

Finite-Temperature Hartree-Fock Exchange and Exchange-Correlation Free Energy Functionals

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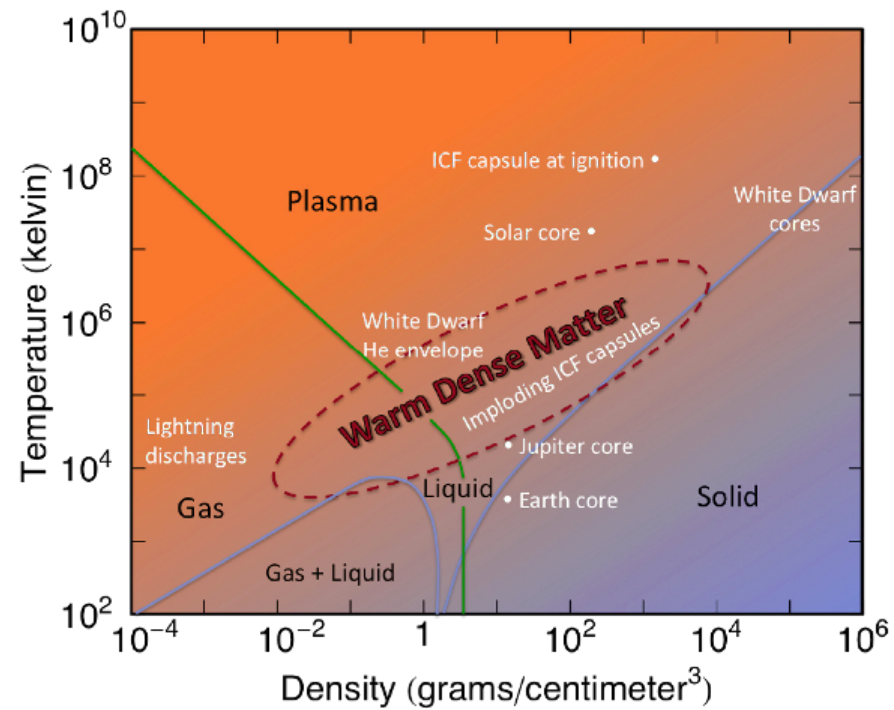
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Overview

- Exchange and Correlation (XC) in DFT
- Introduction to finite temperature XC functionals
- Confined and extended system results
- Future work for finite temperature XC functionals



Exchange and Correlation in DFT

DFT Basics

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i, I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad , \quad \hat{H}\Psi = E\Psi$$

Hohenberg-Kohn (1964)

$$E[n] = T + U^{ee} + U^{ion}$$

Kohn-Sham (1965)

$$n(\mathbf{r}) = \sum_i^{\text{occ}} \int \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r}$$

$T[n] \rightarrow T_s[\phi_i]$, KS single particle equations

$$E_H = \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad , \quad U^{ion} = -\sum_I \int \frac{n(\mathbf{r})Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

$$E = T_s + E_H + U^{ion} + E_{xc}$$

$$E_{xc} = (T - T_s) + (U^{ee} - E_H)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$



W. Kohn

E_{xc} approximations

LDA (local density approximation)

Prior to 1980 approximate electron gas calculations:

RPA, high-low density interpolation, GW, local field corrections (i.e. STLS)

Post 1980 Ceperley-Alder QMC calculation parameterizations:

Vosko-Wilk-Nusair (1980) VWN

Perdew-Zunger (1981) PZ81

Perdew-Wang (1992) PW92



D.M. Ceperley

E_{xc} approximations

Gradient expansions as proposed by Kohn-Sham implemented by several others.

Often not better or worse than LDA results.

GGA (generalized gradient approximation)

Can include corrections beyond second order expansion and enforce various constraints on XC.

Becke (1988) B88

Perdew-Wang (1991) PW91

Perdew-Burke-Ernzerhof (1996) PBE

Perdew's Jacob's Ladder...



J.P. Perdew

Extension to Finite Temperature

Finite Temperature DFT

Mermin (1965) extension of Hohenberg-Kohn to finite temperature.
Development through the grand canonical ensemble.

$$F[n, T] = T + U^{ee} + U^{ion} - TS$$

KS scheme also applies

$$n(\mathbf{r}) = \sum_i f_i \int \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r}, \quad f_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

$$T \rightarrow T_s = -\frac{1}{2} \sum_i f_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r}$$

$$S \rightarrow S_s = -k_B \sum_i f_i \ln(f_i) + (1 - f_i) \ln(1 - f_i)$$

$$F = T_s + E_H + U^{ion} - TS_s + F_{xc}$$

$$F_{xc} = (T - T_s) + (U^{ee} - E_H) + (S - S_s)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta F_{xc}}{\delta n(\mathbf{r})}$$



N.D. Mermin

F_{xc} approximations - LDA

No finite temperature benchmarks equivalent to ground state QMC results.

Again interpolation and approximate theoretic methods are required.

Known $T = 0$ and High T limits
QMC and Debye-Hückel, respectively.

Useful thermodynamics
for the UEG

$$\Omega = -pV = F - \mu N$$

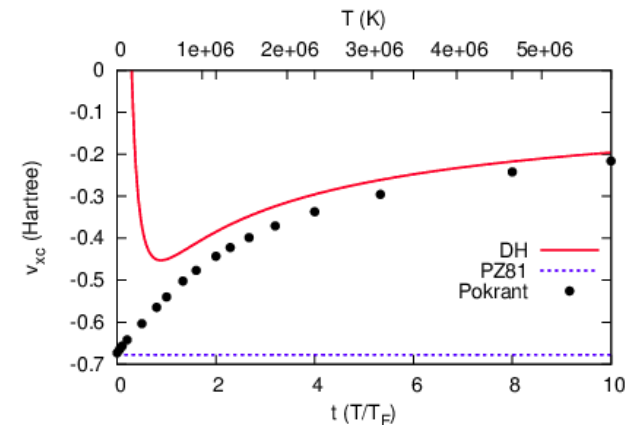
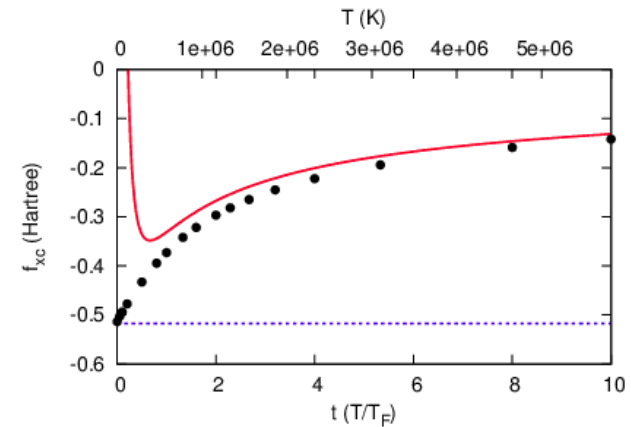
$$p_{xc}/n = f_{xc} - \mu_{xc}$$

$$\mu_{xc} = v_{xc}, \quad f_{xc} = F_{xc}/N$$

$$t = T/T_F = 1/\beta\epsilon_F$$

$$\frac{4\pi}{3} r_s^3 = \frac{1}{n} = \frac{3\pi^2}{k_F^3}$$

$$r_s = 1 \quad \longrightarrow$$



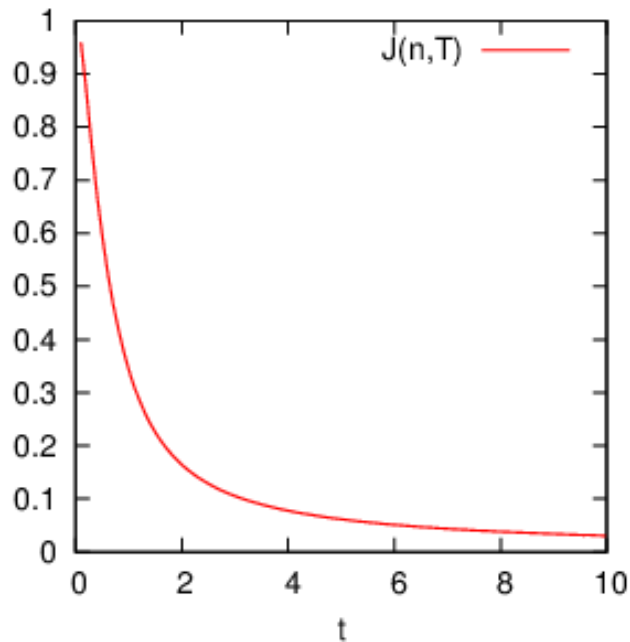
Exchange only F_x

$$F_x^{\text{HEG}} = -\frac{V}{(2\pi)^6} \iint d\mathbf{k} d\mathbf{k}' \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|} f(\mathbf{k})f(\mathbf{k}')$$

$$= -\frac{1}{2\pi^3\beta^2} \int_{-\infty}^{\beta\mu_0} I_{-1/2}^2(x) dx, \quad I_\alpha(x) = \int_0^\infty \frac{z^\alpha}{e^{z-x}+1} dz$$

$$f_x^{\text{LDA}}(n) = \varepsilon_x(n) = \frac{3}{4} \left(\frac{3n}{\pi}\right)^{1/3}$$

$$f_x^{\text{LDA}(T)}(n, T) = \varepsilon_x(n)J(n, T)$$



Temperature dependence of the Hartree-Fock approximation

Suklyun Hong*

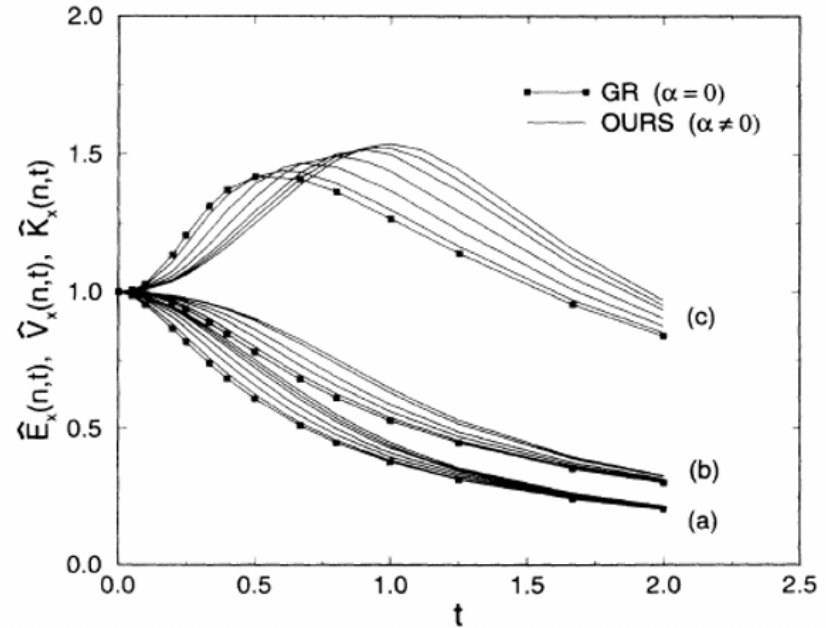
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(Received 17 March 1994)

The Hartree-Fock exchange energy of the electron gas is calculated at nonzero temperatures. The calculation is done self-consistently in that the Hartree-Fock self-energy is included self-consistently in the Fermi-Dirac occupation numbers. We also calculate the first and second derivatives of the Hartree-Fock exchange energy with respect to density, which are useful for density-functional calculations at nonzero temperatures.



