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Gradient corrections to the exchange-correlation free energy

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We develop the first order gradient correction to the exchange-correlation free energy of the homogeneous electron gas for use in finite temperature density functional calculations. Based on this we propose and implement a simple temperature dependent extension for functionals beyond the local density approximation. These finite temperature functionals show improvement over zero temperature functionals as compared to path integral Monte Carlo calculations for deuterium equations of state and perform without computational cost increase compared to zero temperature functionals and so should be used for finite temperature calculations. While the present functionals are valid at all temperatures including zero, non-negligible difference with zero temperature functionals begin at temperatures above 10000 K.

PACS numbers:

I. INTRODUCTION

Understanding of matter in extreme conditions represents a significant and current challenge of high energy density physics^{1,2}. Some particular systems of interest include dense astrophysical plasmas as exist in the interiors of giant planets, as well as warm dense matter, which is increasingly studied in high energy density laboratory experiments. In these conditions of elevated temperature and density relative to the ambient condensed matter state, ions can be strongly coupled and electrons are at least partially degenerate. These conditions have proven difficult to describe theoretically and necessitate numeric simulations³.

One key approach is molecular dynamics simulations via density functional theory (DFT). In this approach the ions are treated classically and propagated according to Newton's equations where the force is determined from the ions interaction with each other and the electron density. The electron density is solved for at each ionic configuration in accord with the Born-Oppenheimer approximation using DFT methods. In particular the electron free energy is minimized subject to conservation of the number of electrons in order to determine the electron density. This free energy is given by the density functional

$$F[n] = F_s[n] + F_H[n] + F_{xc}[n] + F_{ei}[n] \quad (1)$$

where F_s is the non-interacting free energy comprised of both kinetic and entropic parts, F_H is the Hartree energy or direct Coulomb interaction between the electrons, F_{ei} is the electron-ion Coulomb interaction, and F_{xc} is defined as the remainder of the total free energy, which includes the quantum mechanical exchange and correlation as well as the excess kinetic and entropic terms. F_{xc} is a key contribution for which there is not an exact expression and, hence, it must be approximated by a density functional that is in general temperature dependent. However, while the DFT approach is increasingly used to study higher temperature systems⁴⁻⁶, zero temperature exchange-correlation functionals are most commonly em-

ployed, even at significant temperature, as opposed to explicitly temperature dependent functionals.

Recently fits were provided for F_{xc} in the local density approximation (LDA)⁷ which is the simplest type of density functional. At zero temperature the LDA has seen significant improvements made upon it over the past 40 years. In the first step beyond LDA density gradient expansions were examined, then generalized gradient approximations were developed, and later even more complex, orbital-dependent functionals were considered^{8,9}. While a similar effort has not been seen at finite temperature, Geldart and co-workers¹⁰ did derive the gradient expansion for the exchange only contribution. In this paper we examine the gradient expansion for the full exchange-correlation functional and based on that provide a simple finite temperature extension for generalized gradient functionals. In addition we perform self-consistent calculations to determine the overall importance of temperature dependence in exchange-correlation functionals.

II. GRADIENT CORRECTIONS TO THE EXCHANGE-CORRELATION FREE ENERGY

A. Development of the gradient expansion

In order to determine the gradient expansion we consider the relation of density functional theory to dielectric theory for the uniform electron gas. Following Kohn and Sham we first write the gradient expansion of the exchange-correlation free energy as

$$F_{xc}[n] = \int d\mathbf{r} f_{xc}(n, T) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} g_{xc}^{(2)}(n, T) |\nabla n(\mathbf{r})|^2 + \dots, \quad (2)$$

where n and T are the electron density and temperature. The first term of the RHS on its own is the local density approximation, with f_{xc} the exchange-correlation free energy per electron in the uniform electron gas. The coefficient of the gradient correction term, $g_{xc}^{(2)}$, is the piece

determined in this work, and it is related to the static local field correction $G(k)$ of the homogeneous electron gas by^{11–14}

$$g_{xc}^{(2)}(n, T) = \frac{1}{2} \left(\frac{\partial^2 [-v_k G(k)]}{\partial k^2} \right)_{k \rightarrow 0} = -4\pi e^2 \delta / k_F^4, \quad (3)$$

where $v_k = 4\pi e^2 / k^2$ is the Coulomb potential, $k_F = (3\pi^2 n)^{1/3}$, and in the second line we consider the small k expansion of $G(k) = \gamma(k/k_F)^2 + \delta(k/k_F)^4 + \dots$. Here the dependence of G , γ and δ on n and T is suppressed for convenience.

