

Warming Up Density Functional Theory

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Abstract Density functional theory (DFT) has become the most popular approach to electronic structure across disciplines, especially in material and chemical sciences. Last year, at least 30,000 papers used DFT to make useful predictions or give insight into an enormous diversity of scientific problems, ranging from battery development to solar cell efficiency and far beyond. The success of this field has been driven by usefully accurate approximations based on known exact conditions and careful testing and validation. In the last decade, applications of DFT in a new area, warm dense matter, have exploded. DFT is revolutionizing simulations of warm dense matter including applications in controlled fusion, planetary interiors, and other areas of high energy density physics. Over the past decade or so, molecular dynamics calculations driven by modern density functional theory have played a crucial role in bringing chemical realism to these applications, often (but not always) with excellent agreement with experiment. This chapter summarizes recent work from our group on density functional theory at non-zero temperatures, which we call thermal DFT. We explain the relevance of this work in the context of warm dense matter, and the importance of quantum chemistry to this regime. We illustrate many basic concepts on a simple model system, the asymmetric Hubbard dimer.

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1 Introduction

Warm dense matter: The study of warm dense matter (WDM) is a rapidly growing multidisciplinary field that spans many branches of physics, including for example astrophysics, geophysics, and attosecond physics[MD06; DOE09; LHR09; KDBL15; KD09; KDP15; HRD08; KRDM08; RMCH10; SEJD14; GDRT14]. Classical (or semiclassical) plasma physics is accurate for sufficiently high temperatures and sufficiently diffuse matter[I04]. The name WDM implies too cool and too dense for such methods to be accurate, and this regime has often been referred to as the malfunction junction, because of its difficulty[DOE09]. Many excellent schemes have been developed over the decades within plasma physics for dealing with the variety of equilibrium and non-equilibrium phenomena accessed by both people and nature under the relevant conditions[BL04]. These include DFT at the Thomas-Fermi level (for very high temperatures) and use of the local density approximation (LDA) within Kohn-Sham (KS) DFT at cold to moderate temperatures (at very high temperatures, sums over unoccupied orbitals fail to converge). The LDA can include thermal XC corrections based on those of the uniform gas, for which simple parametrizations have long existed[SD13b; KSdT14].

Electronic structure theory: On the other hand, condensed matter physicists, quantum chemists, and computational materials scientists have an enormously well-developed suite of methods for performing electronic structure calculations at temperatures at which the electrons are essentially in their ground-state (GS), say, 10,000K or less[B12]. The starting point of many (but not all) such calculations is the KS method of DFT for treating the electrons[KS65]. Almost all such calculations are within the Born-Oppenheimer approximation, and ab initio molecular dynamics (AIMD) is a standard technique, in which KS-DFT is used for the electronic structure, while Newton's equations are solved for the ions[CP85].

DFT in WDM: In the last decade or so, standard methods from the electronic structure of materials have had an enormous impact in warm dense matter, where AIMD is often called QMD, quantum molecular dynamics[GDRT14]. Typically a standard code such as VASP is run to perform MD[KRDM08]. In WDM, the temperatures are a noticeable fraction of the Fermi energy, and thus the generalization of DFT to thermal systems must be used. Such simulations are computationally demanding but they have the crucial feature of including realistic chemical structure, which is difficult to include with any other method while remaining computationally feasible. Moreover, they are in principle exact[M65; KS65], if the exact temperature-dependent exchange-correlation free energy could be used because of Mermin's theorem establishing thermal DFT(thDFT). In practice, some standard ground-state approximation is usually used. (There are also quantum Monte Carlo calculations which are typically even more computationally expensive[MD00; FBEB01; M09b; SBFH11; DM12; SGVB15; DGSM16]. The beauty of the QMD approach is that it can provide chemically realistic simulations at costs that make useful applications accessible[MMPC12].) There have been many successes, such as simulation of Hugoniot curves measured by the Z machine[RMCH10] or a new phase diagram for high density water which resulted in improved predictions for the

structure of Neptune[MD06]. Because of these successes, QMD has rapidly become a standard technique in this field.

Missing temperature dependence: However, the reliability and domain of applicability of QMD calculations are even less well understood than in GS simulations. At the equilibrium level of calculation, vital for equations of state under WDM conditions and the calculation of free-energy curves, a standard generalized gradient approximation (GGA) calculation using, e.g., PBE[PBE96], is often (but not always) deemed sufficient, just as it is for many GS materials properties. Such a calculation ignores thermal exchange-correlation (XC) corrections, i.e., the changes in XC as the temperature increases, which are related to entropic effects. We believe we know these well for a uniform gas (although see the recent string of QMC papers[SGVB15; DGSM16] and parametrizations[KSDT14]), but such corrections will be unbalanced if applied to a GGA such as PBE. So how big a problem is the neglect of such corrections?

(A little) beyond equilibrium: On the other hand, many experimental probes of WDM extract response functions such as electrical or thermal conductivity[MD06]. These are always calculated from the equilibrium KS orbitals, albeit at finite temperature. Work on molecular electronics shows that such evaluations suffer both from inaccuracies in the positions of KS orbitals due to deficiencies in XC approximations, and also require further XC corrections, even if the *exact* equilibrium XC functional were used[TFSB05; QVCL07; KCBC08].

Acronym	Meaning	Acronym	Meaning
GGA	Generalized Gradient Approx.	RPA	Random Phase Approximation
GS	ground-state	TDDFT	Time-dependent DFT
HXC	Hartree XC	thDFT	thermal DFT
KS	Kohn-Sham	unif	uniform gas
LDA	Local Density Approx.	XC	exchange-correlation
PBE	Perdew-Burke-Ernzerhof	ZTA	Zero-Temperature Approx.
QMC	quantum Monte Carlo		

Table 1 Acronyms frequently used in this chapter.

2 Background

Generalities: Everything described within uses atomic units, is non-relativistic and does not include external magnetic fields. Unless otherwise noted, all results are for the electronic contributions within the Born-Oppenheimer approximation. While all results are stated for density functionals, in practice, they are always generalized to spin-density functionals in the usual way.

