

Thermal Corrections to Density Functional Simulations of Warm Dense Matter

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(Dated: September 11, 2015)

Present density functional calculations of warm dense matter often use the Mermin-Kohn-Sham (MKS) scheme at finite temperature, but employ ground-state approximations to the exchange-correlation (XC) free energy. In the simplest solvable non-trivial model, an asymmetric Hubbard dimer, we calculate the exact many-body energies, the exact Mermin-Kohn-Sham functionals for this system, and extract the exact XC free energy. For moderate temperatures and weak correlation, we show this approximation is excellent, but fails for stronger correlations. We plot various free energy correlation components and the adiabatic connection formula.

Recent decades have seen enormous advances in the use of DFT calculations[1] of warm dense matter, a highly energetic phase of matter that shares properties of solids and plasmas[2]. Materials under the extreme temperatures and pressures necessary to generate WDM can be found in astronomical bodies, within inertial confinement fusion capsules, and during explosions and shock physics experiments[3]. These calculations are used in the description of planetary cores[4, 5], for the development of experimental standards[6, 7], for prediction of material properties[8–10], and in tandem with experiments pushing the boundaries of accessible conditions[11].

In almost all of these calculations, a crucial approximation is made: The exchange-correlation (XC) free energy depends on the temperature[12, 13], but is approximated by a standard ground-state approximation (GSA). Since most calculations are for extended systems, these often (but not always) use the PBE generalized gradient approximation[14]. These Mermin-Kohn-Sham (MKS) [15, 16] calculations predict several key properties, such as the free energy and density for a given distribution of the nuclei, and any properties that can be extracted from these, such as equations of state of materials and Hugoniot shock curves[17]. If the exact temperature-dependent XC free energy were known, such properties would be exact[18]. In some of these calculations, a further approximation is made when response properties are extracted from the thermal KS orbitals[8], but that is not one we examine here. We note that although no-one has shown that the lack of thermal XC corrections is a fatal flaw in a given calculation, the pervasive use of this uncontrolled approximation is an underlying concern.

The only thermal XC approximation commonly used is thermal LDA (TLDA), i.e., a local density approximation using the XC free energy of a uniform gas at finite temperature[16], though recent work has proposed a method that generates gradient corrections to XC[19]. Recent quantum Monte Carlo calculations[20] have been devoted to accurate calculation of the uniform gas XC free energy, and improved parameterizations have resulted[21]. But since chemically realistic calculations require a GGA-level treatment for sufficient accuracy at zero temperature[22], inclusion of thermal effects at the

LDA-level alone can never resolve this question unambiguously (and might even worsen results).

Tremendous progress and insight has been gained in ground-state DFT from use of exactly solvable model systems, against which not just the energy, but also its individual components and the density can be compared. Examples include the benchmark calculations of Umrigar and coworkers for spherical atoms[23], the Hooke's atom[24], and many recent works in time-dependent DFT[25–27]. But even the simplest system, such as an isolated atom with a thermal average of one electron per atom, is difficult to imagine solving exactly as the exact partition function includes sums over *all* electron numbers, with important many-body effects for all $N > 1$. Without an exact solution, it is difficult to determine when the GSA is a good one in MKS calculations.

In the present work, we calculate the exact thermal energy and density of a simple model, an asymmetric two-site Hubbard dimer[28]. We use the site-occupation functional theory[29] to construct an MKS system and calculate the KS quantities. Subtraction yields exact XC free energies and their individual components. We choose parameters loosely corresponding to the warm dense matter regime and show that both free energies and densities are highly accurate in this regime, suggesting that errors due to GSA are typically irrelevant. We also plot several key correlation components, illustrating recent theorems, and show what happens when correlation is stronger.