F_x beyond LDA

Geldart (1993) has provided a closed form expression (in Fermi integrals) for the first term in the finite temperature gradient expansion.

Developed in grand canonical ensemble, analogous to KS original proposal for gradient expansion.

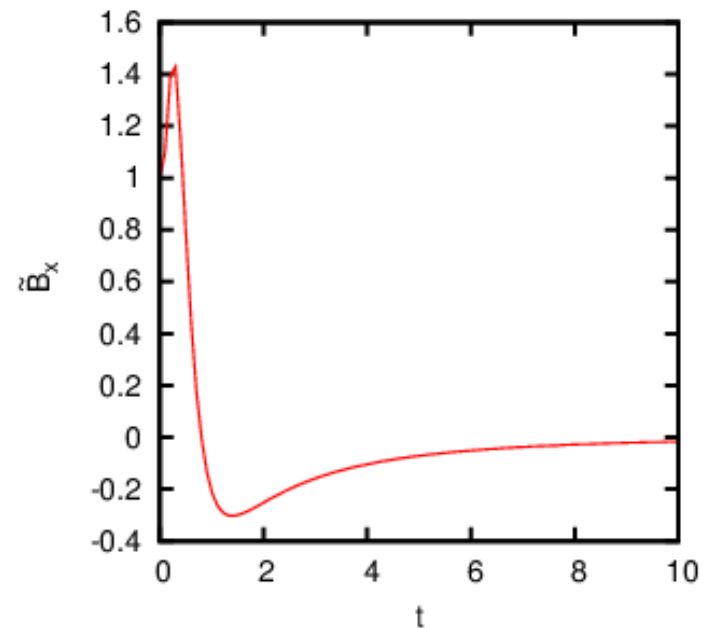
$$B_x(n, T) = -\frac{\pi\beta^2}{72} \left[\left(\frac{I'_{-1/2}(\eta)}{I_{-1/2}(\eta)} \right)^2 - 3 \left(\frac{I''_{-1/2}(\eta)}{I_{-1/2}(\eta)} \right)^2 \right]$$

$$F_x^g = \int B_x(n, T) |\nabla n(\mathbf{r})|^2 d\mathbf{r}$$

$$\eta = \beta\mu_0$$

$$n = \frac{\sqrt{2}}{\pi\beta^{3/2}} I_{1/2}(\beta\mu_0)$$

$$\tilde{B}_x(t) = (-18k_f^4/\pi) B_x$$



Finite temperature Correlation

RPA

Originally calculated by Gupta and Rajagopal (1980), revised by Perrot and Dharma-wardana (1984).

$$\Omega(\mu, T) = \Omega_0 + \Omega_x + \Omega_c$$

$$\Omega_x = -\frac{V}{2\pi^3\beta^2} \int_{-\infty}^{\beta\mu} I_{-1/2}^2(x) dx$$

$$\Omega_c \approx \Omega_r = \frac{V}{(2\pi)^3} \sum_n \frac{1}{2\beta} \int_0^{\infty} \{\ln[1 - u_q \pi^0(v_n, \mathbf{q})] + u_q \pi^0(v_n, \mathbf{q})\} d\mathbf{q}$$

Linearized inversion for μ_{xc} , direct inversion will differ.

$$F_{xc}(n, T) = \Omega_{xc}(\mu_0, T)$$

$$\mu_{xc}(n, T) = \frac{(\partial\Omega_{xc}/\partial\mu)_{\mu=\mu_0}}{(\partial n/\partial\mu)_{\mu=\mu_0}}$$

STLS type Dielectric

Finite temperature version of Singwi-Tosi-Land-Sjölander local field corrections.

Calculated and fit by Ichimaru et. al. (1985)

$$S(x) = \frac{3}{2} t \sum_{l=-\infty}^{\infty} \frac{\Phi(x,l)}{1+(2\Gamma t/\pi\alpha x^2)[1-G(x)]\Phi(x,l)}$$

$$G(x) = -\frac{3}{4} \int_0^{\infty} y^2 [S(y) - 1] \left(1 + \frac{x^2 - y^2}{2xy} \ln \left| \frac{x+y}{x-y} \right| \right) dy$$

$$\Gamma = \beta/r_s, \quad \alpha = (4/9\pi)^{1/3}, \quad x = q/q_F$$

After self-consistent solutions fit,

$$\varepsilon_{int} = \frac{\Gamma}{\pi\alpha\beta} \int_0^{\infty} [S(x) - 1] dx, \quad f_{xc}(n, T) = \frac{1}{\beta} \int_0^{\Gamma} \frac{d\Gamma}{\Gamma} (\beta\varepsilon_{int})_t$$

Classical Mapping

Idea is to map quantum variables to classical variables, for which classical calculation results are equivalent/correct for the quantum system.

Perrot and Dharma-wardana realization through CHNC.

At $T = 0$, given density n , the CHNC equations are solved with T_{cf} which is adjusted until $T_{cf} = T_q$ is found which produces the same $\varepsilon_c(n)$ as the benchmark QMC.

The CHNC calculation also produce pair distribution functions in good agreement with the benchmarks, and are always non-negative.

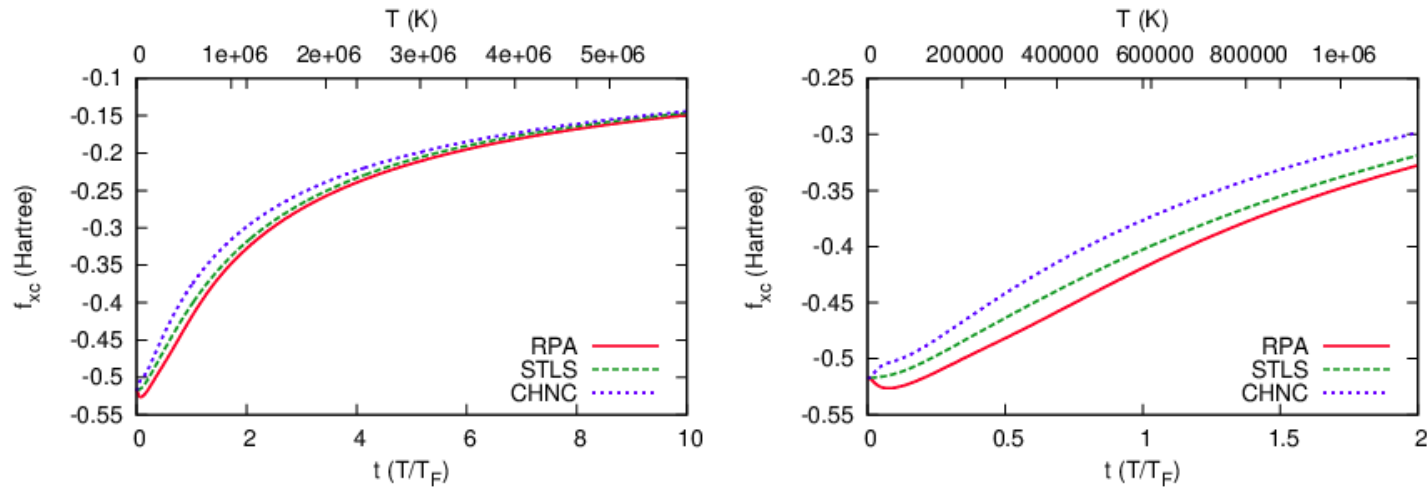
$$T_q/E_F = 1/(a + b\sqrt{r_s} + cr_s)$$

For $T > 0$

$$T_{cf} = \sqrt{T^2 + T_q^2},$$

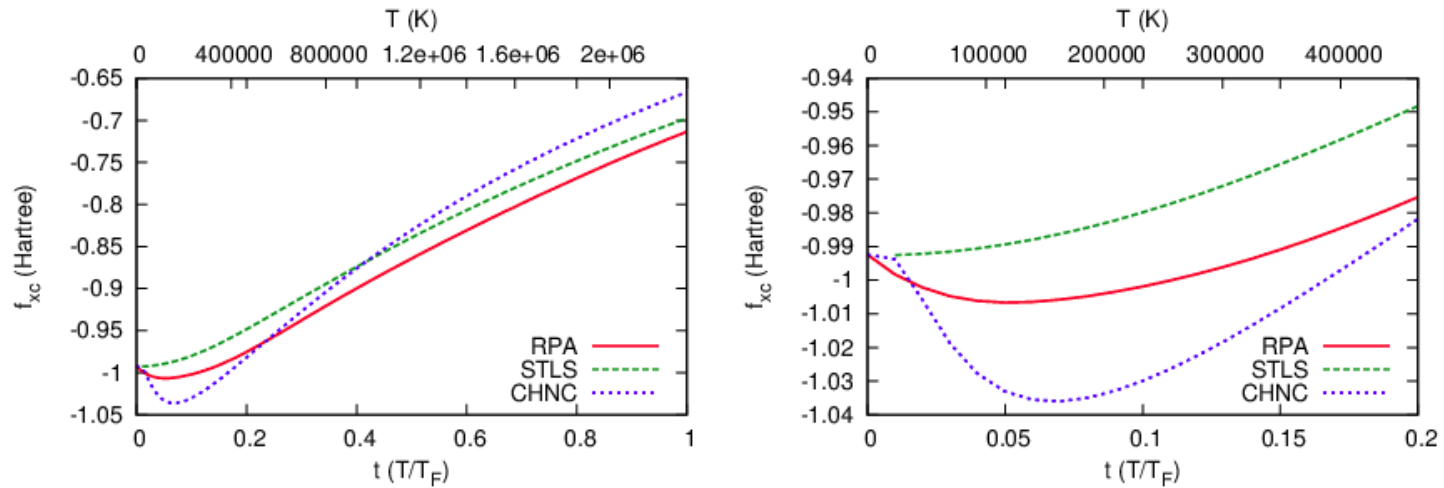
interpolates between 0 and high T .