2.1 Ground-state DFT

Hohenberg-Kohn functional: Just over 50 years ago, in 1964, Hohenberg and Kohn wrote down the foundations of modern DFT[HK64]. They start with the many-body Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}, \quad (1)$$

where \hat{T} , \hat{V}_{ee} , and \hat{V} are the kinetic, electron-electron, and potential energy operators, respectively. Assuming a non-degenerate ground-state, they proved by *reductio ad absurdum* that the external potential, $v(\mathbf{r})$ is a unique functional of the density $\rho(\mathbf{r})$, and therefore all observables are also density functionals. More directly Levy defines the functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (2)$$

where Ψ is normalized and antisymmetric, and uses it to define the energy functional

$$E_v[\rho] = F[\rho] + \int d^3r v(\mathbf{r})\rho(\mathbf{r}), \quad (3)$$

whose minimization over normalized non-negative densities with finite kinetic energy yields the ground-state energy and density[L81].

Kohn-Sham scheme: In 1965, Mermin generalized the Hohenberg-Kohn theorems for electrons in the grand canonical potential with fixed non-zero temperature τ and chemical potential μ [M65]. Later in 1965, Kohn and Sham created an exact method to construct the universal functional (see Eq. (6)). The Kohn-Sham scheme imagines a system of N non-interacting electrons that yield the electronic density of the original interacting N electron system. These fictitious electrons sit in a new external potential called the KS potential. The KS scheme is written as a set of equations that must be solved self-consistently:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad \rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2, \quad (4)$$

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}), \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \quad (5)$$

where $\phi_i(\mathbf{r})$ and ε_i are the KS orbitals and energies, $v_H(\mathbf{r})$ is the classical Hartree potential, and $v_{xc}(\mathbf{r})$ is the exchange-correlation potential defined by the unknown XC energy, E_{xc} , in Eq. (5). These must be solved self-consistently since the Hartree potential and E_{xc} depend explicitly on the density. Lastly, the total energy can be found via

$$F[\rho] = T_s[\rho] + U_H[\rho] + E_{xc}[\rho] \quad (6)$$

where T_s is the kinetic energy of the KS electrons and U_H is the Hartree energy.

In practice, an approximation to E_{xc} must be supplied. There exists a wealth of approximations for E_{xc} [MOB12]. The simplest, LDA, uses the XC per electron of the homogeneous electron gas[PW92]:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int d^3r e_{\text{xc}}^{\text{unif}}(\rho(\mathbf{r})) \quad (7)$$

where $e_{\text{xc}}^{\text{unif}}$ is the XC energy density of a uniform gas with density $\rho(\mathbf{r})$. We can imagine going up a ladder by adding in more ingredients (like gradients of the density[PBE96]) and obeying different or additional conditions to make more complicated and more accurate functionals[PRCS09]. For the exact E_{xc} , these equations have been proven to converge[WSBW13].

2.2 Asymmetric Hubbard dimer and its relevance

Throughout this chapter we illustrate results with the simplest interesting model of an interacting system. This model is the asymmetric Hubbard dimer[CFSB15]. The Hubbard dimer crosses the divide between the weakly and strongly correlated communities. Previous work has shown that the basic concepts of ground-state KS-DFT apply to this model and here we demonstrate similar applicability to thermal DFT. The Hamiltonian is given by

$$\hat{H} = -t \sum_{\sigma} (\hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + H.c.) + \sum_{i=1}^2 (U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + v_i \hat{n}_i) \quad (8)$$

where $\hat{c}_{i\sigma}^{\dagger}$ ($\hat{c}_{i\sigma}$) 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 is the ultra-short range Coulomb repulsion for when both electrons are on the same site, and v_i is the on-site external potential. We choose, without loss of generality, $v_1 + v_2 = 0$ then $\Delta v = v_2 - v_1$ and the occupation difference, the analog of density, is $\Delta n = n_2 - n_1$.

In Fig. 1 we plot the density Δn versus asymmetry Δv in the Hubbard dimer. The Hohenberg-Kohn theorem applies to this Hamiltonian, and guarantees $\Delta n(\Delta v)$ is an invertible function for any value of U . The main physics is a competition between asymmetry and interaction strength. The weakly correlated regime is $U < \Delta v$ and the opposite is strong correlation. Increasing Δv pushes the electrons onto a single site, thus Δn approaches 2. Likewise, for small Δv or large U the electrons are apart and Δn tends to 0. This is made most clear by the extreme cases, i.e.,

$$|\Delta n_{U=0}(\Delta v)| = 2\Delta v / \sqrt{(2t)^2 + \Delta v^2}, \quad |\Delta n_{U \rightarrow \infty}(\Delta v)| \rightarrow 2\theta(\Delta v - U). \quad (9)$$

The ability to vary U and move continuously from weak to strong correlation in a model that is analytically solvable makes the Hubbard dimer an excellent illustrator of how KS-DFT works[CFSB15].

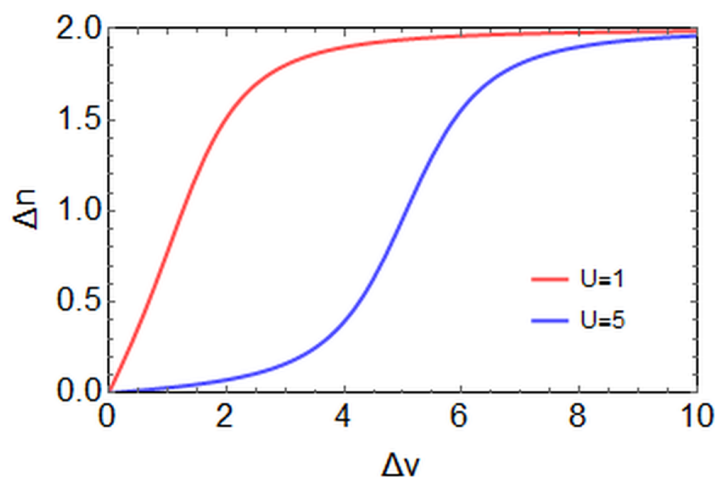


Fig. 1 On-site occupations as a function of on-site potential difference for $U = 1$ and 5 in the asymmetric Hubbard dimer. The HK theorem guarantees that each function is invertible. There is a simple analytic result for $U = 0$, and for large U , the relation tends toward a (smoothed) step function, with the step at $\Delta v = U$.