It is known that G may be well represented for small and large k , though not for intermediate values, by the function^{15,16}

$$G(q) = A \left(1 - e^{Bq^2} \right) \quad (4)$$

with $q = k/k_F$. Then for small q

$$G(q) = ABq^2 - \frac{1}{2}AB^2q^4 + \dots, \quad (5)$$

and so,

$$\gamma = AB \quad \delta = -AB^2/2. \quad (6)$$

Next from the compressibility sum rule we have

$$\gamma = -\frac{k_F^2}{4\pi e} \frac{\partial^2 (n f_{xc})}{\partial n^2}, \quad (7)$$

which we may evaluate by the recent analytic fits⁷ for f_{xc} which are based on the quantum Monte Carlo (QMC) data¹⁷ for the internal exchange-correlation energies of the homogeneous electron gas at finite temperatures. This leaves us needing still A or B independently to determine δ and hence $g_{xc}^{(2)}$. This is completed then by the relation for the large q limit of $G(q)$ to the pair distribution function¹⁸, $g(r)$,

$$A = G(q \rightarrow \infty) = 1 - g(0). \quad (8)$$

In order to determine the gradient coefficient, we now need only $g(0)$ further (again T and n dependence is suppressed). This we obtain from the same QMC results of Brown et al.¹⁷ that the f_{xc} fit is based on, in which they also provide $g(r)$ for the unpolarized system. However, their grid does not include $g(0)$ so we have extrapolated their $g(r)$ data to obtain $g(0)$ by fitting $g(r) = a + ar + br^2$ for small r in accord with the cusp condition¹⁹ at each density and temperature point given in the QMC results. Next we perform a separate fit for $g(0)$ as a function of r_s at each temperature $t = k_B T / E_F = \{0.0625, 0.125, 0.25, 0.5, 1.0, 2.0, 4.0, 8.0\}$, according to the following equation²⁰

$$g(0) = \frac{1}{2} \frac{1 + a\sqrt{r_s} + br_s}{1 + cr_s + dr_s^3} \quad (9)$$

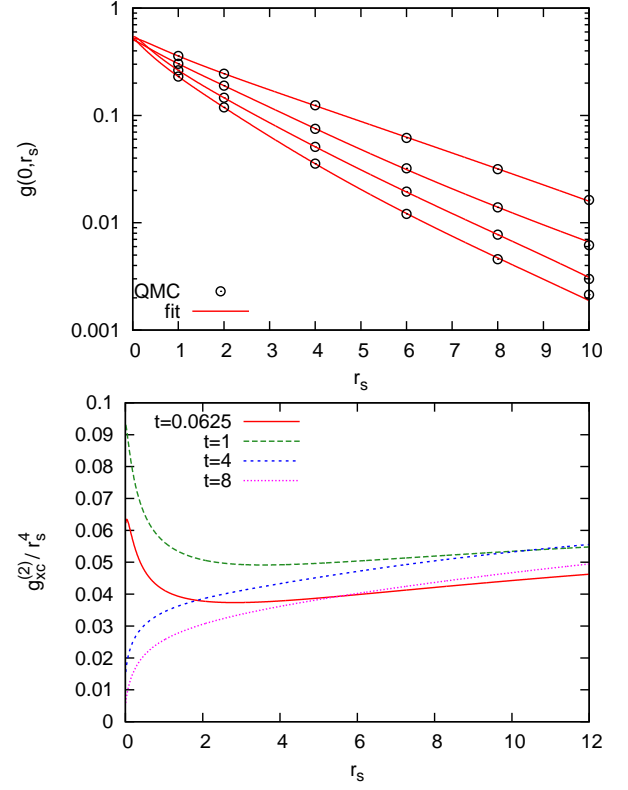


FIG. 1: Top: QMC data points for $g(0)$ and our fit as a function of r_s for a given $t = k_B T / E_F$, with the curves being $t = 8, 4, 0.0625, 1$ from top to bottom. Bottom: Coefficient of the gradient expansion $g_{xc}^{(2)}$, for given t as derived from QMC fits for f_{xc} ⁷ and $g(0)$ (top).

