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Phys. Rev. Lett. **116**, 233001 — Published 8 June 2016

DOI: [10.1103/PhysRevLett.116.233001](https://doi.org/10.1103/PhysRevLett.116.233001)

Thermal density functional theory: Time-dependent linear response and approximate functionals from the fluctuation-dissipation theorem

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(Dated: April 20, 2016)

The van Leeuwen proof of linear-response time-dependent density functional theory (TDDFT) is generalized to thermal ensembles. This allows generalization to finite temperatures of the Gross-Kohn relation, the exchange-correlation kernel of TDDFT, and fluctuation dissipation theorem for DFT. This produces a natural method for generating new thermal exchange-correlation (XC) approximations.

PACS numbers: 31.15.E-, 71.15.Mb, 05.30.Fk

Kohn-Sham density functional theory (KS-DFT) is a popular and well-established approach to electronic structure problems in many areas, especially materials science and chemistry[1]. The Kohn-Sham method imagines a fictitious system of non-interacting fermions with the same density as the real system[2] and from which the ground-state energy can be extracted. Only a small fraction of the total energy, called the exchange-correlation (XC) energy, need be approximated to solve any ground-state electronic problem[1], and modern approximations usually produce sufficient accuracy to be useful[3]. The advent of TDDFT generalized this method to time-dependent problems[4]. Limiting TDDFT to linear-response yields a method for extracting electronic excitations[5, 6], once another functional, the XC kernel, is also approximated.

But there is growing interest in systems in which the electrons are not close to zero temperature. Warm dense matter (WDM) is partially ionized, solid-density matter having a temperature near the Fermi energy. It has wide-ranging applications including the astrophysics of giant planets and white dwarf atmospheres[7–14], cheap and ultra-compact particle accelerators and radiation sources[15–17], and the eventual production of clean, abundant energy via inertial confinement fusion[18, 19]. One of the most successful methods for simulating equilibrium warm dense matter combines DFT[2, 20] and molecular dynamics[21] to capture quantum mechanical effects of WDM electrons and the classical behavior of ions[7–14, 22–24]. Such simulations use the Mermin theorem[25] to generate a KS scheme at finite temperature, defined to generate the equilibrium density and free energy. In practice, the XC free energy is almost always approximated with a ground-state approximation, but formulas for thermal corrections are being developed[26–30].

Many processes of interest involve perturbing an equilibrium system with some time-dependent (TD) perturbation, such as a laser field[31] or a rapidly moving

nucleus as in stopping power[32–34]. Of great interest within the WDM community are calculations of spectra, dynamic structure factors, and the flow of energy between electrons and ions[35–38]. Spectra expose a material’s response to excitation by electromagnetic radiation, which would facilitate experimental design and analysis. Dynamic structure factors can be related to the x-ray scattering response, which is being developed as a temperature and structural diagnostic tool for WDM[39]. Thus it would appear that a TD version of the Mermin formalism is required. A theorem is proven in Li et al.[40, 41], but the formalism assumes the temperature is fixed throughout the process, and so cannot describe e.g., equilibration between electrons and ions. Moreover, the proof requires the Taylor expansion of the perturbing potential as a function of time, just as in the Runge-Gross (RG) theorem[4]. This can be problematic for initial states with cusps[42], such as at the nuclear centers. (Recent efforts[43, 44] have focused on avoiding these complications at zero temperature.) Finally, the RG proof requires invocation of a boundary condition to complete the one-to-one correspondence between density and potential[45], which create subtleties when applied to extended systems[46].

In the present work, we prove the RG theorem at finite temperature within linear response by generalizing the elegant linear response proof of van Leeuwen[43] to thermal ensembles. Our proof avoids several of the drawbacks mentioned above, while still providing a solid grounding to much of WDM theoretical work. We then define the exchange-correlation kernel at finite temperature and generalize the Gross-Kohn equation. Finally, we extend the fluctuation-dissipation theorem of ground-state DFT to finite temperatures, and show how this provides a route to *equilibrium* free energy XC approximations.