Exchange-correlation energy per electron for $r_s = 1$.



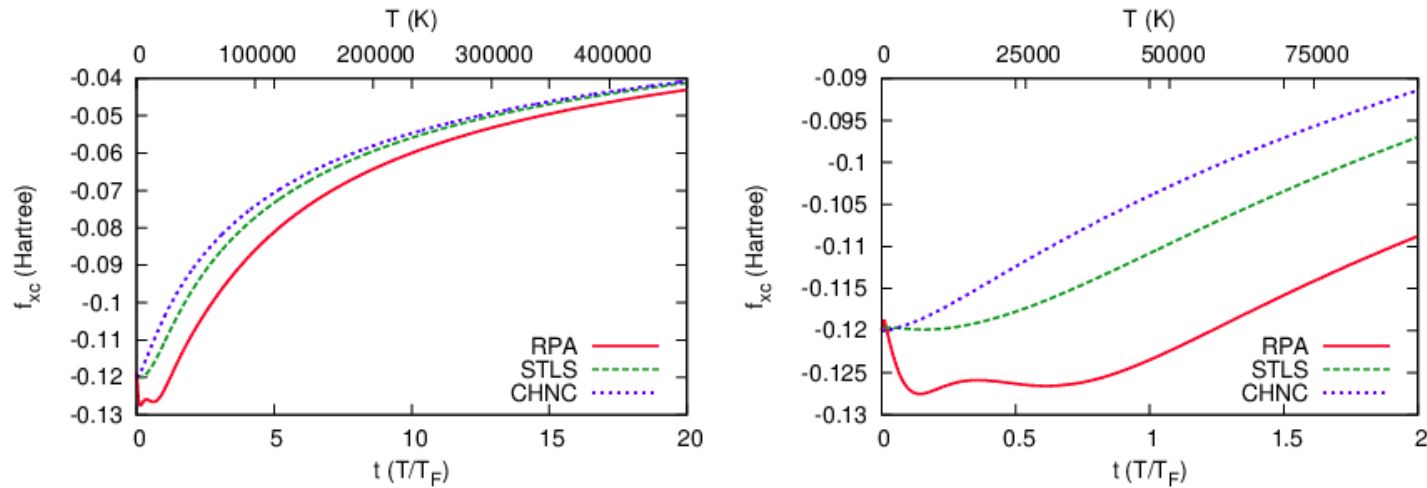
Approximately 5% difference at $T = 200000$ K from ground state.

Exchange-correlation energy per electron for $r_s = 0.5$.

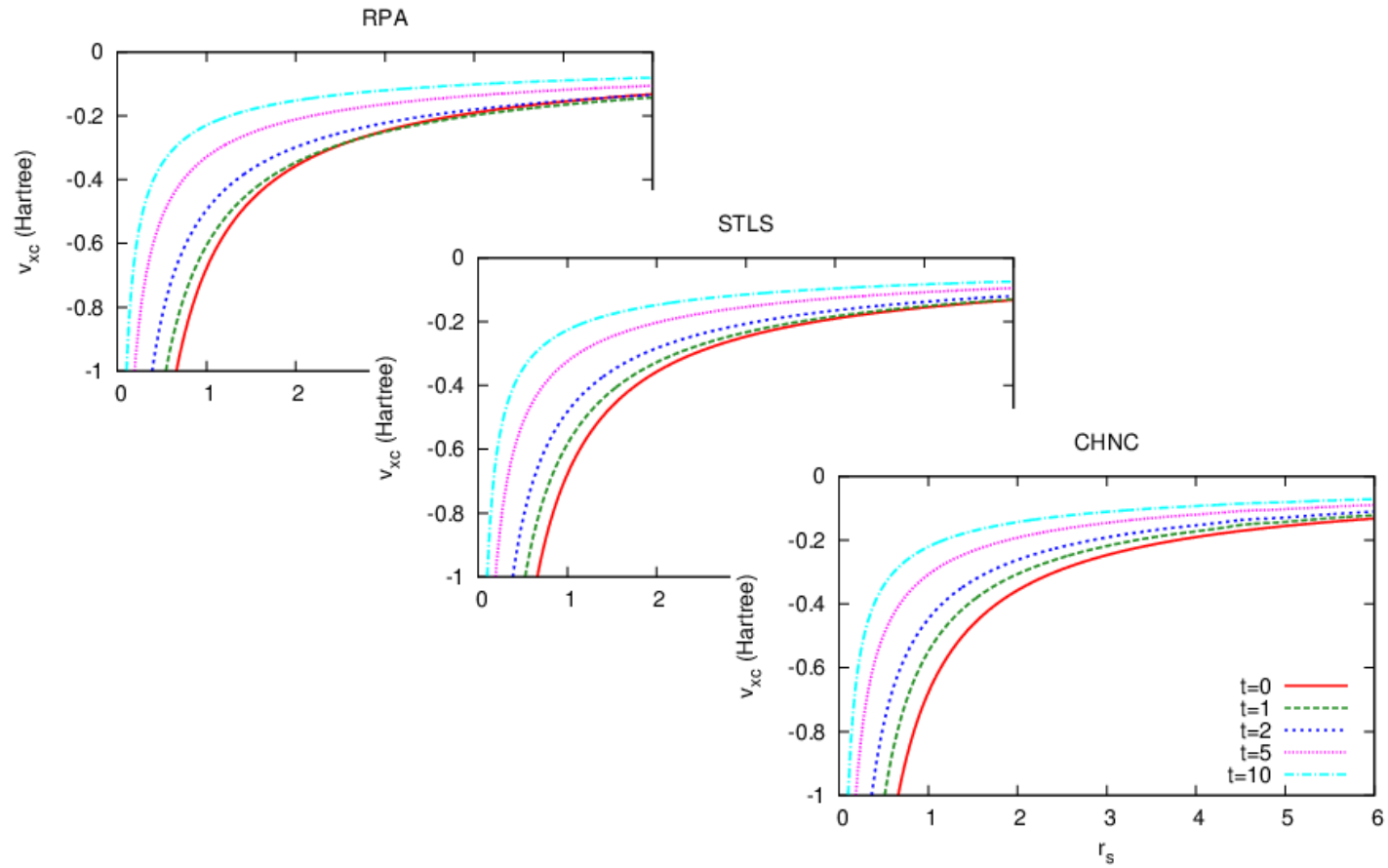


Approximately 2% difference at $T = 200000$ K from ground state.

Exchange-correlation energy per electron for $r_s = 5$.



Approximately 50% difference at $T = 200000$ K from ground state.



$$v_{xc} = \frac{\partial(nf_{xc})}{\partial n}$$

Not necessarily related to temperature dependence.

Finite temperature Hartree-Fock

Mermin (1963) examined finite temperature Hartree-Fock, showing in the grand ensemble that there is an ensemble of Slater determinants that minimizes the Hartree-Fock free energy and provides an upper bound as at zero temperature.

$$F_{HF} = T_{HF} - TS_{HF} + U^{ion} + E_H + F_{HF}^x$$

$$T_{HF} = T_s, \quad S_{HF} = S_s, \quad \text{with respective orbitals and } f_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$$

$$F_{HF}^x = -\frac{1}{2} \sum_{i,j} f_i f_j \delta(\sigma_i, \sigma_j) \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Single particle equations

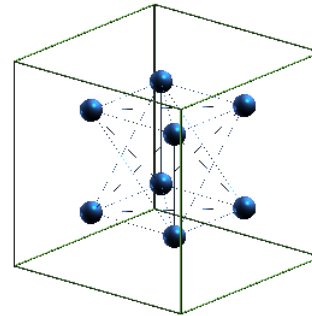
$$\begin{aligned} \varepsilon_i \phi_i(\mathbf{r}) = & \left(-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) \right) \phi_i(\mathbf{r}) + \sum_j f_j \int d\mathbf{r}_2 \frac{\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} \phi_i(\mathbf{r}) \\ & - \sum_j f_j \delta(\sigma_i, \sigma_j) \int d\mathbf{r}_2 \frac{\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} \phi_j(\mathbf{r}) \end{aligned}$$

Confined hydrogen

Model Problem

- Hard-wall rectangular parallelepiped containing a few (1-32) hydrogen atoms, where fixed atomic positions are sampled.
- Box size is from 1 au^3 (Bohr³) to free limit (arbitrarily large).
- Temperatures range from 0 to 300,000 K ($0 \rightarrow \approx 26 \text{ eV}$)
- Methods: Finite Temperature Hartree-Fock (FTHF) and Kohn-Sham density functional theory (DFT).
- Unique truncated Gaussian type orbital basis is employed.

8 Hydrogen atoms in cubic arrangement of spacing a confined within a hardwall cube of side length L .



Truncated Gaussian Type Orbitals

Basis Requirements

- Large number of orbitals for thermal occupation.
- Matching of hardwall boundary condition.
- Efficient calculation of electron repulsion integrals.