2.3 Ensemble DFT as a route to excitation energies

In this section we take a quick aside to overview ensemble DFT (eDFT), a close cousin of thermal DFT.

Excitations in DFT: Although time-dependent DFT (TDDFT) is the standard method used to determine the excited states of a system [M16], there are still many deficiencies, due to crude approximations to the XC functional as well as being unable to approximate multiple excitations, charge transfer excitations, canonical intersections, and polarizabilities of long-chain polymers; all things that can be important for photochemistry [MZCB04; DWH03; T03; LKQM06; FBLB02]. Ensemble DFT is a time-independent alternative to the standard TDDFT that can be a useful method for extracting excited states. Naturally, since eDFT and TDDFT are based on two different fundamental theories, it is possible to use eDFT on different systems to those of the traditional method and expect different successes and likewise different failures.

Ensemble variational principle: eDFT is based on a variational principle made up of ensembles of ground and excited states [T79]. These ensembles are made of decreasing weights, with the ground state always having the highest weight.

$$E^{\mathbf{w}} \leq \sum_{k=0}^{M-1} w_k \langle \Psi_k | \hat{H} | \Psi_k \rangle, \quad w_0 \geq w_1 \geq \dots \geq w_k \geq 0 \quad (10)$$

where all Ψ_k are normalized, antisymmetric, and mutually orthogonal, $\mathbf{w} = (w_0, w_1, \dots, w_k)$, and the sum of all weights is 1. The ensemble-weighted density is

$$\rho^w(\mathbf{r}) = \sum_{k=0}^{M-1} w_k \rho_{\psi_k}(\mathbf{r}). \quad (11)$$

Just as in the ground-state case, a one-to-one correspondence from the weighted density to the potential can be established [GOK88], and applying this to a non-interacting system of the same weighted density can be used to construct a KS eDFT. From this KS system it is in principle possible to extract the exact excited states of the system.

Relation to thermal DFT: The connection to thermal DFT is natural and straight forward. Thermal DFT is a special case of eDFT. In thDFT, one chooses the ensemble to be the grand canonical ensemble with the usual Boltzmann factors for the weights. However, unlike eDFT, the weights themselves depend on the eigenvalues of the Hamiltonian, including the strength of the interaction. Thus the weights in the KS system are different from those of the interacting system. In most applications of eDFT, the weights are chosen to be the same in both the physical and non-interacting systems.

History: Ensemble DFT was originally proposed by Gross-Olivera-Kohn in 1988[GOK88], but, like thermal DFT, there has been slow progress over the last 30 years due to a lack of useful approximations to the XC functional. Many of these difficulties arise from the so-called ghost interaction errors that occur in the Hartree energy[GPG96]. More specifically these ghost-interaction errors appear when only using the ground state definition of the Hartree energy, which causes unphysical contributions and must therefore be accounted for by using a more accurate definition of the Hartree energy for ensembles[PYTB14; YTPB14].

Recent progress: More recently, work has been done to extract the weight dependence of the KS eigenvalues, which are required in order to extract accurate transition frequencies[PYTB14; YTPB14]. It was also found that a large cancellation of the weight-dependence occurs in the exact ensembles. Further, a new numerical method for inverting ensemble densities was derived for spherically symmetric systems, and this method was also tested for cylindrically symmetric systems. This inversion of densities to extract potentials provides a useful test of eDFT approximations.

Recent work combines linear interpolation with an extrapolation method in eDFT to extract excited states that are independent of ensemble weights[SHMK16]. Also, an exact analytical expression for the exchange energy was derived, and a generalized adiabatic connection for ensembles (GACE) was used to connect the ensemble XC functional with the ground state functional[DMF16]. Finally, a ghost interaction correction has been developed for range-separated eDFT[AKF16].

A simple exercise: Here we show an example of the importance of the weight-dependence of functionals in eDFT, in a seemingly simple system. We put only one electron in the Hubbard dimer, so there is no interaction, and its a simple tight-binding Hamiltonian. We will derive the exact kinetic energy functional, which is an example of the non-interacting KS kinetic energy functional. We will also approximate it, as if we were interested in orbital-free eDFT.

There are only two levels, the ground state and a first excited state. Thus we can make only a bi-ensemble. The ensemble-weighted ground-state density is

$$\Delta n^w = (1-w)\Delta n_0 + w\Delta n_1 = (1-2w)\Delta n_0(x), \quad (12)$$

where Δn_0 , and Δn_1 correspond to the occupational difference of the two sites for the ground and first-excited state, respectively, and $\Delta n_0(x)$ is given by Eq. (9) with $U = 0$. This last result is true only because $\Delta n_1 = -\Delta n_0$ in this simple model. The weight as previously stated is $w \leq 0.5$. Similarly, the kinetic energy for a single particle in the ground-state is known, and $T_{S,1} = -T_{S,0}$, so

$$T_S^w = (1-w)T_{S,0} + wT_{S,1} = (1-2w)T_{S,0} = (1-2w)\frac{-1}{2\sqrt{1+x^2}} \quad (13)$$

where $x = \Delta v/(2t)$. Using $V^w = \Delta v\Delta n^w/2$ and adding it to T_S^w yields the ensemble energy, which is exactly linear in w , and passes through E_0 at $w = 0$ and (would pass through) E_1 at $w = 1$.

This simple linearity with w is true by construction of the ensemble, when energies are plotted against w for a fixed potential. But now we show that things get complicated when we consider them as density functionals. Inverting the relation between potentials and densities we find

$$x = \frac{\Delta n^w}{\sqrt{(-\Delta n^w)^2 + (1-2w)^2}} \quad (14)$$

and inserting this into the kinetic energy yields

$$T_S^w[\Delta n] = \sqrt{-\Delta n^2 + (1-2w)^2}/2 \quad (15)$$

Even in this trivial case, the the w -dependence of the kinetic energy density functional is non-linear.

Next, we make the most naive approximation, namely to replace $T_S^w[\Delta n]$ with its ground-state counterpart. This yields an approximate eDFT theory from which, in principle, we can estimate the energy of the first excited state. To do this, we insert the exact w -dependent density of Eq. (12) into the ground-state functional, add the exact V^w , and plot the resulting energy. The exact and approximate results are shown in Fig. 2. The approximation is very bad, yielding an excited state energy of about -0.3 instead of 0.71 , by using the value at $w = 1/2$. But it at least illustrates the difficulties of capturing an accurate w -dependence in an ensemble density functional.