The fit results are plotted for selected t in the upper panel of Fig. 1 along with the $g(0)$ extrapolated from the QMC data. Then using Eqs. (3)–(8) along with the fits for $g(0)$ we find $g_{xc}^{(2)}$ as a function of r_s for the given t values. The results are plotted for $t = 0.0625, 1, 4, 8$ in the lower panel of Fig. 1. It is worth noting that the $g(0)$ curve for $t = 0.0625$ is nearly identical to that for the $t = 0$ QMC result of Spink et al.²⁰.

B. Analysis of the temperature dependence

To examine the effects of the temperature dependent gradient coefficient, $g_{xc}^{(2)}$, we calculate its relative contributions on various systems at different temperatures and densities. Specifically we solve all electron hydrogen, aluminum, and iron systems at each t for which we have fit $g_{xc}^{(2)}$ and at selected densities from ambient to several times ambient compression. We first solve the system in an average atom model²¹ using an orbital-free functional for the non-interacting contribution, namely the finite temperature Thomas-Fermi plus von Weizsäcker approximation²², and a zero temperature LDA for the exchange-correlation energy. The average atom model

consists of a nucleus at the center of a spherical cavity of volume that is determined by prescribing the density of the material. The spherically symmetric electron density is then found by density functional theory, subject to the condition that the integrated electron density in the cavity is equal to the charge of the nucleus. This gives us a realistic average density around each ion. Then using this density we evaluate the different exchange-correlation free energy contributions to determine their relative effects, with the results shown in Fig. 2. The relative effect of the temperature dependence of the local density term is shown in the red curves given by

$$\frac{\int d\mathbf{r} n (f_{xc} - \epsilon_{xc})}{\int d\mathbf{r} n \epsilon_{xc}}, \quad (10)$$

where $\epsilon_{xc} = f_{xc}(t=0)$ is the zero temperature exchange-correlation energy. While the total relative contribution due to the gradient term as well as that portion due to its finite temperature contribution are given by

$$\frac{\int d\mathbf{r} |\nabla n|^2 g_{xc}^{(2)}/2}{\int d\mathbf{r} n f_{xc}}, \quad (11)$$

$$\frac{\int d\mathbf{r} |\nabla n|^2 [g_{xc}^{(2)}(t) - g_{xc}^{(2)}(t=0)]/2}{\int d\mathbf{r} n f_{xc}}, \quad (12)$$

and shown in the blue and green curves respectively. These results show that at high temperature, dependence of the local density term provides the dominant correction, however at low temperature the gradient correction is most important. By comparison the temperature dependent correction coming from the gradient term is always negligible. This is not unexpected when considering Fig. 1 where for $g_{xc}^{(2)}$ although the different temperature curves do vary they remain relatively close to the lowest temperature case for all t .

C. Beyond the gradient expansion

In considering an improved gradient corrected functional for the exchange-correlation free energy we reiterate that the previous analysis shows that temperature dependence in the gradient term is in fact negligible. That is using a zero temperature gradient correction at finite temperature is in fact a good approximation. However this applies only to the gradient term, the local density term does show a significant temperature dependence and a proper finite temperature functional should be used in that case. It is also clear, though, that gradient corrections are important at low temperature. Beyond this generality it is well known from zero temperature development that gradient expansions for the exchange-correlation yield poor results often not better or worse than the local density approximation^{11,23,24}. Generalized gradient approximations (GGAs), such as PBE²⁵

have proven to perform significantly better than gradient expansions at zero temperature. Given the quality GGA's available at zero temperature and with our current analysis of the gradient corrections *non*-temperature dependence, we therefore propose a temperature dependent GGA as follows

$$F_{xc}^{GGA}[n] = E_{xc}^{GGA}[n] - E_{xc}^{LDA}[n] + F_{xc}^{LDA}[n]. \quad (13)$$

Here the zero temperature GGA term, $E_{xc}^{GGA}[n]$ includes the local density contribution. Then the zero temperature local density contribution is removed and replaced with the finite temperature version. Thus capturing all significant temperature and density gradient dependence in the exchange-correlation free energy.

D. Self-consistent results

We have implemented the finite temperature exchange-correlation free energy in both the local density approximation as given in Ref. 7, as well as in finite temperature modification of the zero temperature PBE functional according to Eq. (13) in the plane wave density functional theory code Quantum-Espresso²⁶ as well as in our orbital-free code. We then applied this to cases of warm dense deuterium, for which there exists path integral Monte Carlo (PIMC) equation of state results²⁷ that do not require an approximate input for the exchange-correlation free energy.