We begin with thermal DFT[15]. For an ensemble in thermal equilibrium with a bath at temperature τ , the free energy may be found from:

$$A = \min_n \left(F[n] + \int d^3r (v(\mathbf{r}) - \mu) \right) \quad (1)$$

where $v(\mathbf{r})$ is the one-body potential, μ is the chemical potential, and the minimization is over all positive densities with finite kinetic energy. The Mermin functional is

$$F[n] = \min_{\Gamma \rightarrow n} Tr \left\{ (\hat{T} + \hat{V}_{ee} - \tau \hat{S}) \Gamma \right\} \quad (2)$$

where \hat{T} is the kinetic energy operator, \hat{V}_{ee} the electron-electron repulsion operator, \hat{S} the entropy operator, and

the minimization is over all statistical density matrices with density $n(\mathbf{r})$. The average particle number is determined uniquely by μ . Then one can construct the MKS equations[18]

$$\left\{ -\frac{1}{2}\nabla^2 + v_s^\tau(\mathbf{r}) \right\} \phi_i^\tau(\mathbf{r}) = \epsilon_i^\tau \phi_i^\tau(\mathbf{r}), \quad (3)$$

$$v_s^\tau[n](\mathbf{r}) = v(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{\text{xc}}^\tau[n](\mathbf{r}), \quad (4)$$

where $v_H[n](\mathbf{r})$ is just the usual Hartree potential. The density is the sum over all orbitals,

$$n^\tau(\mathbf{r}) = \sum_i f_i^\tau |\phi_i^\tau(\mathbf{r})|^2, \quad (5)$$

where $f_i^\tau = (1 + e^{(\epsilon_i^\tau - \mu)/\tau})^{-1}$ are their Fermi occupations. When solved with the exact $v_{\text{xc}}^\tau[n](\mathbf{r})$, these reproduce the exact density of the physical system.

We apply this technology to the asymmetric Hubbard dimer. The DFT version of a lattice model is called site-occupation functional theory (SOFT)[30] and has been thoroughly explained for the ground state in a recent review[28]. The Hamiltonian is

$$\hat{H} = -t \sum_\sigma (\hat{c}_{1\sigma}^\dagger \hat{c}_{2\sigma} + h.c.) + \sum_i (U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + v_i \hat{n}_i) \quad (6)$$

where $\hat{c}^\dagger(\hat{c})$ are electron creation (annihilation) operators and $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$ are number operators, t is the strength of electron hopping between sites, U the Coulomb repulsion when two electrons are on the same site, and v_i is the external potential on each site. Without loss of generality, we choose $v_1 + v_2 = 0$, $\Delta v = v_2 - v_1$, and denote the occupation difference $\Delta n = n_2 - n_1$. The hopping term plays a role logically analogous to the kinetic energy of Eq. (2) but it is in fact always negative. We choose units where $2t = 1$ and we vary U and Δv .

Next we calculate the finite-temperature many-body energy and density for the Hubbard dimer. Begin with the (grand-canonical) partition function

$$Z_G = \sum_{i,N} e^{(\mu N - E_i(N))/\tau} \quad (7)$$

where $E_i(N)$ is the i -th energy level of the Hamiltonian with N particles. The energy for 0 through 4 particles are calculated explicitly, yielding the exact partition function and, from that, the exact free energy via $A = \mu N - \tau \log(Z_G)$. We can also calculate the exact occupation difference from the ensemble average of $\hat{\Delta n}$,

$$\Delta n = Z_G^{-1} \sum_{i,N} \Delta n_{i,N} e^{(\mu N - E_{i,N})/\tau}. \quad (8)$$

where $\Delta n_{i,N}$ is the occupation difference of the i -th state for N particles.

To construct the MKS system for the Hubbard dimer within SOFT, we simply repeat the exercise for $U = 0$, i.e., a tight-binding dimer. Then

$$\Delta n = -2 \sin \phi \tanh \alpha \quad (9)$$

where $\alpha = (4\tau \cos \phi)^{-1}$, $\sin \phi = x/\sqrt{1+x^2}$, τ is in units of $2t$, and $x = \Delta v_s/2t$. This inverse of this relation yields $\Delta v_s(\Delta n)$, the exact KS site-potential difference that yields a given occupation density. The Hartree(-exchange) energy (in the standard DFT definition) is (for this model)

$$U_{\text{HX}}(\Delta n) = \frac{U}{2} \left(1 + \frac{\Delta n^2}{4} \right) \quad (10)$$

and this definition is independent of the temperature. The thermal MKS hopping energy is just that of this tight-binding problem:

$$T_s^\tau(\Delta n)/(2t) = \Delta n/x(\Delta n) \quad (11)$$

and the MKS entropy is

$$S_s^\tau(\Delta n) = \log \{ 16 \cosh^4 \alpha - \tanh \alpha / (4\tau \cos \phi) \} \quad (12)$$