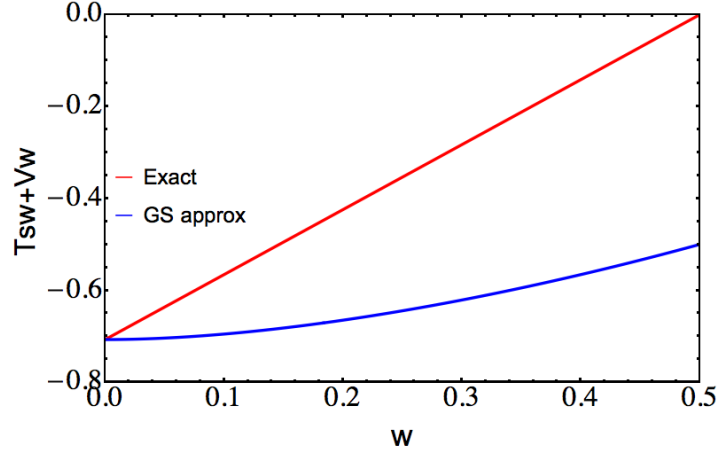


Fig. 2 The exact energy curve for a single particle in a Hubbard dimer $E_{exact} = T_s^w[\Delta n^w] + V^w$ (red), when $x = 1$, in units of $2t$. The blue line is the approximate energy when T_s^w is replaced by its ground-state analog, T_s^0 . Notice that $w = 0$ corresponds to E_0 , which is $1/\sqrt{2}$ in these units.

2.4 Thermal DFT in a nutshell

Mermin-Kohn-Sham equations: In a thermal system, Eq. (4) and (5) are generalized such that the density and XC potential become $\rho^\tau(\mathbf{r})$ and $v_{XC}^\tau(\mathbf{r})$, i.e. temperature dependent, and $E_{XC}[\rho]$ in Eq. (5) becomes $A_{XC}^\tau[\rho]$, the exchange-correlation *free* energy density functional. The density becomes

$$\rho^\tau(\mathbf{r}) = \sum_i f_i |\phi_i^\tau(\mathbf{r})|^2 \quad (16)$$

where the sum is now over all states and $f_i = (1 + e^{(\epsilon_i^\tau - \mu)/\tau})^{-1}$, the Fermi occupation factors. One of the core difficulties in thermal DFT calculations is this sum, since a huge number of states are required once the temperature is sufficiently high. This leads to large computational demands and convergence issues. We call these the Mermin-Kohn-Sham equations.

To extract the total free energy from the MKS equations, we write

$$A^\tau[\rho] = A_S^\tau[\rho] - U_H[\rho] + A_{XC}^\tau[\rho] - \int d^3r \rho(\mathbf{r}) v_{XC}^\tau[\rho](\mathbf{r}), \quad (17)$$

where the MKS free energy is

$$A_S^\tau[\rho] = \sum_i \epsilon_i^\tau[\rho] - \tau S_S^\tau[\rho], \quad S_S^\tau[\rho] = -\sum_i [f_i \log(f_i) + (1 - f_i) \log(1 - f_i)], \quad (18)$$

and S_S is the MKS entropy.

Exchange-correlation free energy: Compared to ground-state DFT, relatively few approximations have been developed for A_{XC}^T . In active use are two approximations: thermal LDA (thLDA) and the Zero-Temperature Approximation (ZTA). The former uses the temperature-dependent XC free energy of the uniform gas instead of its ground-state analog in Eq. (7). The ZTA means simply using any ground-state XC functional instead of a temperature-dependent one. We denote use of the exact ground-state XC functional as exact ZTA (EZTA).

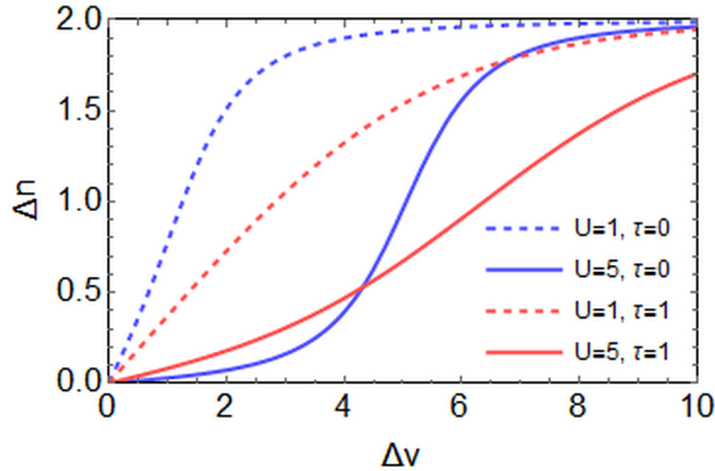


Fig. 3 Effects of temperature on the on-site occupations as a function of on-site potential difference for $U = 1$ and 5 in the asymmetric Hubbard dimer (see Sec. 3.2) with and without temperature. Increasing temperature pushes the electrons towards opposite sites and lowers Δn while increasing Δv pushes electrons to the same site and raises Δn .

In Fig. 3 we demonstrate the effects of turning on temperature for the Hubbard dimer (see Sec. 3.2 for more information). Even a small increase in temperature can have a big impact on a system regardless of the strength of correlation.

3 Some recent developments in thermal DFT

The formalism for thermal DFT was originally developed alongside that of ground-state DFT, but in the intervening decades ground-state DFT (and TDDFT, for that matter) has received significantly more attention and consequently more developments [WGB05; B12]. However, in the past couple decades thermal DFT has seen more use, and with that much more development in the past ten years. In this section we outline some recent developments to thermal DFT from our group.

3.1 Exact conditions and their relevance

Zero temperature: One of the most crucial steps in understanding and developing functionals beyond LDA is exact conditions. These conditions take many forms with some common examples being coordinate and interaction scaling conditions[LP85], and bounds on the XC energy[LO81]. There are well over a dozen conditions in ground-state DFT (a recent meta-GGA functional even uses seventeen[SRP15]!), but the use of exact conditions is much more nascent in thermal DFT.