Specifically we ran both Kohn-Sham and orbital-free DFT based molecular dynamics simulations for warm dense deuterium. For the Kohn-Sham calculations a non-local pseudopotential was used and a local pseudopotential was used for the orbital-free calculations, these are as given in Ref. 22. The orbital-free functional is that given in Ref. 28. In both cases 128 atoms were simulated with periodic boundary conditions for at least 5000 time steps, where the time step varied from 0.5 fs at 10 kK to 0.0125 fs at 1000 kK. Also only the gamma-point was used in the Kohn-Sham calculations.

In Fig. 3 we plot the resulting pressure relative to the pressure from a zero temperature LDA calculation for deuterium at 4.05 g/cc and up to nearly 200 kK (1000 K = 1 kK), where we have subtracting out the ion kinetic pressure $P_{ion} = N_{ion}k_B T/V$. Using the standard zero temperature PBE it is clear that the gradient correction becomes less and less as temperature increases, by contrast both finite temperature functionals show first a small increase in pressure at low temperature, then a more significant decrease in pressure as the temperature is elevated to 200 kK. This can be understood in terms of f_{xc} , which is always negatively valued. For a given density, f_{xc} becomes slightly more negative to a minimum, and then increase towards zero as temperature becomes very high. The net result at high temperature then is to reduce the exchange-correlation contribution to the pressure. Again we note the gradient effects diminish with increasing temperature.

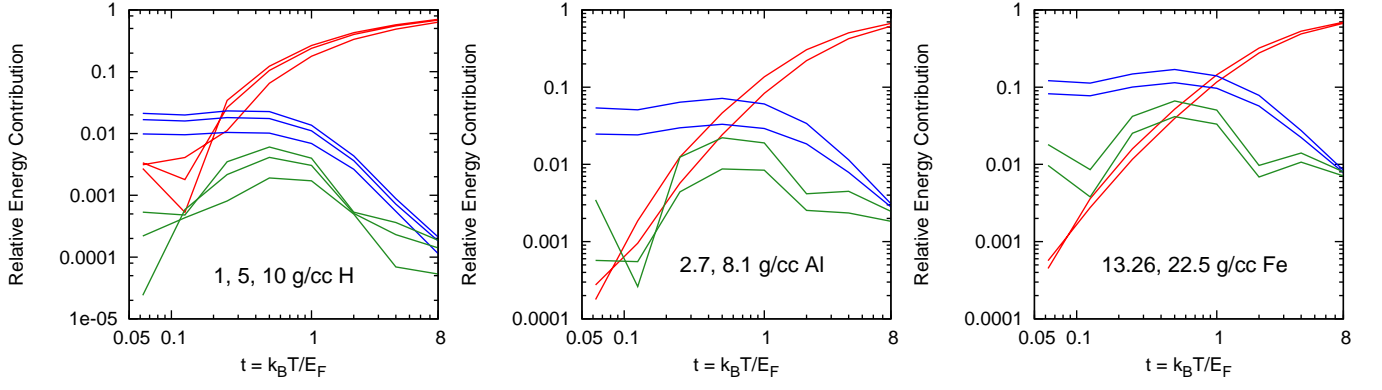


FIG. 2: Relative effects of the terms of the gradient expansion for the exchange-correlation free energy. The temperature dependence of the local density term becomes dominant at high temperatures (red curves, Eq. (10)), and the gradient term is most important at lower temperatures (blue curves, Eq. (11)), while the temperature dependence of the gradient term is always negligible (green curves, Eq. (12)). Different curves of the same color represent the different densities.

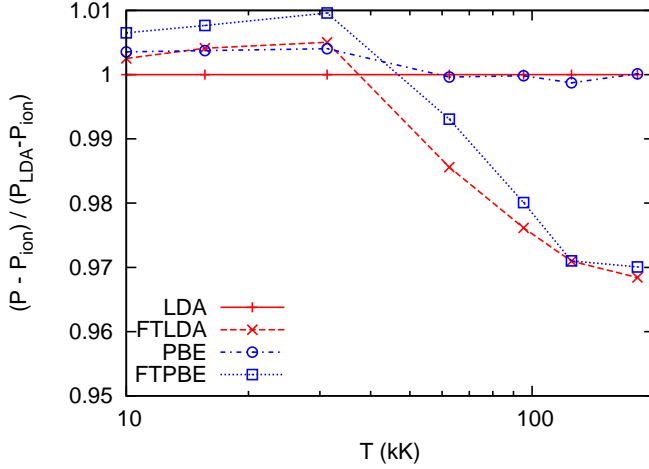


FIG. 3: Deuterium pressure, excluding the ion kinetic contribution, at 4.05 g/cc for the LDA and GGA functionals with and without temperature dependence plotted relative to the zero temperature LDA results. Increased significance of the temperature dependent functionals, and decreased effect from the gradient terms for higher temperatures are shown.