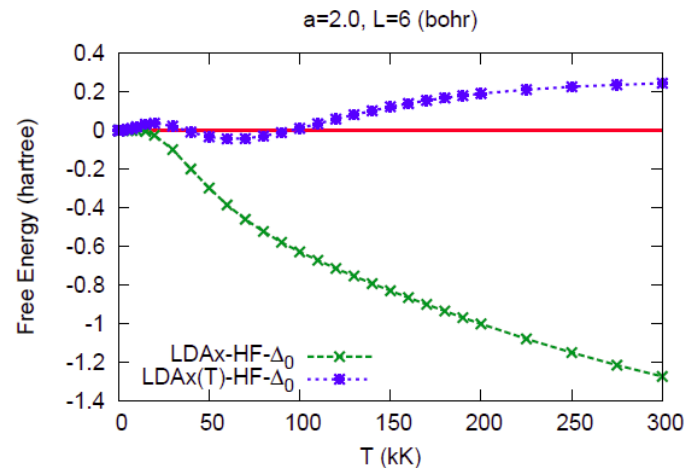
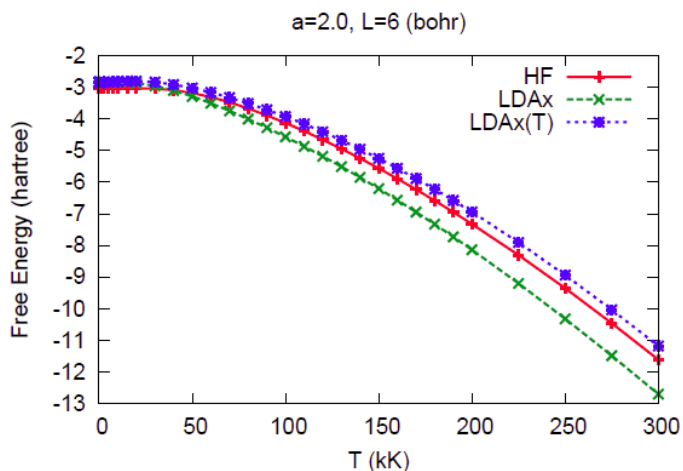
Cartesian Gaussians truncated to match BCs. Coefficients a_0 and a_L set by requiring continuity of basis functions.

$$g_{\text{box}}^n = \begin{cases} a_0 [g^n(x) - g^n(0)] & 0 \leq x \leq x_c \\ a_L [g^n(x) - g^n(L_x)] & x_c \leq x \leq L_x \end{cases}$$

$$g^n(x) = (x - x_c)^n e^{-a(x-x_c)^2}$$

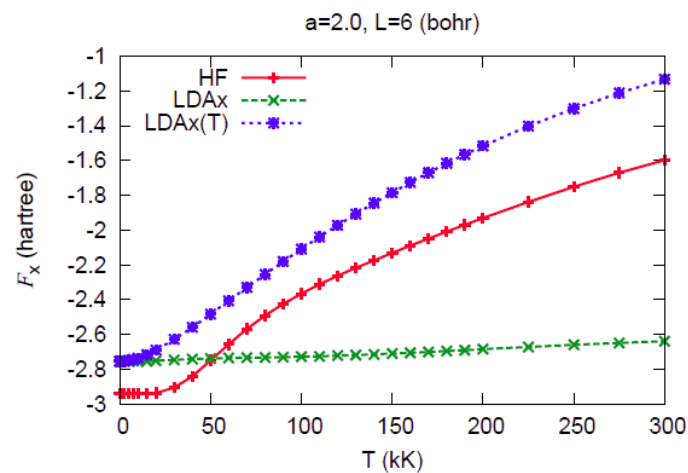
x_c is nucleus position.

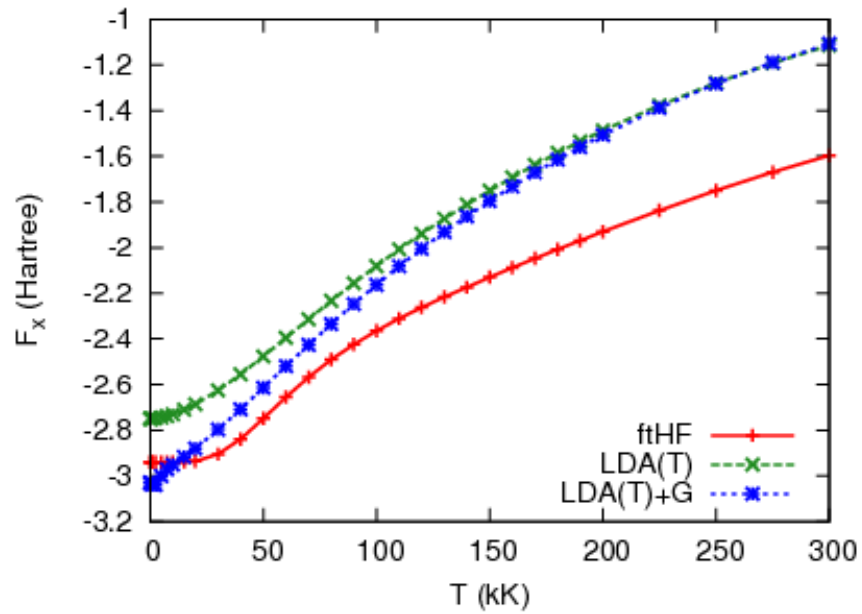
Results - Free Energy



$T = 0$ to 300000 K.
 $a = 2.0$ au; for simple cubic lattice
 this corresponds to $r_s = 1.24$.

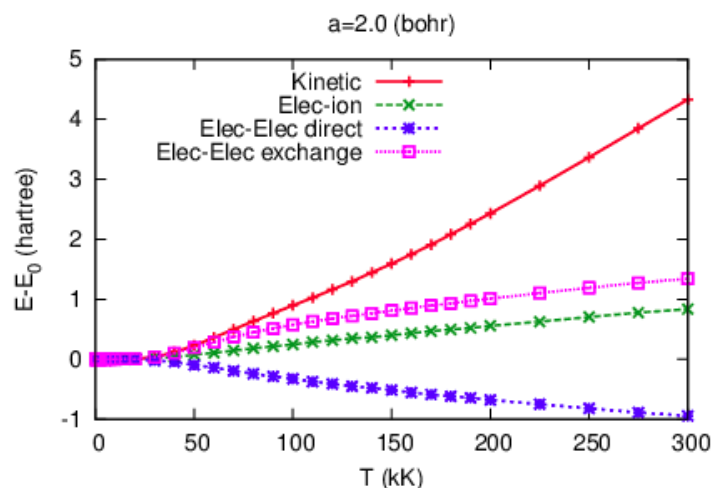
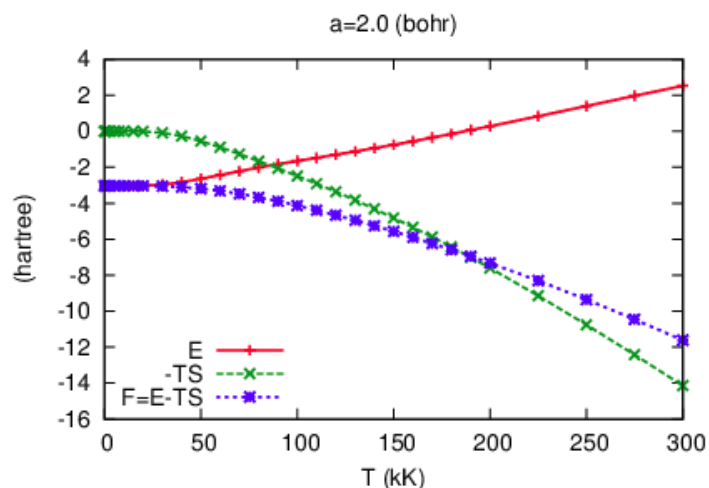
HF free energy is better approximated
 by temperature dependent LDA
 exchange functional.





Comparison of previous with Geldart finite temperature exchange gradient correction included.

Free Energy Components



Entropic and kinetic terms contribute most to overall change in free energy, but change in exchange free energy is not negligible.

At 300 kK ΔF_x is 25% of ΔE and 14% of ΔF .

ftHF for solid Li

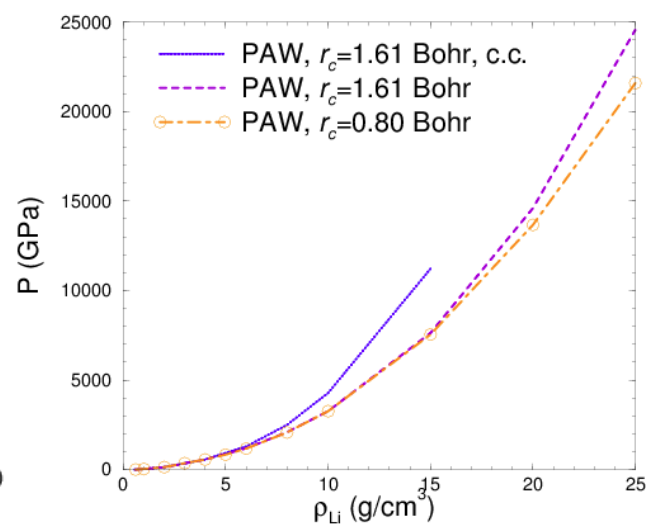
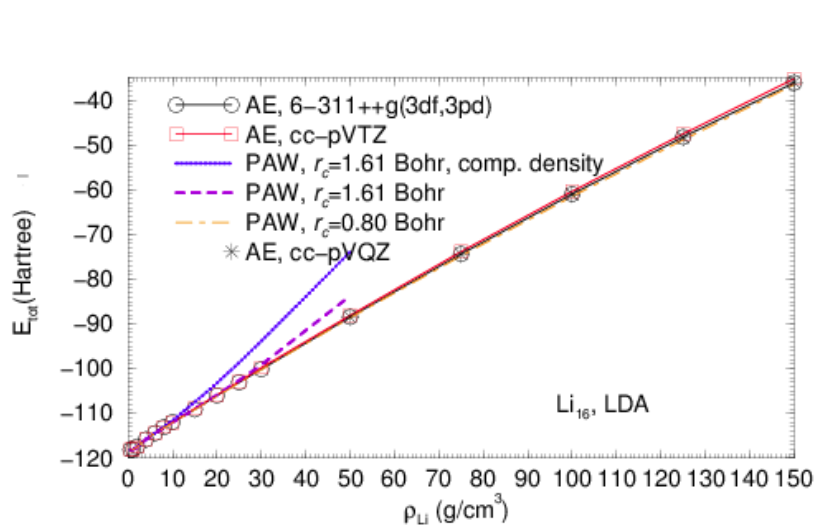
Pseudopotentials

PPs are required, but must be specialized for WDM systems.