3.1.1 Coordinate-temperature scaling and the thermal connection formula

Uniform coordinate scaling: The most straightforward application of exact conditions to thermal DFT is by uniform scaling of the density[LP85]. The very basic conditions that this procedure generates in ground-state DFT are built in to almost all modern approximations. In a sense, this is simply dimensional analysis, but while keeping the density fixed (which is the tricky bit).

Early work on exact conditions for thermal DFT[PPFS11; PPGB13] derived basic conditions such as the signs of correlation quantities, including the separation into kinetic and potential contributions, and the adiabatic connection formula at finite temperature. More conditions come from coordinate scaling of the density, showing that is intimately related to temperature dependence. Examples of a few of these conditions are

$$F_s^\tau[\rho] = \gamma^2 F_s^{\tau/\gamma^2}[\rho_{1/\gamma}], \quad S_s^\tau[\rho] = S_s^{\tau/\gamma^2}[\rho_{1/\gamma}], \quad A_x^\tau[\rho] = \gamma A_x^{\tau/\gamma^2}[\rho_{1/\gamma}], \quad (19)$$

where $\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma\mathbf{r})$. For any of these functionals, this means that, if you know the functional at *any* one finite temperature, the functional at *all* possible temperatures is available via scaling of the density.

New formulas: In recent work, many new formulas relating correlation components of the energy to one another were derived[PB16], such as

$$K_c^{\tau,\lambda}[\rho] = A_c^{\tau,\lambda}[\rho] - \lambda \frac{dA_c^{\tau,\lambda}[\rho]}{d\lambda}, \quad (20)$$

where $K_c^{\tau,\lambda}[\rho] = T_c^{\tau,\lambda}[\rho] - \tau S_c^{\tau,\lambda}[\rho]$ is the correlation entropy. There was also a rewriting of the adiabatic connection formula[PPFS11; LP75], using the relation to scaling mentioned above, yielding the XC free energy at temperature τ :

$$A_{xc}^\tau[\rho] = \frac{\tau}{2} \lim_{\tau'' \rightarrow \infty} \int_\tau^{\tau''} \frac{d\tau'}{\tau'^2} U_{xc}^{\tau'}[n_{\sqrt{\tau'/\tau}}], \quad \rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma\mathbf{r}), \quad (21)$$

where $U_{xc}^\tau[\rho]$ is the purely potential contribution to the XC free energy, and the scaling is the usual coordinate scaling of the density introduced by Levy and Perdew[LP85] for the GS problem. Note that this thermal connection formula uses

only information between the desired temperature and higher ones, allowing approximations that begin from the high-temperature end instead of the low-temperature end[PB16]. A second set of formulas give the many relations among the different correlation energy components (total, potential, and entropic). These are very important in ground-state DFT[FTB00; PEB96] for understanding the origins of different physical contributions to the correlation free energy and have guided the construction of many approximations.

Entropy: Lastly for this section, we look at a new set of exact conditions for the electronic entropy as a functional of the density[BSGP16]. The most important is that the universal functional can be written solely in terms of a temperature integral over entropy, such as

$$F^\tau[\rho] = F^0[\rho] - \int_0^\tau d\tau' S^{\tau'}[n], \quad A_{xc}^\tau[\rho] = E_{xc}[\rho] - \int_0^\tau d\tau' S_{xc}^{\tau'}[\rho], \quad (22)$$

i.e., the universal contribution to the free energy functional is a simple integral over the electronic entropy, and the second shows that all thermal corrections to the XC free energy are given by an integral over the XC entropy. These formulas have no analog in ground-state DFT. They also lead to fundamental inequalities on the various thermal derivatives of both interacting and KS quantities. Such conditions have long been known for the uniform gas[I82], but our results are their generalization to inhomogeneous systems. Analogs are also easily derived from statistical mechanics, but again, the tricky part is to deduce their behavior as functionals of the density rather than the external potential. This is why, for example, all derivatives are total with respect to temperature. The particle number is fixed by the density, so temperature is the sole remaining variable. Our work uses the formalism and methods of ground-state DFT, generalized to finite temperature, but the same results can also be extracted in the language of statistical mechanics[DT11; DT16].

Tiny violations: A minor illustration of the relevance of these conditions is that we found that a recent parameterization of the thermal XC free energy of the uniform gas[KSdT14] violates one of our conditions for low densities[BSGP16]. This violation is slight, and unlikely to ever influence the results of any thLDA calculation. Nonetheless, it is always better to build parameterizations that satisfy known conditions, so that the corresponding approximate calculations are guaranteed to satisfy such conditions[SGVB15; DGSM16].

Zero-temperature approximations: This work also showed that any ZTA calculation automatically satisfies most of our conditions, whereas the inclusion of thermal XC corrections risks violating them for specific systems. For example, all approximations in Fig. 5 (discussed below) are guaranteed to satisfy these conditions. But practical calculations including approximate thermal XC corrections should be checked for possible violations of exact conditions in the future.

3.2 Exact calculations on a simple model system

Importance for ground-state DFT: A crucial step in all DFT development is the exact solution of simple systems and the test of approximate functionals against exact quantities. There are large databases of molecular properties, based either on highly reliable and accurate experimental measurements, or on far more accurate quantum chemical calculations[SGB97; ZKP98; KPB99; TS09]. But these databases usually contain at most a few numbers per system, such as the atomization energy and bond length(s). A substantially more sophisticated test occurs when a highly accurate calculation is performed such as QMC[CKB79; NU99] or DMRG[W92], and an inversion of the KS equations[SV09], so that essentially exact KS potentials, eigenvalues, orbitals, etc, can all be deduced. This is a much more powerful test of a DFT approximation, and usually provides detailed insight into its limitations. The QMC calculations of Umrigar and collaborators[UG94; FUT94; HU97] and their high impact, testify to this fact.

Difficulty of exact thermal calculations: Although almost all practical calculations of WDM are in a condensed phase (with hot ions), almost all high level inversions yielding exact KS quantities are for atoms or small molecules. But even for such systems, it is difficult to imagine accurate inversions at finite temperature, as only the average particle number is fixed, and all possible particle numbers must be considered.

