S.B. Trickey, J.Chem. Phys. 142, 045105 (2015)

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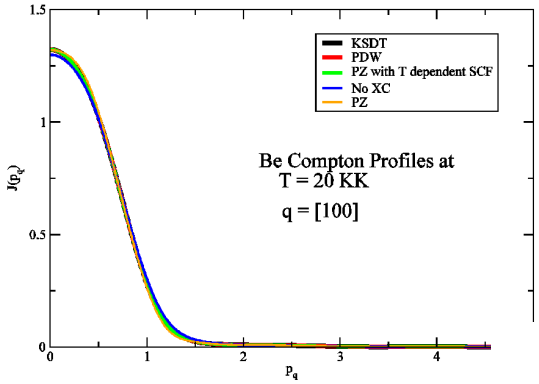
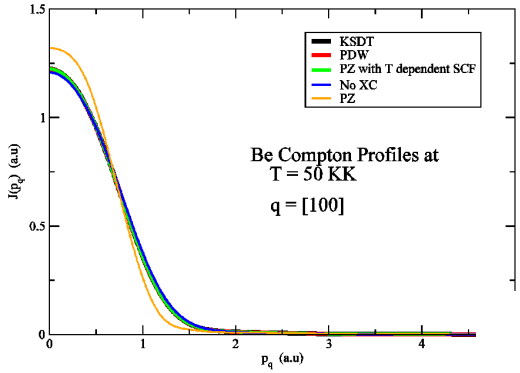
Implementation: finite-T LDA in FEFF9



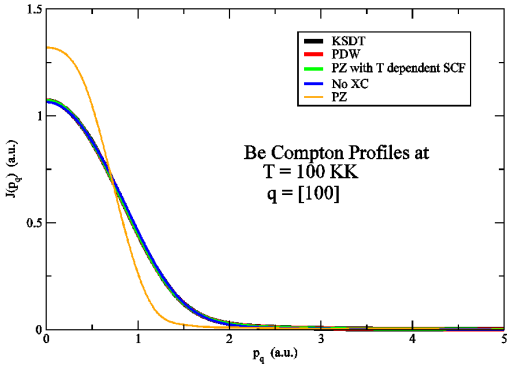
HCP Beryllium Compton profiles at fixed, T=0 K crystal structure from various XC approximations.



Huh?

No XC is the same as Finite-T XC?

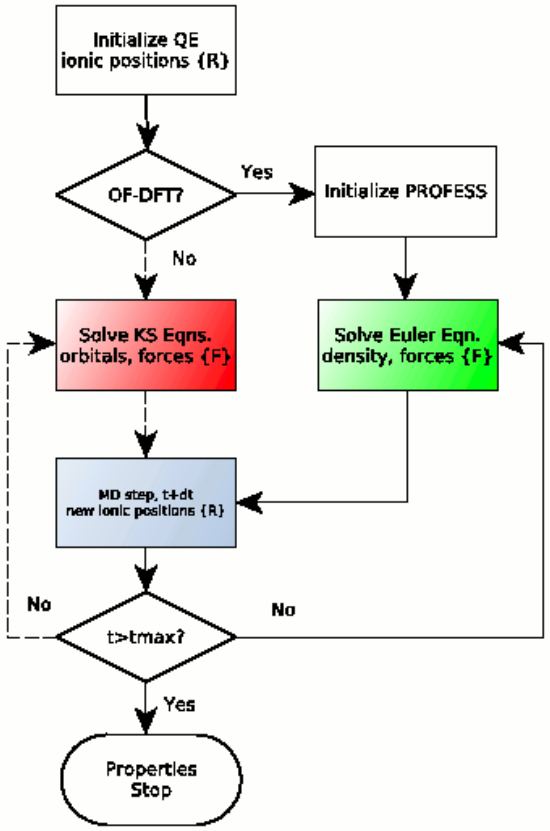
Approaching correct high-T limit?
Under examination.



L. Calderín, May 2015, unpublished

Software: PROFESS@QuantumEspresso

- **Drives QuantumEspresso with OFDFT forces from modified PROFESS**
- **Includes our finite-T functionals**
- **Provided as patch files and libraries, plus test cases.**
- **Download from www.qtp.ufl.edu/ofdft and give it a try (GPL).**
- **V. Karasiev, T. Sjostrom and S.B. Trickey, Comput. Phys. Commnun. 185, 3240 (2014)**



New June 2015! The LDA XC free energy module also is downloadable

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

Summary

1. **Explicit T-dependence in XC is important for accurate prediction of properties of electron gas at finite-T and for accurate equations of state at elevated T.**
2. **The KSDT XC functional fitted to Brown et al. data appears to be consistent with the recent Schoof et al. data as well.**
3. **There is major progress on a constraint-based, single-point non-interacting functional (KS KE plus entropy).**
4. **Caveat: The VT84F functional does not work at low densities – underlying reasons are under investigation.**
5. **Caveat: All good OFDFT non-interacting free energy functionals exhibit odd behavior with respect so some pseudopotentials.**
6. **Hugoniot calculations of liquid hydrogen are not sensitive to the LDA(XC)→TLDA(XC) replacement. This may change when our finite-T GGA XC functional (under development) is used.**
7. **Progress on lower-rung XC functionals still is possible.**
8. **Introduction of finite-T functionals into spectroscopic and response function calculations is in its infancy, with some initial surprises.**

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