Consider a system of electrons in thermal and particle equilibrium with a bath at some temperature, τ , and with static equilibrium density $n^\tau(\mathbf{r})$. The system extends throughout space with a finite average density, i.e.,

the thermodynamic limit has been taken. The limit of isolated atoms or molecules is achieved by then taking the separation between certain nuclei to infinity. In this sense, no surface boundary condition need be invoked[45], as the density never quite vanishes, while the average particle number per atom or molecule molecule is finite. These electrons are perturbed at $t = 0$ by a potential $\delta v(\mathbf{r}, t)$ that is Laplace-transformable. To avoid complex questions of equilibration, we consider only the linear response of the system, so that the perturbation does not affect the temperature of the system as, e.g., Joule heating is a higher order effect[47]. The Kubo response formula for the density change in response to δv is

$$\delta n^\tau(\mathbf{r}, s) = \int d^3 r' \chi^\tau(\mathbf{r}, \mathbf{r}', s) \delta v(\mathbf{r}', s), \quad (1)$$

where the Laplace transform

$$\delta v(\mathbf{r}, s) = \int_0^\infty dt e^{-st} \delta v(\mathbf{r}, t) \quad (2)$$

is assumed to exist for all $s > 0$. Within the grand canonical ensemble[48, 49], the equilibrium density-density response function is[50]:

$$\chi^\tau(\mathbf{r}, \mathbf{r}', s) = i \sum_{ij} \mathbf{w}_i \frac{\Delta n_{ij}^{\tau*}(\mathbf{r}) \Delta n_{ij}^\tau(\mathbf{r}')}{s - i\omega_{ji}} + c.c., \quad (3)$$

where

$$\Delta n_{ij}^\tau(\mathbf{r}) = \langle i | \hat{n}(\mathbf{r}) | j \rangle - \delta_{ij} n^\tau(\mathbf{r}) \quad (4)$$

are matrix elements of the density fluctuation operator. The energy-ordered indices i, j run over all many-body states (both bound and continuum[51]) with all particle numbers, but Δn_{ij}^τ vanishes unless $N_i = N_j$. The transition frequencies $\omega_{ji} = E_j - E_i$, and the statistical weights \mathbf{w}_i are thermal occupations for the equilibrium statistical operator $\hat{\Gamma}^\tau = \sum_i \mathbf{w}_i |\Psi_i\rangle \langle \Psi_i|$ and obey $\mathbf{w}_i < \mathbf{w}_j$ if $E_i > E_j$ and $N_i = N_j$. This condition is satisfied by the grand canonical ensemble of common interest with $\mathbf{w}_i = \exp[-(E_i - \mu N_i)/\tau] / \sum_i \exp[-(E_i - \mu N_i)/\tau]$.

We also need the (Laplace-transformed) one-body potential operator:

$$\delta \hat{V}(s) = \int d^3 r \hat{n}(\mathbf{r}) \delta v(\mathbf{r}, s), \quad (5)$$

and its matrix elements:

$$\delta V_{ij}(s) = \langle i | \delta \hat{V}(s) | j \rangle. \quad (6)$$

Its expectation value is

$$\delta V^\tau(s) = \sum_i \mathbf{w}_i V_{ii}(s) = \int d^3 r n^\tau(r) \delta v(\mathbf{r}, s), \quad (7)$$

so that matrix elements of its fluctuations are

$$\Delta V_{ij}^\tau(s) = \delta V_{ij}(s) - \delta_{ij} \delta V^\tau(s). \quad (8)$$

Then consider the expectation value:

$$m^\tau(s) = \int d^3 r \delta n^\tau(\mathbf{r}, s) \delta v(\mathbf{r}, s). \quad (9)$$

Inserting Eq. (1) and using the definitions, we find

$$m^\tau(s) = - \sum_{ij} \mathbf{w}_i | \Delta V_{ij}^\tau(s) |^2 \frac{2\omega_{ji}}{s^2 + \omega_{ji}^2}. \quad (10)$$

This is rearranged as

$$m^\tau(s) = -2 \sum_{i=0}^\infty \sum_{j=i+1}^\infty \frac{(\mathbf{w}_i - \mathbf{w}_j)\omega_{ji}}{s^2 + \omega_{ji}^2} | \Delta V_{ij}^\tau(s) |^2. \quad (11)$$

We have ordered all states by energy regardless of particle number here for simplicity, though this is not strictly necessary since different particle number subsystems do not interact. For now, we assume no degeneracies. Then the above expression, $m^\tau(s)$, vanishes only if every $\Delta V_{ij}^\tau(s)$ does for $i \neq j$ because of our assumption that $(\mathbf{w}_i - \mathbf{w}_j)\omega_{ji} > 0$ if $i \neq j$.