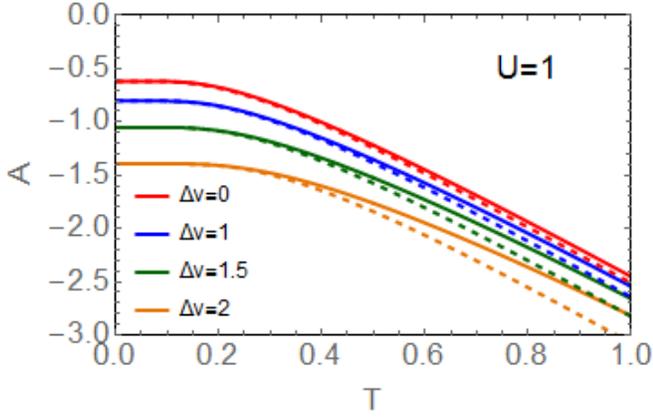
With these simple results, we can now extract the correlation free energy for this problem as

$$A_C^\tau = (T_I^\tau - T_s^\tau) - \tau(S^\tau - S_s^\tau) + (V_{\text{ee}}^\tau - U_{\text{HX}}) \quad (13)$$

where T^τ , S^τ , and V_{ee}^τ are calculated from the many-body problem. A_C^τ is what we study and we know of no other exact calculation of this quantity for a finite system.

There is in fact a vast parameter space to be explored in this model as, choosing $2t = 1$, we can vary U , Δv , τ , and $\langle N \rangle$. Our focus is on testing thermal calculations using ground-state approximations. We will always choose $\langle N \rangle = 2$, which in fact means $\mu = 0$ here[31]. We focus on the corner $U, \tau < 1$, so as to mimic WDM calculations of weakly correlated materials. In particular, we avoid warming our model so much that properties are strongly influenced by the very limited Hilbert space. At least at zero temperature and in the symmetric case, the distinction between weak and strong correlation is very well characterized. An expansion in powers of U converges absolutely up to $U = 4t$ and diverges beyond that; similarly, an expansion in $1/U$ converges absolutely only for $U > 4t$.

In Fig. 1, we plot the free energy as a function of temperature for several different values of Δv , both exactly and replacing $A_C^\tau(\Delta n)$ with $E_C(\Delta n) = A_C^{\tau=0}(\Delta n)$ for $U = 1$, evaluated on the exact Δn . We see that the error is extremely small, for $\tau \lesssim 0.5$. Moreover, trends are very well reproduced by the GSA values, and fractional errors shrink for large τ . This suggests that free energies in such calculations can be trusted. The errors grow most rapidly with τ when the dimer is asymmetric. Note that since we have only two electrons, our model is a worst case scenario. In many simulations, there are

FIG. 1. Free energy for different values of Δv .

more valence electrons per site, and (exchange-) correlation components are a much smaller fraction of the total energy. In a realistic DFT simulation of WDM, the error made by approximating the ground-state functional would likely be much larger than the error due to the lack of temperature-dependence.

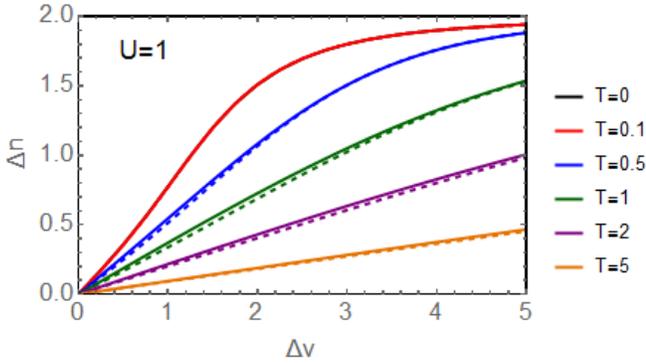


FIG. 2. Densities as a function of temperature for the system of Fig. 1. Solid lines are exact, dashed lines are self-consistent within GSA.

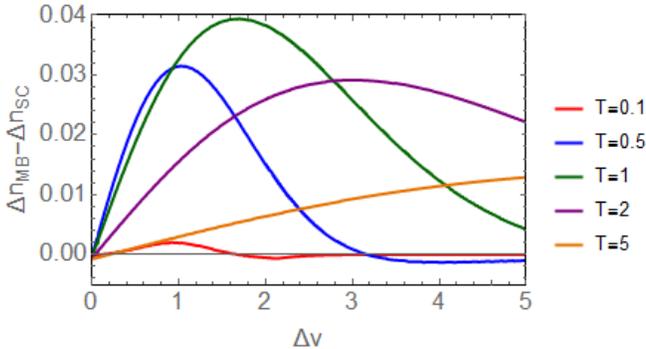


FIG. 3. Error in GSA densities of Fig. 2.

