Linear-response thermal time-dependent density functional theory

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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.

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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[26–32].

Many processes of interest involve perturbing an equilibrium system with some time-dependent (TD) perturbation, such as a laser field [33] or a rapidly moving nucleus as in stopping power [34–36]. Of great interest within the WDM community are calculations of spectra, dynamic structure factors, and the flow of energy between electrons and ions [37–40]. 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 [41]. Thus it would appear that a TD version of the Mermin formalism is required. A theorem is proven in Li et al.[42, 43], 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[44], such as at the nuclear centers. Much effort is focused on avoiding these complications[45] but so far the Coulomb-interacting case remains open. Finally, such proofs require invocation of a boundary condition to complete the one-to-one correspondence between density and potential[46], which create subtleties when applied to extended systems[47].

In the present work, we make a step forward, by proving the Runge-Gross theorem at finite temperature, but only within linear response. We generalize the elegant linear response proof of van Leeuwen[48] to thermal ensembles. Our proof has none 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 equilibrium with a bath at some temperature, τ, with static equilibrium density $n^\tau(\mathbf{r})$. These 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[49]. The Kubo response formula for the density change in response to δv is

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

where the Laplace transform

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

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

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

where

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

are matrix elements of the density fluctuation operator, $\omega_{ji}=E_j-E_i$ are transition frequencies between the i^{th} and j^{th} states of the N_i- and N_j-body systems and $\mathtt{w}_i=\exp[-(E_i-\mu N_i)/\tau]/\sum_i\exp[-(E_i-\mu N_i)/\tau]$ are thermal occupations. Note that since Eqn. 4 is zero for states with $N_i\neq N_j$, only those with identical particle numbers will give non-zero matrix elements as we proceed.

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

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

and its matrix elements:

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

Its expectation value is

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

so that matrix elements of its fluctuations are

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

Then consider the expectation value:

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

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

$$m^{\tau}(s)=-\sum_{ij}\mathtt{w}_i\mid\Delta V^{\tau}_{ij}(s)\mid^2\frac{2\omega_{ji}}{s^2+\omega^2_{ji}}. \tag{10}$$

If we assume no degeneracies and order states by energy, this is easily rearranged as

$$m^{\tau}(s)=\sum_{i=0}^{\infty}\sum_{j=i+1}^{\infty}\frac{(\mathtt{w}_i-\mathtt{w}_j)\omega_{ji}}{s^2+\omega^2_{ji}}\mid\Delta V^{\tau}_{ij}(s)\mid^2. \tag{11}$$

Note that, apart from the $N_i\neq N_j$ cases for which we already know $\Delta V^{\tau}_{ij}(s)$ is zero, every term in this sum is positive, so it can vanish only if every $\Delta V^{\tau}_{ij}(s)$ does for $i\neq j$.

The usual statement of the RG theorem is that no two potentials that differ by more than a trivial time-dependent constant can give rise to the same density (for fixed statistics, interparticle interaction, and initial state). 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 $\Delta V^{\tau}_{ij}(s)$ with $i\neq j$ would also. Finally, note that

$$\sum_k\delta v(\mathbf{r}_k,s)\Psi_j(\mathbf{r}_1\ldots\mathbf{r}_{N_j})=\sum_i\delta V_{ij}(s)\Psi_i(\mathbf{r}_1\ldots\mathbf{r}_{N_i}), \tag{12}$$

with $N_i=N_j$. Then, as $\Delta V^{\tau}_{ij}(s)=\delta V_{ij}(s)$ 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 degeneracies of finite number. For those states, $\omega_{ij}=0$ and the argument above no longer implies $\delta V_{ij}(s)$ vanishes. But consider Eq. (12) for a degenerate subspace $\mathcal{I}_M$ of size M. Then we have M equations of the form

$$\sum_k\delta v(\mathbf{r}_k,s)=\sum_{i\in\mathcal{I}_M}\delta V_{ij}(s)\frac{\Psi_i(\mathbf{r}_1\ldots\mathbf{r}_{N_i})}{\Psi_j(\mathbf{r}_1\ldots\mathbf{r}_{N_j})} \tag{13}$$

for each $j\in\mathcal{I}_M$. The solution of these equations for δv and the $M-1$ independent wave function ratios implies that if $i\neq j$, $\delta V_{ij}=0$ to ensure that the ratios are allowed to have position dependence. The rest of the proof follows as before. Thus we have generalized the van Leeuwen proof to thermal ensembles. Our proof applies to *any* ensemble with weights that monotonically decrease with increasing energy for each particle number[51].