The usual statement of the RG theorem is that no two potentials that differ by more than an inconsequential function of time alone can give rise to the same density (for fixed statistics, interparticle interaction, and initial state[4]). Imagine two such perturbations exist, yielding the same density response. Since, in linear response, the density response is proportional to the perturbation, we can subtract one from the other, and the statement to be proved is that there is no non-trivial perturbation with zero density response. If it did exist, then $m^\tau(s)$ would vanish and our algebra shows that every $\Delta V_{ij}^\tau(s)$ with $i \neq j$ would also. Finally,

$$\sum_{k=1}^{N_i} \delta v(\mathbf{r}_k, s) \Psi_j(\mathbf{r}_1 \dots \mathbf{r}_{N_i}) = \sum_i \delta V_{ij}(s) \Psi_i(\mathbf{r}_1 \dots \mathbf{r}_{N_i}), \quad (12)$$

which can be proven by integrating over all coordinates with Ψ_k^* . Then, as $\Delta V_{ij}^\tau(s) = \delta V_{ij}(s)$ for $i \neq j$, and must vanish if there is no density response, the sum on the right of Eq. (12) collapses to just the j -th term, showing that $\delta v(\mathbf{r}, s)$ must be spatially independent.

We can also include a finite number (M) of degenerate excited eigenstates. (For the complications involved when the ground-state is degenerate, see Ref. [52]). For such states, $\omega_{ij} = 0$ and the argument above no longer implies $\delta V_{ij}(s)$ vanishes, as the perturbation couples degenerate states within the same subspace. But simply choose at least M points in the $3N$ -dimensional coordinate space that are not on any nodal hypersurface of the degenerate subspace. Then the only solution to Eq. (12) is again that $\delta v(\mathbf{r}, s)$ must be independent of \mathbf{r} .

Thus we have generalized the van Leeuwen proof to thermal ensembles, even with finite degeneracies among excited states. Our proof applies to *any* ensemble with

weights that monotonically decrease with increasing energy for each particle number[53, 54]. This avoids complications caused by cusps in initial wavefunctions[42, 55]. Extension to spatially periodic potentials is straightforward, as no boundary condition[45] was invoked[46].

In order for the above result to be of practical use, we consider the KS scheme for finite-temperature, time-dependent systems and provide a method for generating XC approximations. We assume the equilibrium Mermin-Kohn-Sham (MKS)[2, 25] potential exists. At this point, we switch to using the more familiar Fourier-transform notation, but in fact all results and definitions apply only to Laplace-transformable perturbations. (In practice, this distinction rarely matters, but occasional formal difficulties arise if this restriction is not made, see Ref. [56] and Sec. 3.2 of Ref. [43].) First we generalize the Gross-Kohn response formula[57] to thermal ensembles. Define

$$\chi^\tau(\mathbf{r}, \mathbf{r}', \omega) = \sum_{jk} \mathbf{w}_j \left\{ \frac{\langle j | \hat{n}(\mathbf{r}) | k \rangle \langle k | \hat{n}(\mathbf{r}') | j \rangle}{\omega - \omega_{kj} + i\eta} - \frac{\langle j | \hat{n}(\mathbf{r}') | k \rangle \langle k | \hat{n}(\mathbf{r}) | j \rangle}{\omega + \omega_{kj} + i\eta} \right\}, \quad (13)$$

where $\eta \rightarrow 0^+$ [58].