Issues are transferability to higher densities and temperatures.

Inclusion of more core orbitals in calculation is necessary.

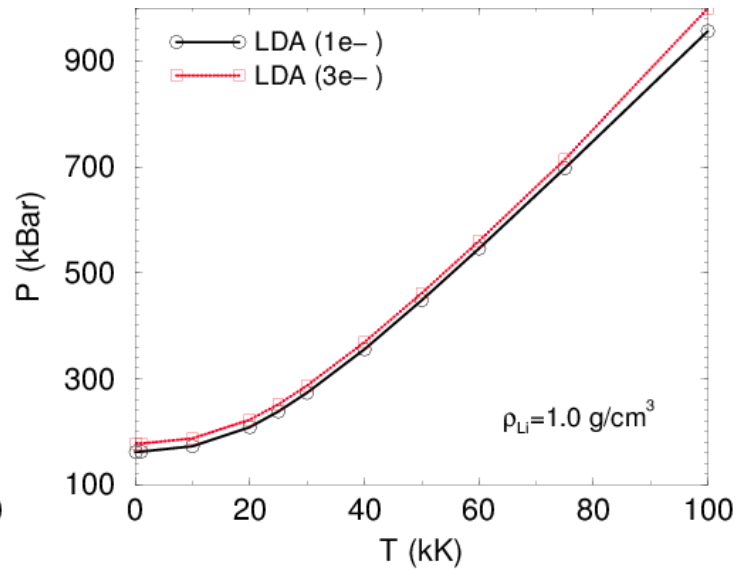
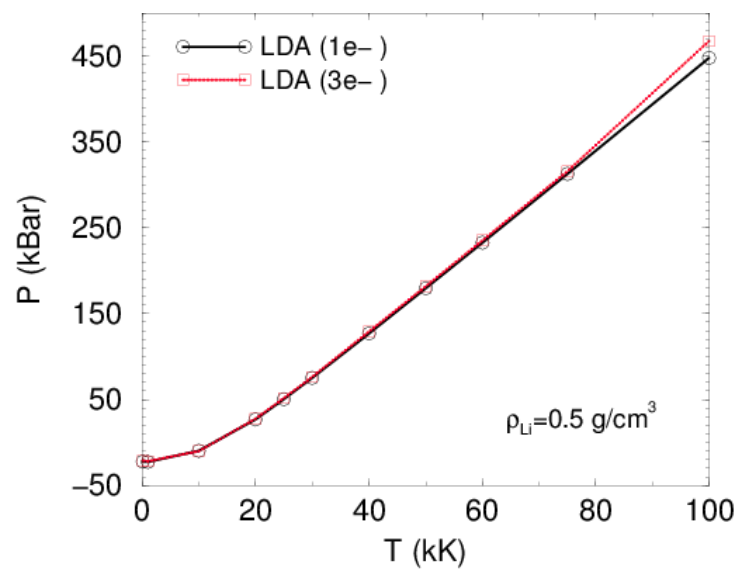
All electron zero temperature calculations for clusters can benchmark PP calculations.



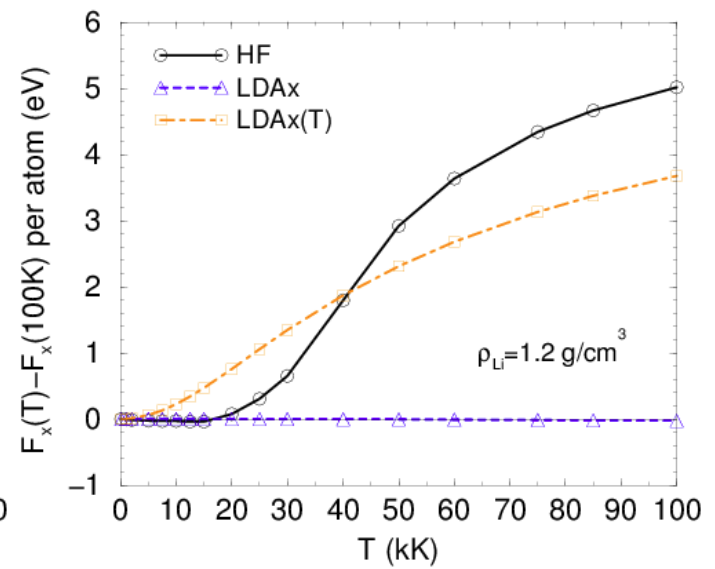
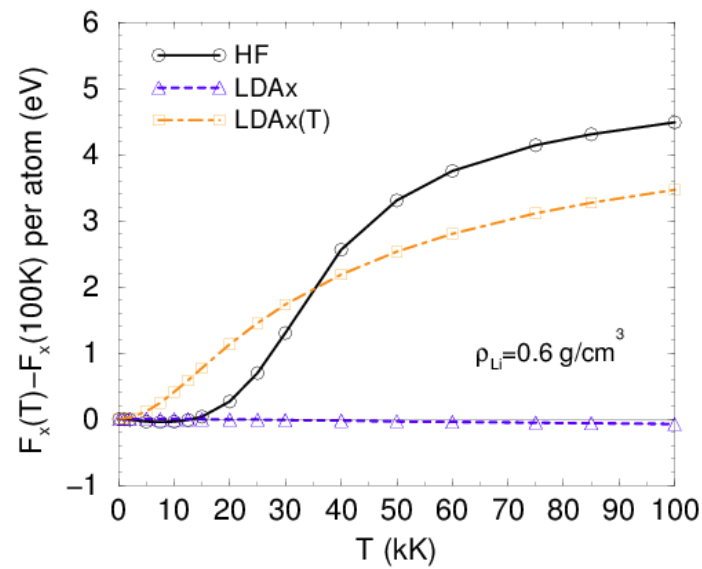
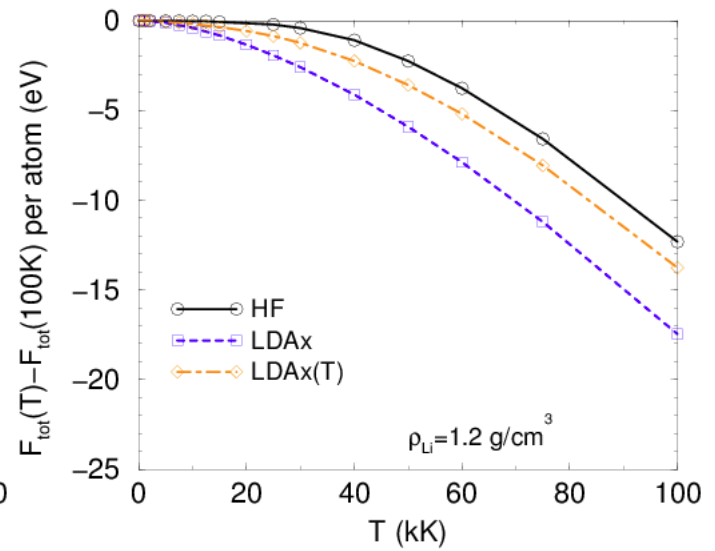
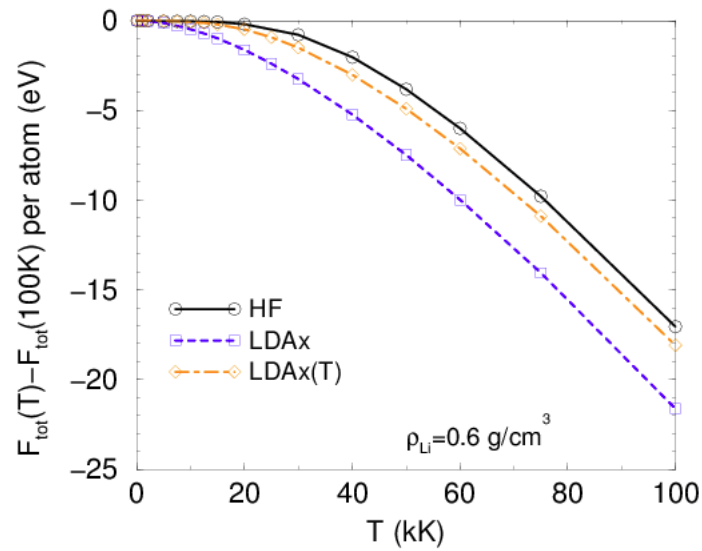
PP for Hartree-Fock

ftHF calculation will be for Li densities $\rho = 0.5 - 1.2$ g/cc.
and temperatures up to 100 kK