Exact calculations for Hubbard dimer: Exact calculations are only possible for this model because the Hilbert space is severely truncated which allows us to compute all energies analytically (see Fig. 4 for complete diagram of the energy spectrum). However, this means the model is not even a qualitatively realistic representation of very high temperatures (though we choose parameters such that the ceiling of the Hilbert space does not effect results). But we are able to do the inversion exactly, and so extract all the different contributions to X and C as a function of both τ and U . These are the first exact inversions of an interacting system at finite temperature. They show us the structure of the underlying functionals, but cannot tell us which approximations will be accurate. For example, there is no real analog of LDA for this system (although BALDA[LSOC03] somewhat plays this role).

Paradox: To see why such simplistic calculations are important, consider the bottom panel of Fig. 5. The black line shows the exact density difference in the dimer versus temperature for moderate correlation and asymmetry. The blue curve is a Hartree-Fock calculation, while the red curve adds in the high-density limit of GS correlation. Finally, EZTA in green uses the exact GS functional (i.e. the best possible ZTA), which we had already found in Ref. [CFSB15], in the MKS equations, which therefore is the best possible calculation that ignores thermal XC contributions. By construction, this becomes exact in the zero-temperature limit. But, to our surprise, we found that the relative error in the free energy and density vanishes in the *high* temperature limit. In fact, as temperature increases, the fractional errors at first increase, and then start to lessen.

Resolution of paradox: How can this counterintuitive result be right? The answer is very simple. For high temperatures, the XC components of the energy remain

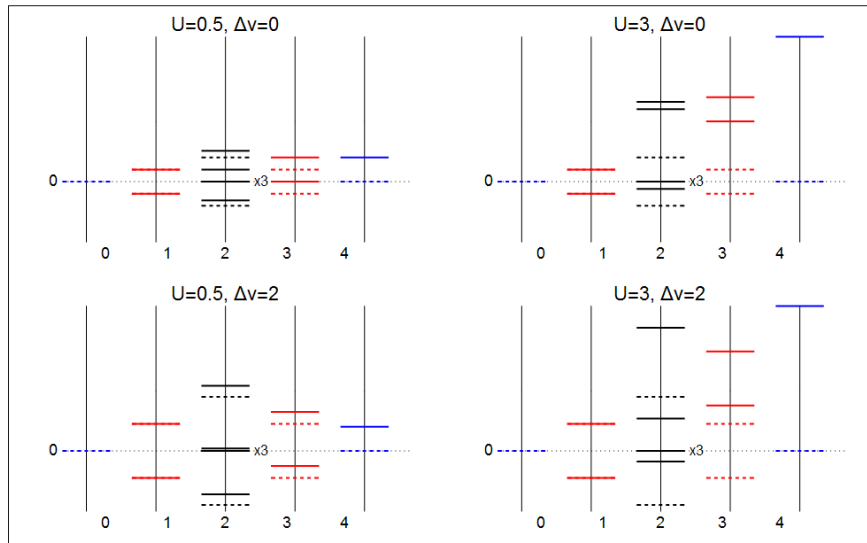


Fig. 4 Energy spectrum for the Fock space of the asymmetric Hubbard dimer at various parameters ranging from weakly to strongly correlated. The x-axis is labeled by the number of particles. The dashed lines correspond to the non-interacting (tight-binding) symmetric case. The labels in the figures denote degeneracy. The triplet for $N = 2$ is always at $E = 0$ due to symmetry. The top left is symmetric and weakly correlated, so the spectral lines are close to the dashed ones. The top right is symmetric but strongly correlated, and the energies for $N = 2$ are substantially raised. We also see pairs of levels pushed together. The Hubbard bands of the infinite chain roughly run between these levels. In the lower left panel, we turn on asymmetry, and show that it lessens the effects of U shown in the upper panels.

finite (and actually shrink, see Fig. 6), while the KS contributions grow, at least in this simple case. Thus *any* XC approximation will produce the same effect. This is why all the approximations merge onto the exact line in Fig. 5 for sufficiently high temperatures. Of course, there can still be a significant absolute error in the free energy which might have important effects on quantities of interest. But the principle is clear: EZTA becomes relatively exact in both the low- and *high*-temperature limits. This is also trivially true for the uniform gas, once the (infinite) Hartree energy is included, and we suspect it to be true for all systems.

Relevance for response functions: The increasing accuracy of the density with temperature has very important implications for calculations of conductivity. This means that the error in the KS orbitals, used in the construction of KS conductivities, starts to decrease beyond some temperature. This is true for *any* GS approximation for XC (within reason). All these conclusions may explain the tremendous success so far gotten by ignoring the thermal XC effects, especially for conductivities.

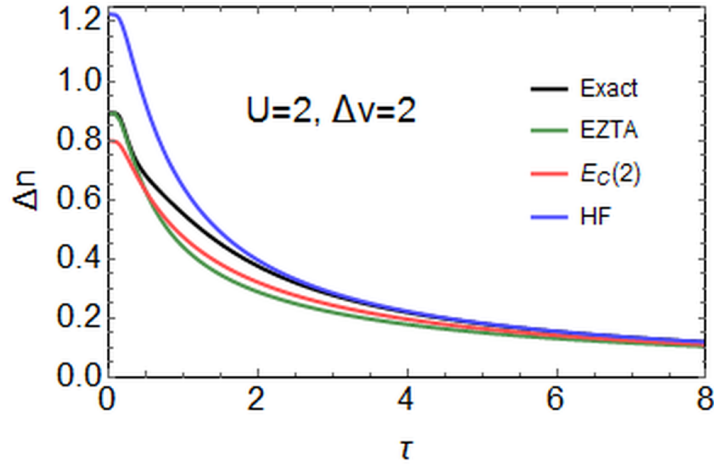


Fig. 5 Difference in on-site densities as a function of temperature for an asymmetric Hubbard dimer with $U = 2$ and site-potential difference 2 (in units where the hopping parameter $t = 1/2$). The approximate calculations are all MKS-DFT-ZTA equilibrium calculations where HF denotes Hartree-Fock, $E_C(2)$ includes the leading correlation correction to HF in powers of the interaction, while EZTA denotes using the exact ground-state XC functional[CFSB15].