However, this is only part of the story. Real calcula-

tions are performed self-consistently within GSA. Then both the density and MKS orbitals are often used to calculate response properties (usually on the MKS orbitals). In Fig. 2, we compare the self-consistent solution using the 'exact' GSA, i.e., the MKS equations solved with the exact ground-state E_C , using the extremely accurate parametrization of Ref. [28]. In Fig. 3, we plot the differences. We see that the errors in the density are small, and appear to lessen as temperature increases, a counterintuitive result, to be explained below.

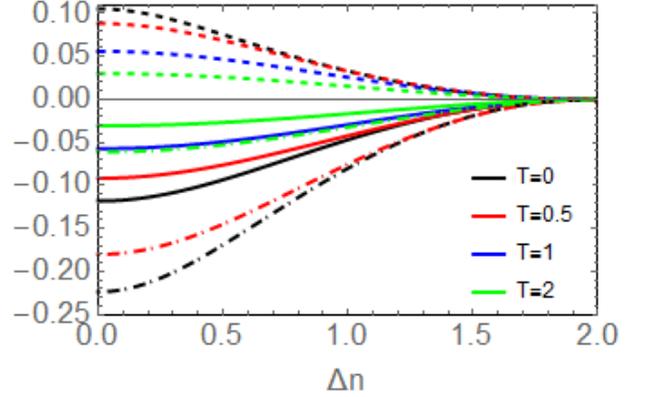


FIG. 4. Correlation free energy functional (solid) and its kentropic (dashed) and potential (dash-dot) contributions.

The most difficult part of DFT approximations is the correlation contribution, and this difficulty is enhanced here by its temperature dependence. A great benefit of the Hubbard dimer[28] is that we can *plot* the 'functional', since it reduces to to a function of Δn . To do this as a function of temperature, we find the one-body potential Δv of the interacting problem that yields Δn for that given temperature. Another great benefit is that we can also calculate all the individual contributions to the correlation free energy by subtracting MKS quantities from their physical counterparts. These are the energy differences appearing in Eq. (13):

$$T_C^\tau = T_I - T_S, \quad S_C^\tau = S^\tau - S_S, \quad U_C^\tau = V_{ee} - U_{HX}. \quad (14)$$

The kentropic correlation is $K_C = T_C - \tau S_C$ and plays a key role in thermal DFT[32]. In Fig. 4, we plot the exact correlation free energy functional and its components as a function of temperature. The kentropic contribution is always positive, the potential always negative, and the correlation free energy always negative, consistent with known conditions[32]. We also see that correlation effects are weakened as the temperature increases for any densities. Moreover, the GSA consists of approximating each of the curves by the corresponding black one. Because all correlation components tend to vanish with increasing temperature, while the total free energy grows in magnitude, the small error made in the GSA becomes less relevant with increasing temperature. This explains the behavior of the self-consistent GSA densities of Fig. 3. Finally, the absolute scale of the correlation free energy

is much smaller than the free energy (even though we have only two electrons), explaining the small errors in the GSA free energies of Fig. 1.

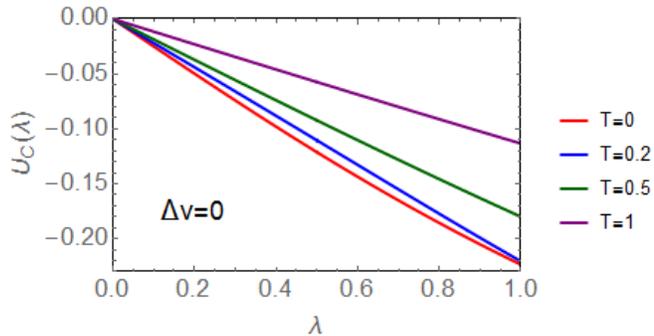


FIG. 5. Adiabatic connection integrands for symmetric dimer at several different temperatures.