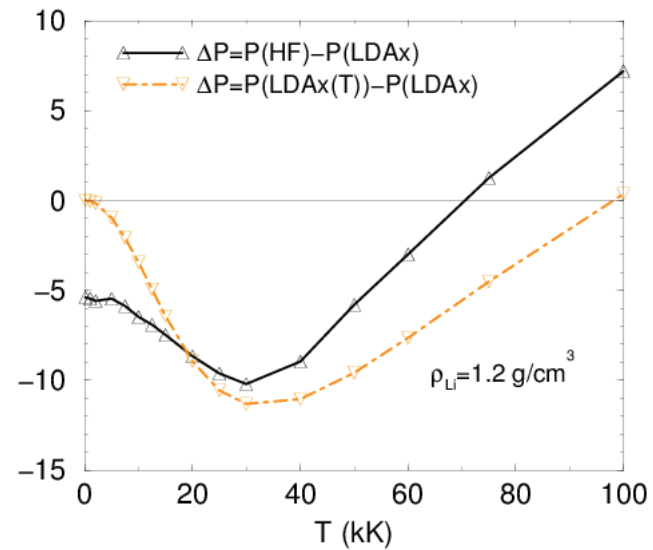
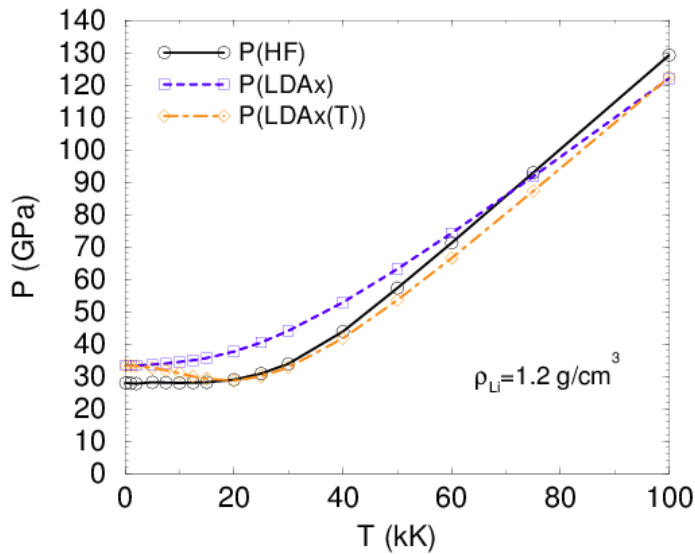
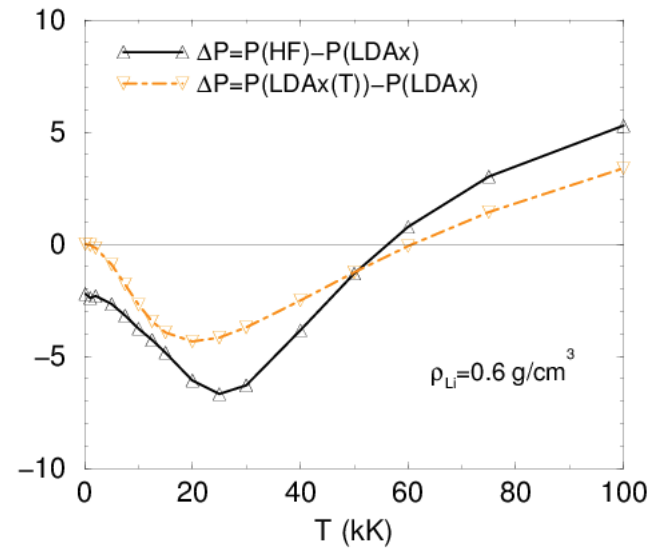
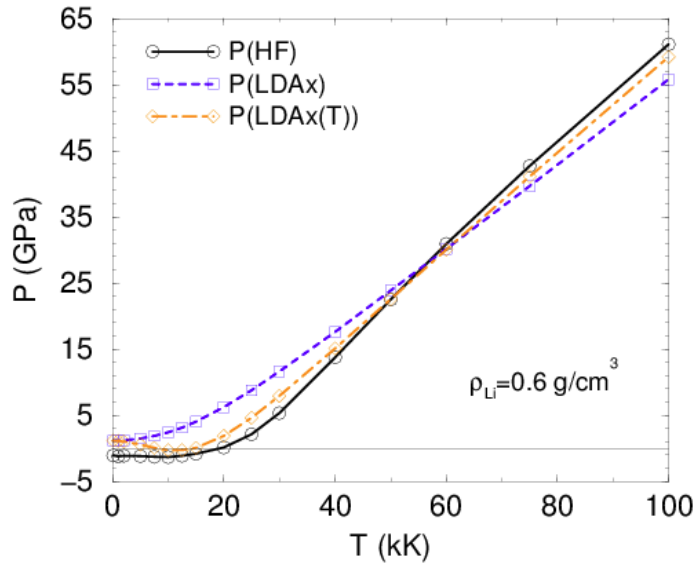
This allows use of standard 1 electron PP



Li ftHF free energy results

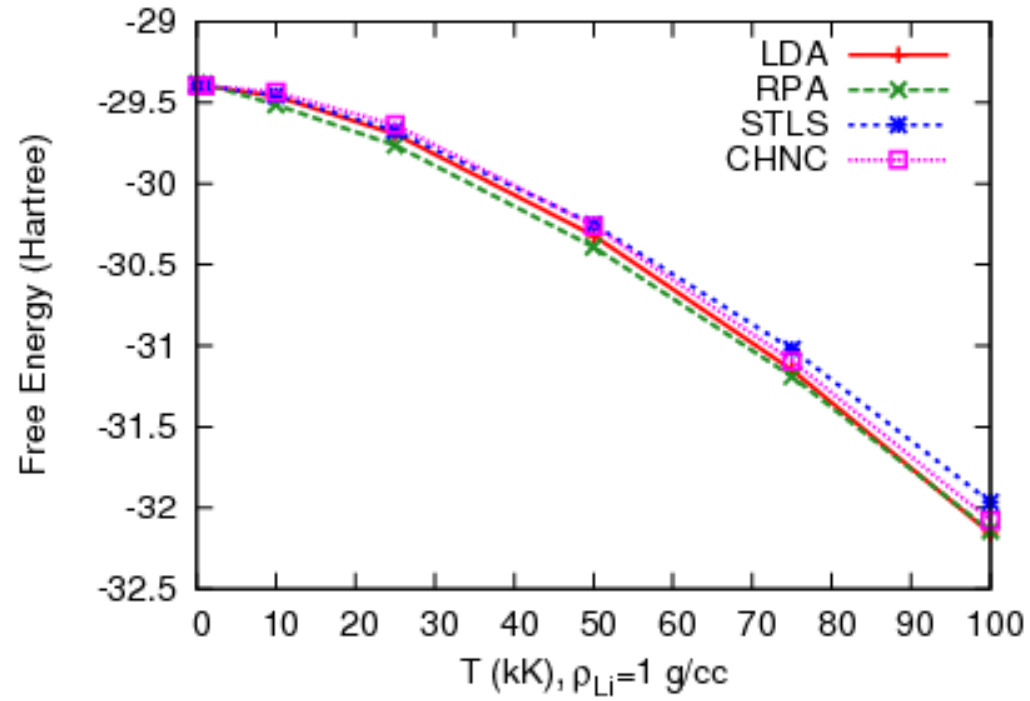


Li ftHF pressure results



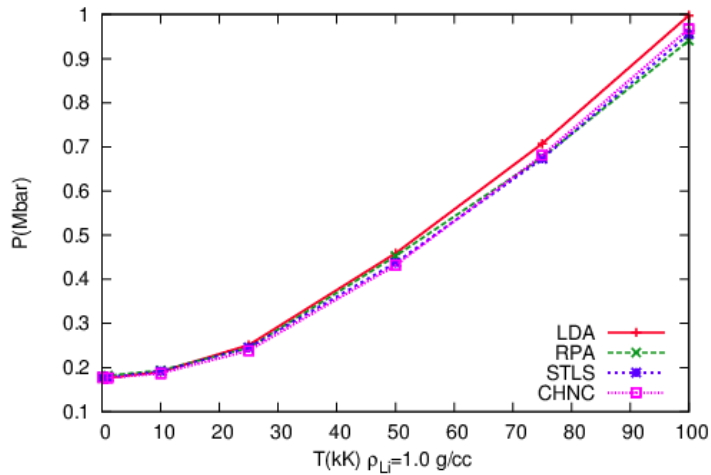
Finite temperature XC results

Li F_{xc} - LDA free energy

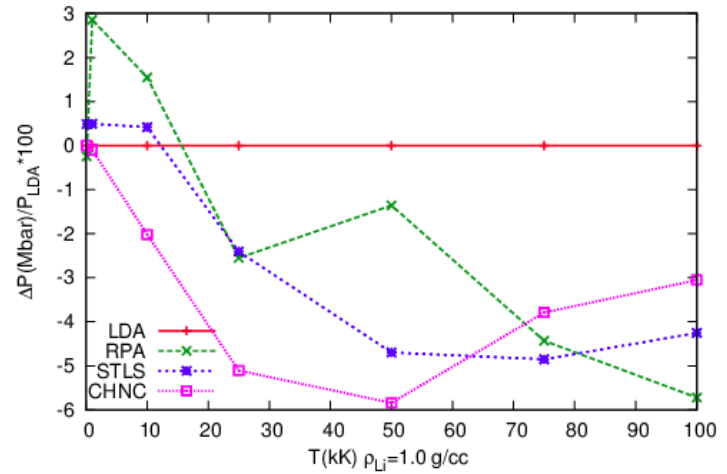
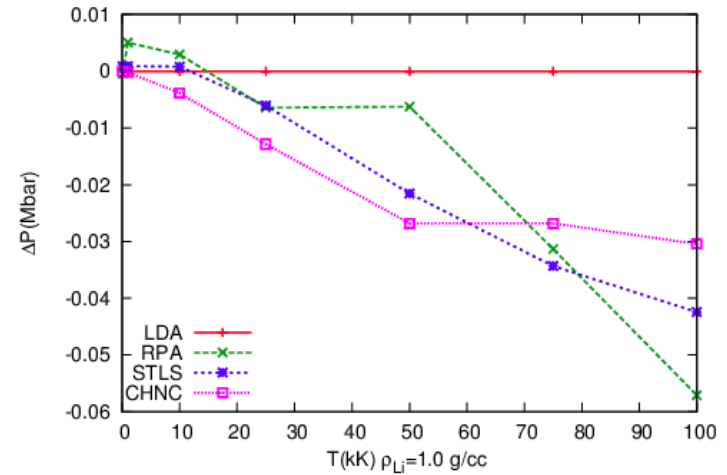


Free energy for ground state LDA and 3 ftXC LDA functionals.

Li LDA pressure



Pressure results for bcc Li at 1 g/cc up to 100 kK. All temperature dependent functionals show about 5% lowering of the pressure at 100 kK.



ftXC beyond LDA

Consider the PBE functional for exchange and correlation.

Replace the uniform energy densities by the finite temperature versions.

$$\varepsilon_x, \varepsilon_c \longrightarrow f_x, f_c$$

The constraint based parameters of the enhancement factors are taken to be temperature independent.