3.3 Beyond equilibrium: Linear response thermal time-dependent DFT

Zero temperature: There are many applications in WDM where the system is perturbed away from equilibrium. At zero temperature, the standard approach to

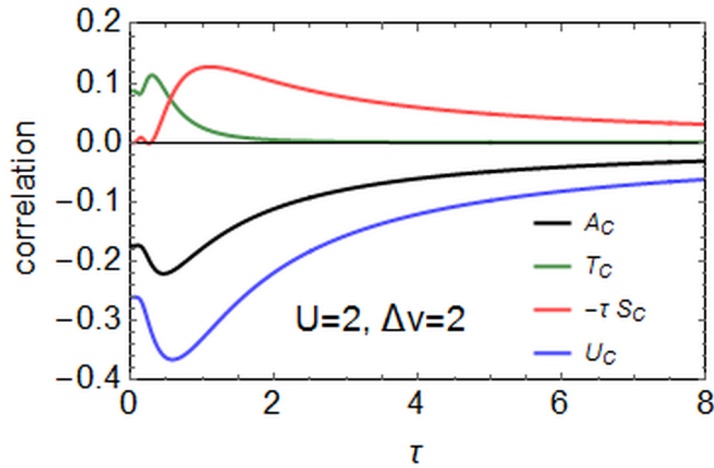


Fig. 6 Correlation energy components as a function of temperature. All inequalities proven in Ref. [PPFS11] are satisfied. This figure shows that the naive assumption that A_C^τ is bounded by $E_C = A_C(\tau = 0)$ is not true. Fig. 1 of Ref. [SPB16] shows that the total free energy increases in magnitude as temperature increases, making the XC contribution relatively less important. Thus ZTA (or any reasonably bounded approximation) will yield relatively exact free energies, densities, and KS orbitals, in the limit of high temperatures.

such problems is to apply TDDFT or many-body non-equilibrium Green's function methods[SV13]. TDDFT in particular[RG84] can handle both strong perturbations, such as atoms and molecules in intense laser fields, and weak perturbations, where the linear response formulation yields excitation energies and oscillator strengths[BWG05].

General case too difficult: Unfortunately, the situation is very complicated if the perturbation is strong, as then a non-equilibrium treatment is needed. Theories in which the temperature is held fixed do not apply. This is the situation for example in calculations of stopping power[GSK96]. There are many fine attempts to overcome these difficulties under a variety of practically useful conditions[RTKC16], but we have not seen a way to construct a general DFT treatment of such problems.

Linear response: For a finite system (which has to be very carefully defined in the thermal case), we proved a limited theorem for the linear density response to a time-dependent external field[PGB16]. This proof allows for (finite numbers of) degeneracies in the excited states, but not in the equilibrium state. Armed with such a theorem, all the usual XC response properties, such as the XC kernel, can be defined at finite temperature. Combined with our thermal connection formula, we have the finite-temperature generalization of the Gross-Kohn response equation[GK85]:

$$\chi^\tau(12) = \chi_s^\tau(12) + \int d3d4 \chi_s^\tau(13) f_{\text{HXC}}^\tau(34) \chi^\tau(42), \quad (23)$$

where 1 denotes the coordinates \mathbf{r}, t , and 2 another pair[KBP94], $\chi^\tau(12)$ is the density-density response function at temperature τ , χ_s its KS counterpart, and $f_{\text{HXC}}^\tau(12)$ the thermal Hartree-XC kernel. This becomes the Random Phase Approximation (RPA) when $f_{\text{XC}} = 0$. Insertion of this into the thermal connection formula yields an RPA-type equation for the XC free energy[PGB16]:

$$A_{\text{XC}}^\tau[\rho] = \lim_{\tau'' \rightarrow \infty} \frac{\tau}{2} \int_\tau^{\tau''} \frac{d\tau'}{\tau'^2} \int_0^\infty \frac{d\omega}{2\pi} \coth\left(\frac{\omega}{2\tau}\right) \int d\mathbf{r} \int d\mathbf{r}' \frac{\Im \chi^\tau[\rho_\gamma](\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}. \quad (24)$$

If XC contributions to the kernel are neglected, this becomes the long-known random-phase approximation to the XC free energy, albeit using the KS orbitals. Since random-phase approximation calculations have become standard within the GS materials world[SHSG10], there is little additional computational demand in performing them at moderate finite temperatures. Inclusion of any approximate treatment of the XC kernel yields an entirely novel approach to XC approximations for equilibrium thermal DFT. In particular, one can consider making a uniform approximation in both space and time, and also decide whether or not to include thermal corrections in an approximate kernel. All such treatments can be first tested on a uniform gas, for which the XC free energy is accurately known from QMC calculations[DGSM16].

4 Recent applications of DFT in WDM

Planetary science: The materials of interest in WDM research span the periodic table. Accurate thermal conductivities for inertial confinement fusion fuel materials such as deuterium and tritium are needed to find the calculated total neutron yield in fusion science (the simulated mixing between the fuel and coating on ICF capsules is very sensitive to thermal conductivities)[HCBK14]. Accurate iron thermal conductivities are used to determine whether the conventional model for how the Earth's core developed is valid because heat flux contributes to the Earth's geomagnetic field. Differential heating experiments at ALS, LCLS, Omega, and Titan facilities are all done slightly differently (heating via optical lasers, XFEL, x-rays, or proton heating), to fit hydrodynamics models because of their high accuracy and because other approaches (SESAME, Purgatorio, and Lee-More) all differ[BJKR78; LM84; WSSI06]. Our work suggesting that ignoring XC thermal corrections nevertheless yields accurate KS eigenstates and eigenvalues[SPB16] helps explain why conductivities can be accurate in these calculations.

Much WDM research is motivated by the desire to understand planetary interiors. The Juno mission is measuring Jupiter's gravitational field extremely accurately, constraining theories of its interior[MGF16], while Kepler has shown that many notions of planetary formation must be rethought with our new data on extrasolar planets[C16]. But there is limited understanding of whether initial planetary protoplanets remain stable during accretion or if they dissolve into outer metallic hydrogen layers. Recent DFT-MD calculations show that MgO is surprisingly soluble in hydrogen under these conditions[WM12]. Similarly, the moon is thought to have formed in an enormous impact, but such a scenario depends crucially on the equation of state of MgO under extreme conditions. Recent DFT calculations and Z-machine experiments have nailed this EOS more accurately than before, and far better than unreliable extrapolations from more mundane conditions[RSLD15].