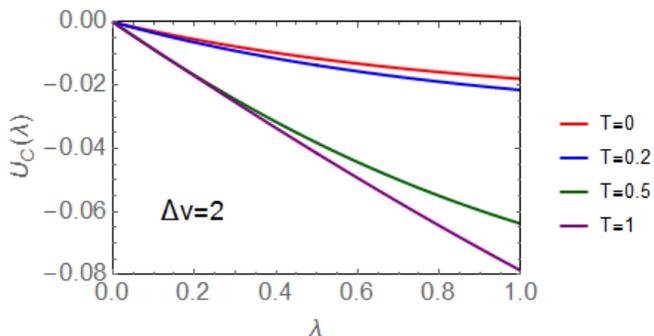


FIG. 6. Same as Fig. 6, except $\Delta v = 2$.

Next, we consider the adiabatic connection formula[33, 34] that has proven so useful in studying and improving density functional approximations. The ground-state version was calculated for the Hubbard dimer in Fig. 21 of Ref. [28]. An alternative version, called the thermal connection formula, was derived in Ref. [35], but that flavor relies on relating the coupling-constant to coordinate scaling. Such a procedure applies to continuum models, but not lattices. So we use the traditional version here, applied to finite temperature[32]:

$$A_C^\tau[n] = \int_0^1 \frac{d\lambda}{\lambda} U_C^{\tau,\lambda}[n] \quad (15)$$

where λ is a coupling constant inserted in front of \hat{V}_{ee} in the Hamiltonian, but (unlike regular many-body theory) the density is held fixed during the variation. Here $U_C^{\tau,\lambda}$ is the potential correlation energy at coupling constant λ , which, for our model, is gotten by replacing U with λU . In Fig. 5, for the symmetric case, turning on temperature clearly reduces both the magnitude of the correlation and the degree of static correlation, as judged by the initial slope of the curves. But Fig. 6, made for the asymmetric dimer, shows that thermal effects can *increase* both

the magnitude and initial slope of the curve, due to the complex interplay between changes of the density and the correlation functional of the density with temperature for a given system.

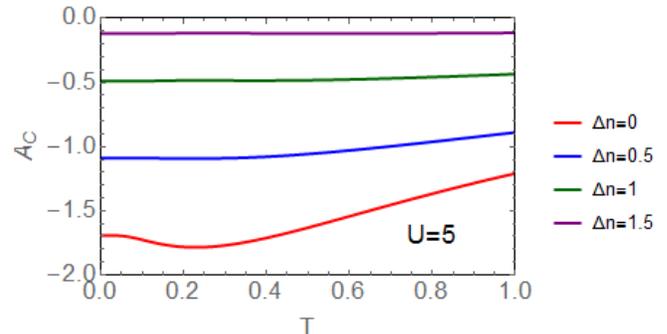


FIG. 7. Correlation free energy for several values of Δn when correlation is strong.

Lastly, we extend beyond the usual conditions for WDM. We do not trust the high-temperature behavior of our model, but the Hubbard model is renowned as model for strong correlation. In Fig. 7, we repeat the A_C^τ curves of Fig. 4 but for $U = 5$, i.e., in the strongly correlated regime. Our previous figures appear to show the magnitude of correlation monotonically decreasing with temperature, i.e., thermal effects reduce correlation effects. One might imagine that this is a general rule, and even attempt to prove it. But the symmetric curve in this figure clearly shows a pronounced minimum at about $\tau = 0.2$. Thus the derivative with respect to temperature is *not* always positive. This one example implies that the correlation free energy is not monotonically decreasing in magnitude in general. This is another value of having an exact calculation, especially one that can be performed beyond the usual conditions of simulations.

In summary, we have solved the simplest possible non-trivial system at finite temperature, exactly both for the many-body case and within MKS density functional theory. We find that for conditions corresponding to weakly correlated warm dense matter, the neglect of temperature dependence in the exchange-correlation functional has relatively weak effect on either the calculated free energies or the self-consistent densities. This should assuage concerns about the validity of this approximation. It seems likely that present limitations of ground-state approximations, such as their inability to treat strongly correlated systems, lead to the greatest source of error in these calculations.

The authors acknowledge support from the National Science Foundation (NSF) under grant CHE - 1464795. J.C.S. acknowledges support through the NSF Graduate Research fellowship program under award # DGE-1321846. A.P.J. acknowledges support through the DOE Computational Science Graduate Fellowship, grant number DE-FG02-97ER25308.

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