Pressure in MD

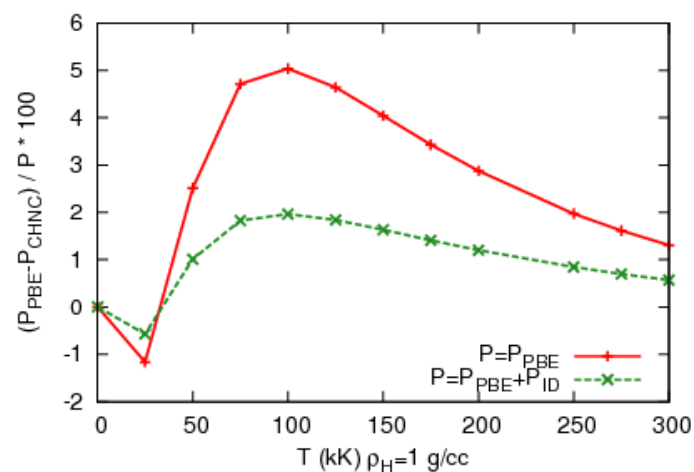
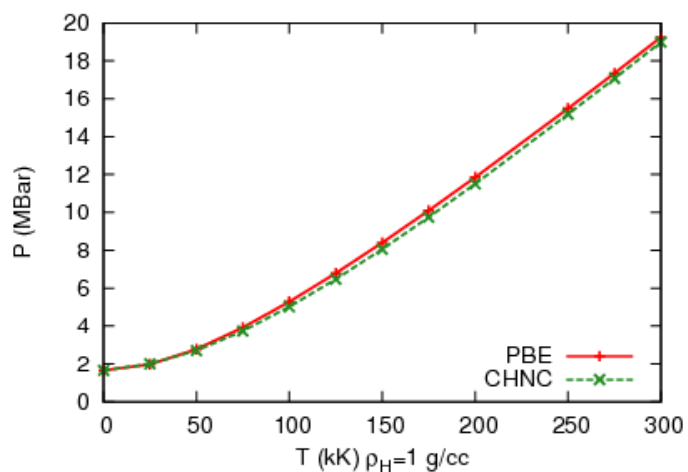
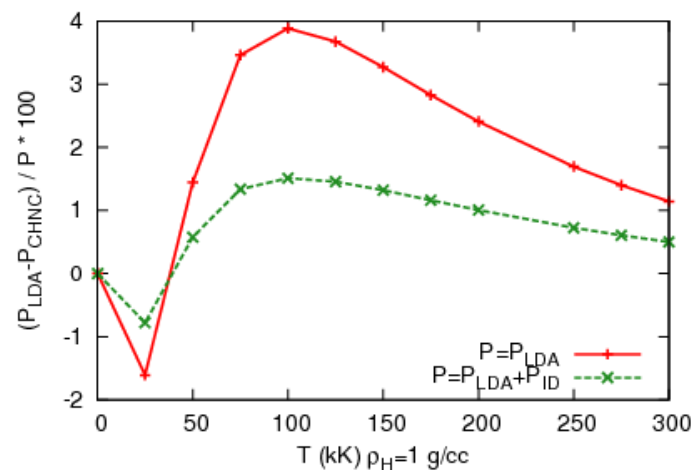
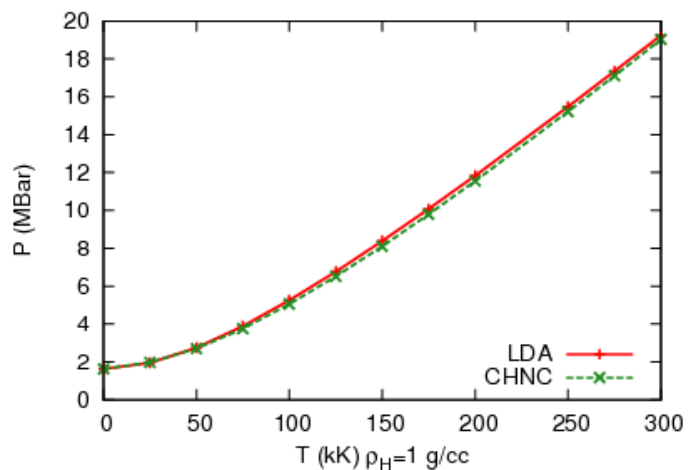
$$P = P_{ID} - \frac{\partial F^{int}}{\partial V}$$

$$P_{ID} = \frac{Nk_B T}{V}$$

Simple cubic hydrogen $\rho_H = 1$ g/cc.

Pressure and percent difference, for LDA and PBE.

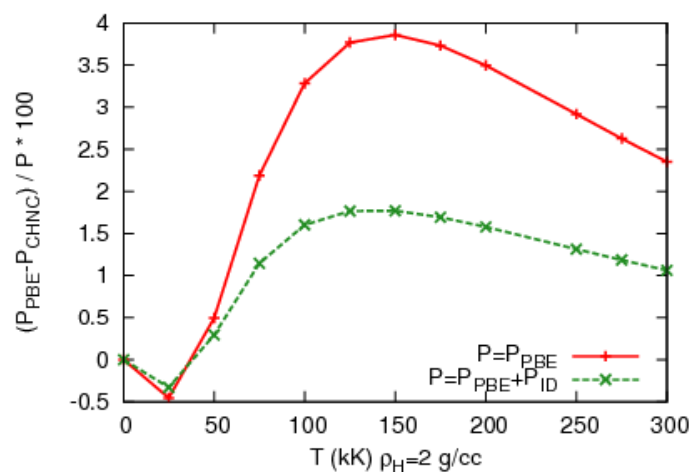
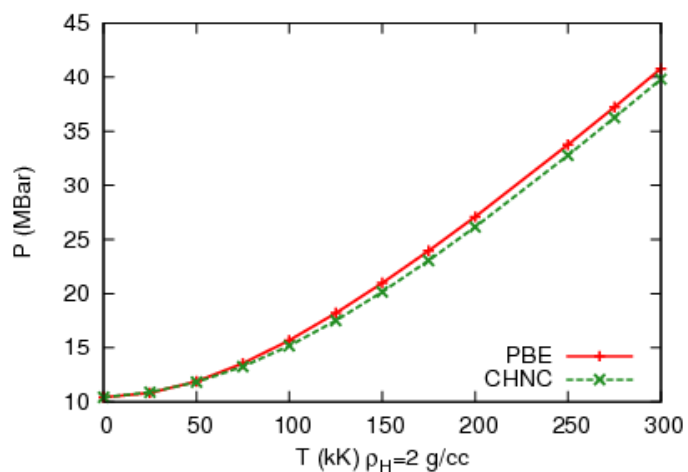
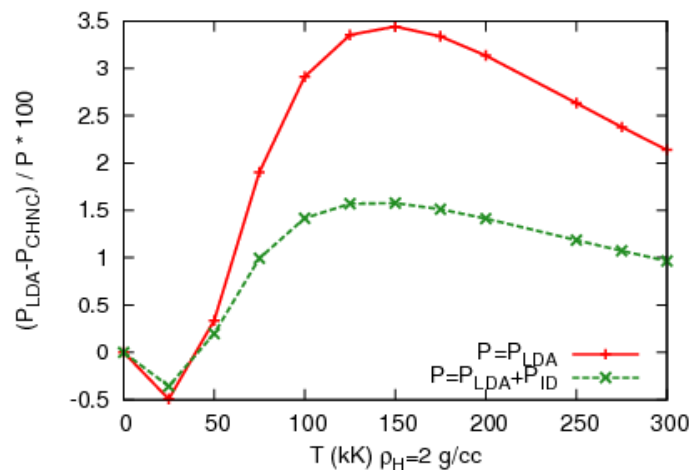
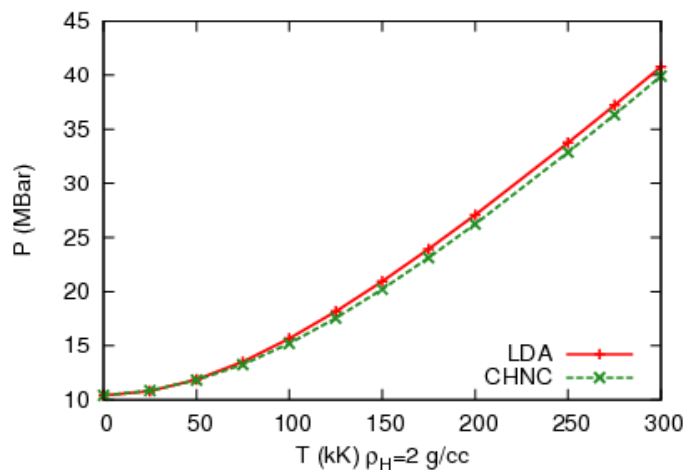
Green is minimum percent difference and red is maximum, for functional.



Simple cubic hydrogen $\rho_H = 2$ g/cc.

Pressure and percent difference, for LDA and PBE.