Because of our proof of one-to-one correspondence, we can invert the response function (excluding a constant), and write

$$(\chi^\tau)^{-1}(12) = \frac{\delta v(1)}{\delta n(2)}, \quad (14)$$

where 1 denotes the coordinates \mathbf{r}, t , and 2 another pair[59]. The standard definition of XC is:

$$v_s(1) = v(1) + v_H(1) + v_{xc}(1), \quad (15)$$

where v_s is the one-body potential of the non-interacting KS system and v_H is the Hartree potential[60]. Differentiating with respect to $n(2)$, this yields

$$(\chi_s^\tau)^{-1}(12) = (\chi^\tau)^{-1}(12) + f_H(12) + f_{xc}^\tau(12), \quad (16)$$

which defines the XC kernel at finite temperature, where χ_s^τ is the KS response function[58] and the traditionally defined Hartree contribution is simply

$$f_H(12) = \frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (17)$$

This follows the definition within the Mermin formalism[25] (but see Refs. [48] and [53] for alternative choices and their consequences). Inverting yields the thermal Gross-Kohn equation[57]:

$$\chi^\tau(12) = \chi_s^\tau(12) + \int d3d4 \chi_s^\tau(13) f_{HXC}^\tau(34) \chi^\tau(42). \quad (18)$$

A simple approximation is then the thermal adiabatic local density approximation (thALDA), in which the thermal XC kernel is approximated using the XC free energy density per particle for a finite-temperature uniform gas, $a_{xc}^{\tau, \text{unif}}$:

$$f_{xc}^{\tau, \text{thALDA}}[n](\mathbf{r}, \mathbf{r}', \omega) = \frac{d^2 a_{xc}^{\tau, \text{unif}}(n)}{d^2 n} \bigg|_{n(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}'), \quad (19)$$

which ignores its nonlocality in space and time, and could be used to generalize ALDA calculations of excitations in metals and their surfaces[61].

We next deduce the fluctuation-dissipation theorem for MKS thermal DFT calculations. This allows us to connect the response function and the Coulomb interaction through the dynamical structure factor[62]. In the MKS scheme, the XC contributions to the free energy are defined via

$$A^\tau[n] = T[n] + V_{ee}[n] + V[n] - \tau S[n] \quad (20)$$

$$= T_s[n] + U[n] + V[n] - \tau S_s[n] + A_{xc}^\tau[n]. \quad (21)$$

By subtraction,

$$A_{xc}^\tau[n] = T_{xc}^\tau[n] + U_{xc}^\tau[n] - \tau S_{xc}^\tau[n] \quad (22)$$

where T denotes kinetic, U denotes potential, and S entropic components. Using many-body theory, the density-density response function determines the potential contribution to correlation[63, 64], just as in the ground state[65]:

$$U_C^\tau = V_{ee}[\hat{\Gamma}^\tau[n]] - V_{ee}[\hat{\Gamma}_s^\tau[n]] \quad (23)$$

$$= - \int d\mathbf{r} \int d\mathbf{r}' \int_0^\infty \frac{d\omega}{2\pi} \coth\left(\frac{\omega}{2\tau}\right) \frac{\Im \Delta \chi^\tau(\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}, \quad (24)$$

where $\Delta \chi^\tau = \chi^\tau - \chi_s^\tau$. By introducing a coupling-constant λ while keeping the density fixed, the thermal connection formula[66] yields

$$A_C^\tau[n] = \lim_{\tau'' \rightarrow \infty} \frac{\tau}{2} \int_\tau^{\tau''} \frac{d\tau'}{\tau'^2} \int d\mathbf{r} \int d\mathbf{r}' \int \frac{d\omega}{2\pi} \coth\left(\frac{\omega}{2\tau}\right) \frac{\Im \Delta \chi^{\tau'}[n_\gamma](\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}, \quad (25)$$

where the scaled density is $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r})$ and $\gamma = \sqrt{\tau'/\tau}$. This is exact, but only if the exact thermal XC kernel is used, as defined by Eq. (16). If the kernel is omitted, the result is the thermal random-phase approximation[67].

Next, we discuss the many applications of Eq. (25). There has been tremendous progress in implementing and testing the random phase approximation for calculating the XC energy in ground-state calculations and

such calculations, while more expensive than standard DFT, are becoming routine[68–70]. Our results provide a thermal generalization that could likewise be used to generate new thermal XC approximations for equilibrium WDM calculations. At finite temperature, the XC hole fails to satisfy the simple sum rules[71] that have proven so powerful in constructing ground-state approximations[72]. But our formula uses instead the XC kernel. Inserting Eqs (18,19) into Eq. (25) yields thALDA-RPA, a new approximation to the equilibrium correlation energy, that can be applied to any system. Another, simpler approximation is ALDA, in which only the zero-temperature XC energy is used in the kernel. Both can be relatively easily evaluated for a uniform gas, and the resulting $a_{xc}^\tau(r_s)$ found from Eq. (25) compared with an accurate parametrization[27]. Even in the uniform gas, thALDA is an approximation because both the q - and ω -dependence of the true f_{xc}^τ are missing; thus the efficacy of these approximations can be tested on the uniform case.