In order to consider the temperature effect in the warm dense regime, we consider just the LDA functional for deuterium at 4.05 g/cc and at 10.0 g/cc. These results are shown in Fig. 4 along with the PIMC data²⁷. In order to extend the calculation from 200 kK up to 1000 kK in temperature we make use of an orbital-free density functional calculation. The plotted results are then the total pressure relative to the total pressure from a zero temperature LDA exchange-correlation calculation in either Kohn-Sham or orbital-free method, hence the LDA and OF LDA curves are exactly one. Note the PIMC results are shown relative to OF LDA. The orbital-free method is seen to be justified as here it overlaps well with the highest temperature Kohn-Sham calculations. These relative pressure results do show better agreement of the

temperature dependent functional to that of the PIMC results versus those of the zero temperature functional at both densities. We can see in these cases there is a maximum difference of 1-2% in the total pressure in the warm dense regime. This effect then diminishes to zero at high temperatures as the total exchange-correlation contribution to the pressure becomes completely negligible compared to the kinetic contributions of the electrons and ions.

Finally we consider the effect of temperature dependent exchange-correlation on the eigenspectrum of a real system. In the upper panel of Fig. 5 we plot for a single random configuration of 128 deuterium atoms at 4.05 g/cc and 181.8 kK the difference in corresponding eigenvalues when using different functionals. The difference between finite temperature and zero temperature functionals here produces about a five times greater difference than the difference between PBE and LDA whether in the finite temperature or zero temperature versions. In the lower panel the ratio of adjacent eigenvalue differences, $(\epsilon_{n+1} - \epsilon_n)$, is taken between the different functionals. The average is clearly seen to always be 1, but there is non-negligible spread seen which is quantified by the standard deviation of 0.12 and 0.09, for the finite temperature to zero temperature functional results of LDA and PBE respectively, and 0.15 and 0.12, for the PBE to LDA results for zero temperature and finite temperature functionals respectively. The significance in addressing the eigenspectrum is that these orbitals (eigenfunctions) and eigenvalues are directly used in various calculation such as for the electrical conductivity through the Kubo-Greenwood formalism, in which the differences in energy levels are required. Here we have shown that the primary effect of temperature dependent exchange-correlation is to shift the eigenspectrum, however there are also changes in the relative spacing. Though we have not performed such calculations here, we suggest that such orbital dependent calculations may also be affected by temperature dependent exchange-correlation.