In order for the above result to be of practical use, we must establish the KS scheme for finite-temperature, time-dependent systems and provide a method for generating XC approximations. To begin, we generalize the Gross-Kohn response formula[52] to thermal ensembles. From this point on, we use the more familiar Fourier transform expressions, though it is more rigorous to apply these results only to the Laplace transform. Because of our proof of one-to-one correspondence, we can invert the response function (excluding a constant), and write

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

where 1 denotes the coordinates $\mathbf{r},t$, and 2 another pair[53]. The standard definition of XC is:

$$v_{\text{S}}(1)=v(1)+v_{\text{H}}(1)+v_{\text{XC}}(1). \tag{15}$$

Differentiating with respect to $n(2)$, this yields

$$\left(\chi^{\tau}_{\text{S}}\right)^{-1}(12)=\left(\chi^{\tau}\right)^{-1}(12)+f_{\text{H}}(12)+f^{\tau}_{\text{XC}}(12) \tag{16}$$

which defines the XC kernel at finite temperature, where $\chi_{\rm S}^\tau$ is the KS response function[54], and the traditionally defined Hartree contribution is simply

$$f_{\rm H}(12) = \frac{\delta(t_1 - t_2)}{|\,\mathbf{r}_1 - \mathbf{r}_2\,|}. \tag{17}$$

This follows the definition within the Mermin formalism[25] (but see Refs. [55] and [56] for alternative choices and their consequences). Inverting yields the thermal Gross-Kohn equation[52]:

$$\chi^\tau(12) = \chi_{\rm S}^\tau(12) + \int d3d4\, \chi_{\rm S}^\tau(13) f_{\rm HXC}^\tau(34) \chi^\tau(42) \tag{18}$$

Finally, we deduce the fluctutation-dissipation theorem for Mermin-Kohn-Sham[2, 25] thermal DFT calculations. Using many-body theory, the density-density response function determines the potential contribution to correlation[50]:

$$U_{\rm C}^\tau = -\int d\mathbf{r} \int d\mathbf{r}' \int_0^\infty \frac{d\omega}{2\pi\,|\mathbf{r} - \mathbf{r}'|} \times \{\Im\,[\chi^\tau(\mathbf{r}, \mathbf{r}', \omega) - \chi_{\rm S}^\tau(\mathbf{r}, \mathbf{r}', \omega)]\} \tag{19}$$

just as for the ground-state[57]. We abbreviate this as

$$U_{\rm C}^\tau = -\int \frac{\overline{d1d2}}{2\pi\,|\mathbf{r} - \mathbf{r}'|}\, \{\Im\,[\chi^\tau(12) - \chi_{\rm S}^\tau(1,2)]\} \tag{20}$$

where the bar denotes the integral over frequency. But we can also use the recently discovered thermal connection formula, which expresses the C free energy of a time-independent thermal system as an integral over temperature[58]:

$$A_{\rm C}^\tau[n] = \frac{\tau}{2} \int_\tau^\infty \frac{d\tau'}{\tau'^2}\, U_{\rm C}^{\tau'}[n_{\sqrt{\tau'/\tau}}]. \tag{21}$$

Here, the density has been coordinate-scaled according to

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r}). \tag{22}$$

Note that this neatly avoids any coupling-constant integral, unlike the adiabatic connection formula. There, the coupling constant λ scales the electron-electron interaction without changing the density. Integrating from $\lambda = 0$ to 1 connects the non-interacting KS system to the fully interacting system and generates correlation energies from potential contributions alone. Here, a similar path to the correlation is provided while bypassing the coupling constant integral.