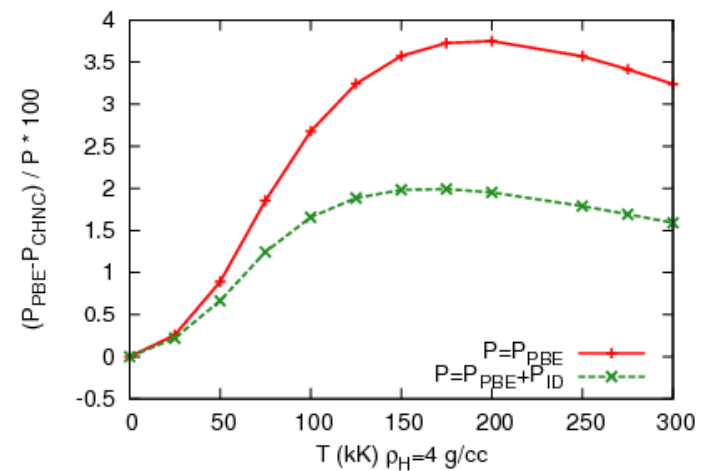
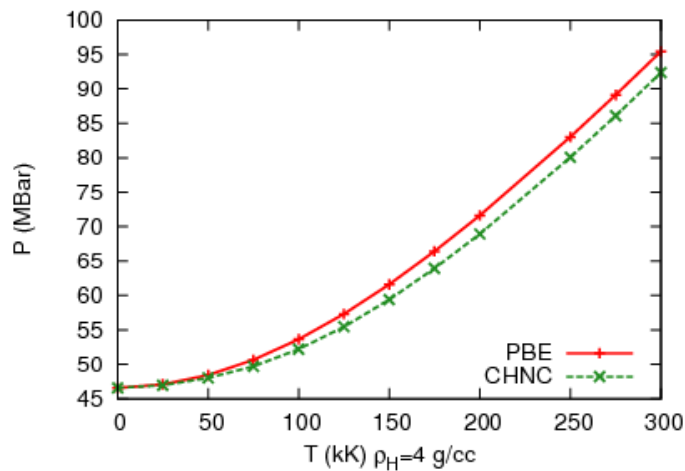
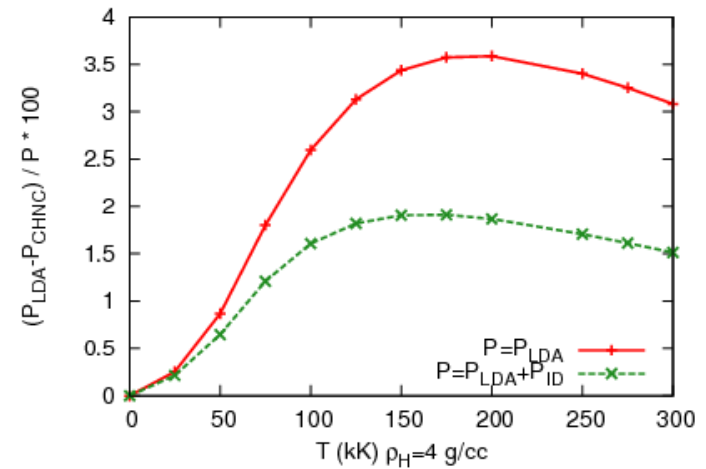
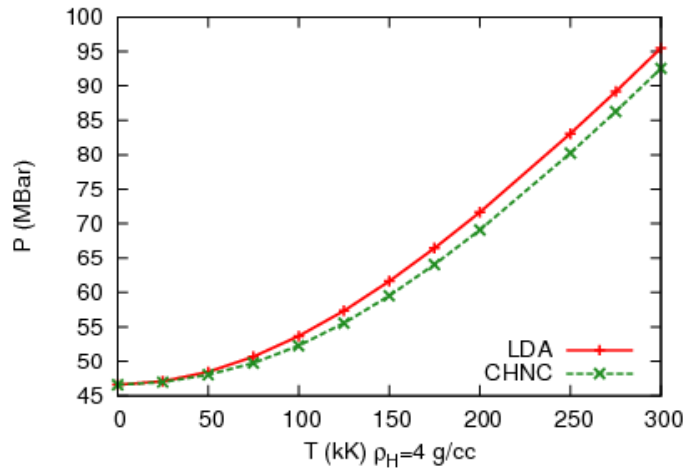
Green is minimum percent difference and red is maximum, for functional.



Simple cubic hydrogen $\rho_H = 4$ g/cc.

Pressure and percent difference, for LDA and PBE.

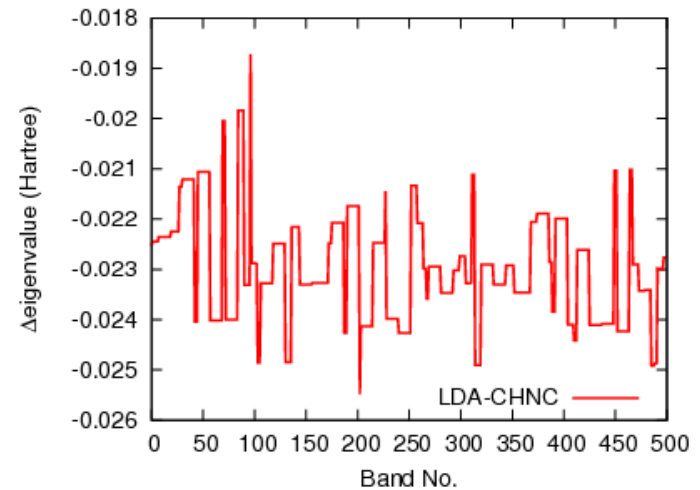
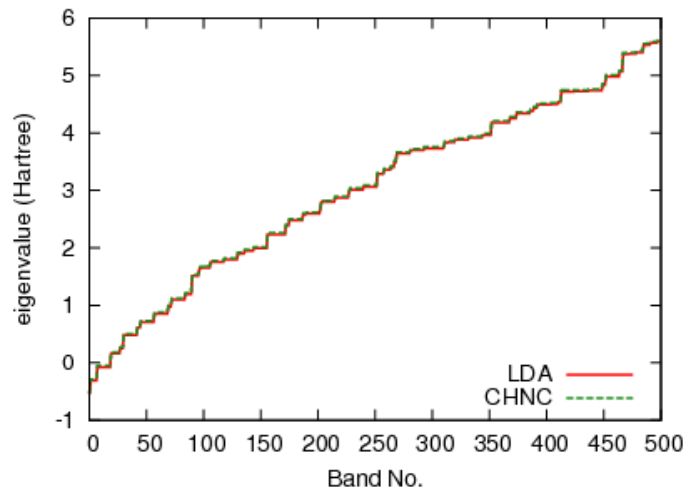
Green is minimum percent difference and red is maximum, for functional.



Temperature dependent XC results for eigenvalues.

Simple cubic hydrogen $\rho_H = 0.981805$ g/cc, $T = 95250K$.

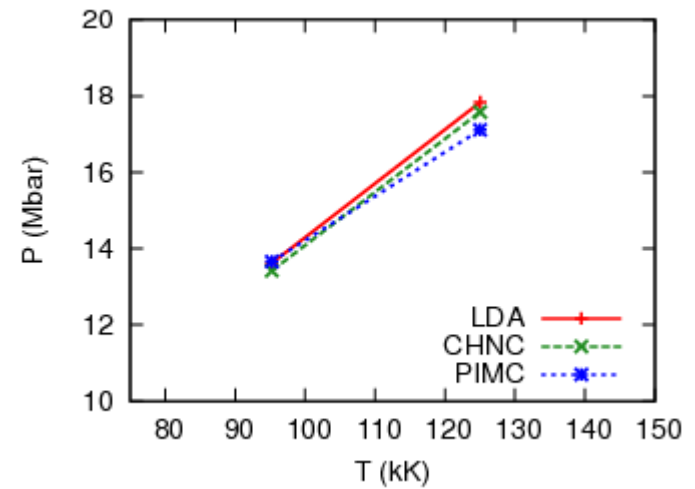
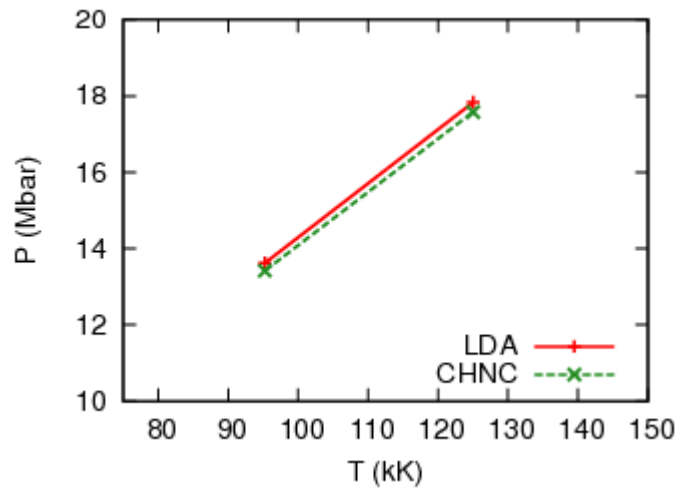
64 atom Gamma point calculation with 500 bands.



Temperature dependent XC QMD results.

Deuterium $\rho_D = 1.96361$ g/cc, at $T = 95250, 125000K$.

64 atom Gamma point calculation.



Summary and Outlook

- Finite temperature exchange-correlation functionals are in infancy with respect to ground state functions.
- This is in part due to lack of high quality LDA data, and lack of benchmark systems.
- Finite temperature Hartree-Fock provides one means of benchmarks for exchange, quantum chemistry post-HF procedures may provide benchmarks for correlation.
- Finite temperature functionals add no real additional cost to DFT methods.
- High accuracy DFT calculations in warm dense matter will require temperature dependent exchange-correlation functionals.

Thank You!

References

1. HEDLP Basic Research Needs Workshop Report, Nov. 15-18, (2009)
2. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)
3. W. Kohn and L.J. Sham, Phys. Rev. 140, A1133 (1965)
4. D.M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980)
5. J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)
6. J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
7. N.D. Mermin, Phys. Rev. 137, A1441 (1965)
8. M.A. Pokrant, Phys. Rev. A 16, 413 (1977)
9. U. Gupta and A.K. Rajagopal, Phys. Rev. A 22, 2792 (1980)
10. E. Dunlap and D.J.W. Geldart, Can. J. Phys. 72, 1-6 (1994)
M.L. Glasser, D.J.W. Geldart, and E. Dunlap, Can. J. Phys. 72, 7-13 (1994)
11. F. Perrot and M.W.C. Dharma-wardana, Phys. Rev. A 30, 2619 (1984)
12. S. Tanaka and S. Ichimaru, J. Phys. Soc. Jpn. 55, 2278 (1986)
13. F. Perrot and M.W.C. Dharma-wardana, Phys. Rev. B 62, 16536 (2000)
14. N.D. Mermin, Ann. Phys. (NY) 21, 99 (1963)
15. T. Sjostrom, F.E. Harris, and S.B. Trickey, Phys. Rev. B 85, 045125 (2012)
16. S.X. Hu, B. Militzer, V.N. Goncharov, and S. Skupsky, Phys. Rev. B 84, 224109 (2011)