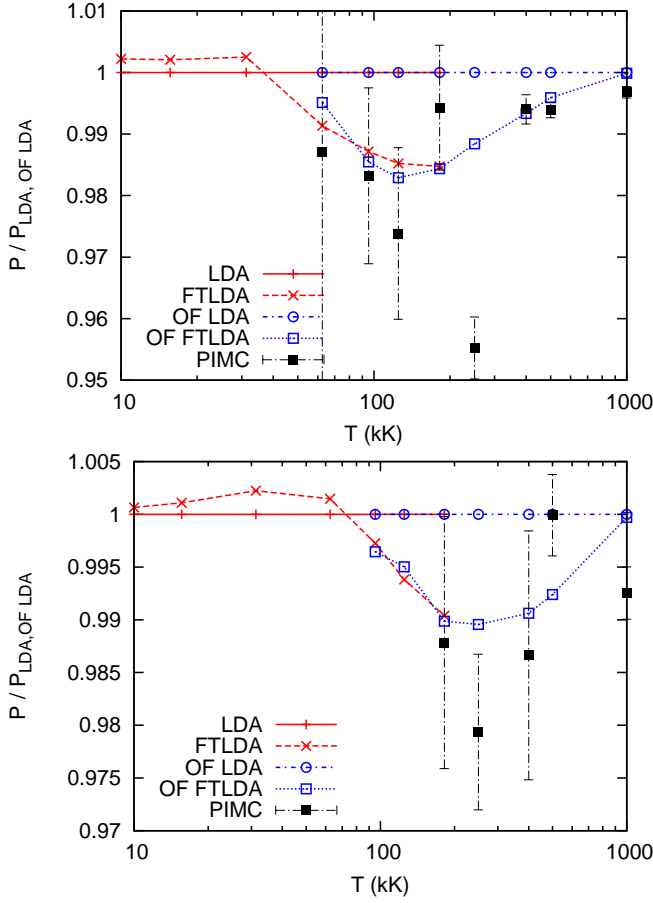


FIG. 4: Deuterium pressure at 4.05 g/cc (top) and 10.0 g/cc (bottom) for the LDA functional with and without temperature dependence, as well as PIMC results, relative to the zero temperature LDA results. At both densities the temperature dependent functional agrees better with the PIMC.

III. SUMMARY

We have derived the finite temperature gradient expansion for the exchange-correlation free energy and then demonstrated that the contribution from the temperature dependence of the gradient term in physical systems is negligible. However the gradient corrections are important at lower temperatures and the finite temperature correction to the local density contribution is important at higher temperatures. We therefore proposed a temperature dependent GGA and showed that the temperature dependence is more significant than gradient dependence in the warm dense matter regime and that better results are achieved using temperature dependent LDA or GGA, as shown by better agreement with PIMC equation of state data for which there is no approximation for the exchange-correlation energy. Finally these finite temperature corrections are easily implemented in any DFT code, through the fit given in Ref. 7 and perform without computational cost increase and so should be used for finite temperature calculations where better accuracy

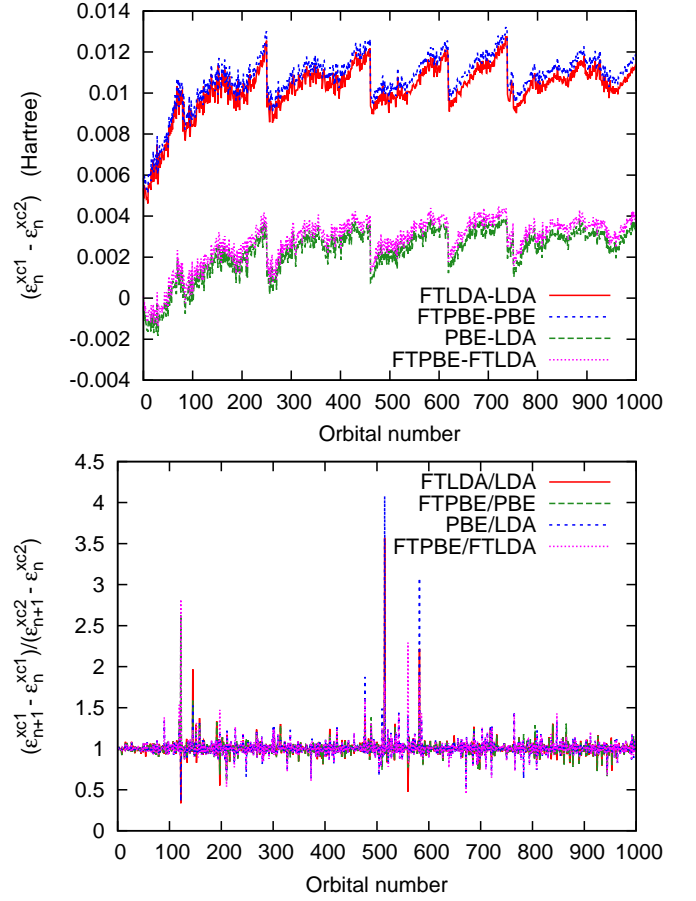


FIG. 5: Differences in corresponding eigenvalue energies between two different exchange-correlation functionals (upper panel) and the ratio of adjacent eigenvalue differences for two functionals (lower panel) are shown for 128 deuterium atoms at 4.05 g/cc and 181.8 kK. The two functional combinations are given in the plot legend. There is non-negligible difference which arises from inclusion of the finite temperature contribution to the exchange-correlation energy.

is desired. We do note that though these finite temperature functionals are valid down to and including zero, for most condensed matter systems below 10000 K, little to no differences will be seen as compared with using zero temperature exchange-correlation functionals.

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