Combination of Eqns. 20 and 21 yields

$$A_{\rm XC}^\tau[n] = \frac{\tau}{2} \int_\tau^\infty \frac{d\tau'}{\tau'^2} \int \overline{d1d2}\, \left\{\Im\left[\chi^{\tau'}[n_\gamma](12) - \chi_{\rm S}^{\tau'}[n](12)\right]\right\} \tag{23}$$

where $\gamma = \sqrt{\tau'/\tau}$.

Next, we discuss the many applications of Eq. (23). First, if we insert $\chi_{\rm S}^\tau$, the KS thermal response function, we generate only $A_{\rm X}^\tau$, the exchange free energy for a finite-temperature system. If we consider the difference between inserting χ^τ and $\chi_{\rm S}^\tau$, we generate precisely $A_{\rm C}^\tau$. The latter is exact, but only if the exact thermal XC kernel is used. If the kernel is omitted, the result is the thermal random-phase approximation[59].

But we can also use this to generate entirely *new* thermal approximations, with novel temperature dependence. At finite temperature, the XC hole fails to satisfy the simple sum rules[60] that have proven so powerful in constructing ground-state approximations[61]. But our formula uses instead the XC kernel, which can be approximated in other ways. We suggest here a thermal adiabatic local density approximation (TALDA), in which the thermal XC kernel is approximated by ALDA, i.e.,

$$f_{\rm XC}^{\tau,\rm TALDA}[n](\mathbf{r}, \mathbf{r}', \omega) = \left.\frac{d^2 a_{\rm XC}^{\tau,\rm unif}(n)}{d^2 n}\right|_{n(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}'), \tag{24}$$

inserted into Eq. (23), and applied to any inhomogeneous system. Another, simpler approximation is ALDA, in which only the ground-state XC energy is used in the kernel. Both can be relatively easily evaluated for a uniform gas, and the resulting $a_{\rm XC}^\tau(r_{\rm S})$ found from Eq. (23) compared with an accurate parametrization[27]. Even in the uniform gas, TALDA is an approximation because both the q- and ω-dependence of the true $f_{\rm XC}^\tau$ are missing.

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 and zero-torque conditions should be satisfied and the kernel should be symmetric in its spatial arguments. However, the simple formulas for one electron are not true at finite temperature, as the particle number is only an average[62].

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. (22), i.e., determined by the functional itself, evaluated at different densities. This is used in both ground-state DFT[63] and in time-dependent DFT[64], and has been generalized to the thermal case[58, 65]. Although the thermal connection formula does not require this relation for the response function, it is useful in many contexts. From the Lehmann representation of χ^τ, we find[50] the λ-dependent response function satisfies:

$$\chi^{\tau,\lambda}[n](\mathbf{r}, \mathbf{r}', s) = \lambda^4\, \chi^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', s/\lambda^2). \tag{25}$$

Insertion into the definition of $f_{\rm XC}$ yields:

$$f_{\rm XC}^{\tau,\lambda}[n](\mathbf{r}, \mathbf{r}', s) = \lambda^2\, f_{\rm XC}^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', s/\lambda^2) \tag{26}$$

and the potential perturbation scales as:

$$\delta v_{\rm XC}^{\tau,\lambda}[n](\mathbf{r},s) = \lambda^2\,\delta v_{\rm XC}^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r},s/\lambda^2). \tag{27}$$

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. (26) produces a rule for scaling of the exchange kernel:

$$f_{\rm X}^{\tau}[n_\gamma](\mathbf{r},\mathbf{r}',\omega) = \gamma f_{\rm X}^{\tau/\gamma^2}[n](\gamma\mathbf{r},\gamma\mathbf{r}',\omega/\gamma^2). \tag{28}$$

Because the poles in $f_{\rm XC}$ are λ-dependent, we expect similar pathologies with zero-temperature TDDFT if the exact frequency-dependent $f_{\rm X}^{\tau}$ is used in Eq. (23)[66]. 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 [67]).

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. In doing so, we have eliminated ambiguities about the relative perturbative and thermal equilibration time scales, allowed for degenerate states more common in finite-temperature ensembles, and avoided restrictive boundary conditions and the requirement of Taylor expandability. 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.

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