Alternate methods: Path integral Monte Carlo is an excellent tool for studying WDM, and has been recently extended beyond small atoms to include water and carbon, and has recently been shown to match reasonably well with DFT calculations at lower temperatures[DM12], validating both. Meanwhile, DFT calculations have predicted new superionic phases of H₂O, under conditions relevant to Uranus and Neptune interiors[WWM13].

DFT failure: A less successful application of DFT in WDM is to the liquid insulator to liquid metal transition in dense D₂, at about 1000K and 300 GPa. DFT calculations with several different functionals yield very different results, none of which are in satisfactory agreement with experiment. The interpretation also depends on the accuracy of the conductivity from the DFT calculations. This system remains a challenge to WDM simulations.

X-ray Thompson scattering: Some of the most exciting recent experiments have been from the LINAC at SLAC, allowing X-ray Thompson scattering (XRTS) measurements of shocked materials. These include the first highly resolved measurements of the plasmon spectrum in an ultrafast heated solid[SGLC15]. Ref. [DDRF16] gives x-ray scattering results from plasmons in dynamically compressed

deuterium, from which one can deduce the ionization state as a function of compression. Ionization begins at about the pressure that DFT-MD calculations show molecular dissociation. In a completely different material, X-ray diffraction showed diamond formation on nanosecond timescales, caused by shock compression to about 200 GPa[KRGG16]. This helps explain why the lonsdaleite crystal structure occurs naturally close to meteor impacts.

XRTS has been performed on a variety of materials including Be, Li, C, CH shells, and Al. Most experiments probe the electron dynamic structure factor, which is decomposed via the somewhat ad-hoc Chihara decomposition into bound, loosely bound, and free electrons[BSDH16]. But by running TDDFT at finite temperatures, one directly calculates the densities, and can then test the accuracy of Chihara for determining the ionization state. The results of Ref. [PGB16] are already being used to justify thTDDFT calculations such as Ref. [BSDH16].

5 Relation of thermal DFT to quantum chemistry

At first glance, it would appear that warm dense matter has little or nothing to do with chemistry. In fact, this is not true, it is simply chemistry in an exciting new regime with which we are relatively unfamiliar.

To see this, we first note that the plasma physicists who usually study WDM think in terms of average properties of their systems, such as mean densities and numbers of electrons ionized. They are familiar with density functional methods, but traditionally only at the level of the LDA. Successes with such an approximation are often attributed to systems being somehow ‘locally uniform’.

But the success of DFT methods in chemistry can be directly correlated with the arrival of the GGA and hybrids of it with Hartree-Fock. These approximations were tested on the G2 data set, and shown to yield much better energetics than LDA, because the G2 data set had already been carefully constructed and benchmarked, using both quantum chemical methods and experimental information[CRRP97; CRRP98; PHMK05]. This vote of confidence led to their widespread adoption in many branches of chemistry, and also led to the confidence that GGAs were better than LDA for many materials problems.

It is the same GGAs, used in MD simulations, that have led to the revolution in WDM simulations over the past decade or so[LBKC00]. The improved accuracy due to GGAs implies that the details of the electronic structure matter, and that these systems are in no way locally uniform. In fact, in many cases, there are large evanescent regions of the HOMO, just as in gas-phase molecules. The KS system is ideal for computing this, and GGAs and hybrid account for the energetic consequences. So the very success of DFT-MD for WDM implies that the detailed chemistry is vital, even if it is happening within simulations of extended systems under high temperature and pressure.

The recent work in our group is almost entirely focused on bringing GGA-level XC technology to the WDM field. Being able to distinguish among different com-

ponents of the correlation energy, and switch from one to another, is a crucial part of the exact conditions that were used to construct GGAs[PB16]. The adiabatic connection formula is often invoked in modern DFT research to understand both exact DFT and approximations, and its recasting as a temperature integral should prove useful in the search for accurate thermal XC approximations.

On the other hand, ground-state DFT has benefited enormously from testing on benchmark data[SGB97; ES99]. But for thermal effects, even a simple H atom is difficult, as one must include sums over all possible particle numbers in the partition function. The asymmetric Hubbard dimer is the simplest imaginable exactly-solvable model, and can be considered a model for H₂ in a minimal basis. While the truncated Hilbert space makes it unrealistic at higher temperatures, it also makes it practical to solve exactly. Thus our calculations on this model demonstrate the behavior of correlation at finite temperatures in one simple case. Unfortunately, due to the lack of a continuum, this cannot be used to check the performance of LDA or GGA.

Thermodynamics tells us simple relations between entropy and free energy and other quantities. But it requires very careful reasoning to deduce the corresponding relations among density functionals, as the density must be held fixed, not the external potential. Our relations between entropy and the universal part of the Mermin functional show this, and subtraction of the corresponding KS contributions yields crucial relations among correlation contributions. They also yield simple inequalities that are not automatically satisfied once thermal XC contributions are approximated.

Lastly, the recent proof of TDDFT for finite temperatures within linear response justifies the extraction of conductivities within the Kubo response formalism from KS orbitals and energies. It also shows that the random-phase approximation, which is now routinely calculated for inhomogeneous systems in many codes in both quantum chemistry and materials science[KF96; F01; F08; EYF10; EBF12; F16], might be an excellent starting point for more accurate approximations to the XC thermal corrections, using approximations to the temperature-dependent XC kernel.

Finally, our recent work explains how ignoring thermal XC effects, which is usually done in practical DFT WDM calculations, might not be as poor an approximation as it first appears. Calculations on the Hubbard dimer show that XC effects become relatively less important as the temperature increases. Thus the errors in the self-consistent density and orbitals caused by any approximation to the XC lessen with increasing temperature, so that calculations of the KS conductance should be more accurate as temperature increases (somewhat counterintuitively).

To summarize, the success of modern density functional approximations in WDM simulations strongly implies the importance of chemical phenomena in such simulations, and the need to accurately approximate the energetics.

6 Conclusion

Thermal density functional theory is an increasingly utilized tool for calculations of hot systems such as warm dense matter. These WDM systems include inertial confinement fusion, planetary interiors, and shock experiments. There have been many recent developments ranging from exact conditions, improved understanding, and extensions beyond equilibrium with more foreseeable, and exciting, improvements on the horizon. These steps forward set up the foundation for further future success of thermal DFT in the years to come.

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