Next we discuss which known exact conditions on the zero-temperature kernel apply to the thermal kernel, and which do not. Because the equilibrium solution is a minimum of the thermal free-energy functional, the zero-force theorem[64]

$$\int d^3r \int d^3r' n^\tau(\mathbf{r}) n^\tau(\mathbf{r}') f_{xc}^\tau(\mathbf{r}, \mathbf{r}', \omega) = 0 \quad (26)$$

should be satisfied and the kernel should be symmetric in its spatial arguments. However, any simple formula for a one-electron system[73] is not true at finite temperature, as the particle number is only an average in the grand canonical ensemble[49, 71].

A last set of conditions is found by considering the coupling-constant dependence in DFT. A parameter λ is introduced that multiplies the electron-electron interaction, while keeping the density constant. Because of simple scaling relations, the λ -dependence can be shown to be determined entirely by coordinate scaling of the density as in Eq. (25), i.e., determined by the functional itself, evaluated at different densities. This is used in both ground-state DFT[74] and in time-dependent DFT[75], and has been generalized to the thermal case[66, 76]. Although the thermal connection formula does not require this relation for the response function, it is useful in many contexts. From the Lehmann representation[50] of χ^τ [63], we find the λ -dependent response function satisfies:

$$\chi^{\tau,\lambda}[n](\mathbf{r}, \mathbf{r}', \omega) = \lambda^4 \chi^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2). \quad (27)$$

Insertion into the definition of f_{xc} yields:

$$f_{xc}^{\tau,\lambda}[n](\mathbf{r}, \mathbf{r}', \omega) = \lambda^2 f_{xc}^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2), \quad (28)$$

and the potential perturbation scales as:

$$\delta v_{xc}^{\tau,\lambda}[n](\mathbf{r}, \omega) = \lambda^2 \delta v_{xc}^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \omega/\lambda^2). \quad (29)$$

Insertion of the scaling relation for the kernel into the thermal connection formula yields a more familiar analog to the ground-state formula.

The exchange kernel must scale linearly with coupling constant, so Eq. (28) produces a rule for scaling of the exchange kernel:

$$f_x^\tau[n_\gamma](\mathbf{r}, \mathbf{r}', \omega) = \gamma f_x^{\tau/\gamma^2}[n](\gamma\mathbf{r}, \gamma\mathbf{r}', \omega/\gamma^2). \quad (30)$$

Because the poles in f_{xc} are λ -dependent, we expect pathologies similar to those in zero-temperature TDDFT if the exact frequency-dependent f_x^τ is used in Eq. (25)[77]. But adiabatic EXX (AEXX), not including frequency-dependence, produces a well-defined approximation to the thermal free energy in which the kernel is non-local. This and the other proposed approximations above could prove useful in WDM simulations when thermal XC effects are relevant (but see [78] for discussion of the subtleties involved in thermal XC approximations).

In conclusion, we have generalized the proofs and constructions of TDDFT within the linear response formalism to thermal ensembles, including those containing a finite number of degeneracies. We have avoided ambiguities about the relative perturbative and thermal equilibration time scales, allowed for degenerate excited states more common in finite-temperature ensembles, avoided invoking boundary conditions and the requirement of Taylor expandability, and provided firm footing for finite-temperature, time-dependent KS-DFT in the linear response regime. Definition of relevant KS quantities led to description of their properties under scaling. Further, we have shown that these quantities, in combination with the thermal connection formula, produce new routes to thermal DFT approximations for use in equilibrium MKS calculations. Implementation and tests of these approximations is ongoing.

APJ acknowledges support from DE-FG02-97ER25308 and the University of California President's Postdoctoral Fellowship, PG from DE14-017426, and KB from CHE-1464795 NSF. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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