Connection formulas for thermal density functional theory

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The adiabatic connection formula of ground-state density functional theory relates the correlation energy to a coupling-constant integral over a purely potential contribution, and is widely used to understand and improve approximations. The corresponding formula for thermal density functional theory is cast as an integral over temperatures instead, ranging upward from the system's physical temperature. We also show how to relate different correlation components to each other, either in terms of temperature or coupling-constant integrations. We illustrate our results on the uniform electron gas.

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The adiabatic connection formula [1–3], often derived via the Hellmann-Feynman theorem [4,5], has been used extensively as an interpretive and development tool in density functional theory (DFT) [6,7]. By scaling the electron-electron interaction with a coupling constant, while keeping the density fixed, one constructs a path from the noninteracting Kohn-Sham (KS) system to the fully interacting system of interest. This yields the exchange-correlation (XC) energy as an integral over only a purely potential contribution.

For equilibrium systems at finite (i.e., nonzero) temperatures, Mermin [8] generalized the Hohenberg-Kohn (HK) theorems of ground-state DFT. Applying the theorem to the KS scheme of fictitious noninteracting electrons with the same equilibrium density, one finds a set of thermal KS equations [7], in which the KS orbitals are thermally occupied via a Fermi function [9]. The relation to the physical system is given by the thermal XC free energy, which now includes an entropic contribution. The dependence of the Hartree and exchange energies on the coupling constant is simple [10], but the thermal correlation free energy is more complicated. Relating scaling to the coupling constant, the thermal adiabatic connection formula was derived in Ref. [10].

Here, we show that the adiabatic connection formula at finite temperature can be recast as an integral over temperatures, *without changing the coupling constant*. This thermal connection formula for the XC free energy at temperature τ is

$$A_{\rm xc}^{\tau}[n] = \frac{\tau}{2}\lim_{\tau''\to\infty}\int_{\tau}^{\tau''}\frac{d\tau'}{\tau'^2}\,U_{\rm xc}^{\tau'}[n_{\sqrt{\tau'/\tau}}] \tag{1}$$

where $U_{\rm xc}^{\tau}[n]$ is the purely potential contribution to the XC free energy, and

$$n_{\gamma}(\mathbf{r}) = \gamma^3\, n(\gamma\mathbf{r}) \tag{2}$$

is the usual coordinate scaling of the density introduced by Levy and Perdew [11] for the ground-state problem. Thus Eq. (1) extracts the XC free energy, including both kinetic and entropic contributions, from the interaction contribution alone. Intriguingly, it is expressed as an integral over all temperatures *higher* than the temperature of interest.

However, just as in ground-state DFT, knowledge of *any* component of the correlation energy as a functional of the density is sufficient to determine *any* other [12]. Thus approximations to the correlation energy can be made for any one of these components, and converted into, e.g., an approximation to the correlation free energy. An example is the "upside-down" adiabatic connection in which, for strongly correlated systems, it can be advantageous to derive approximations to the kinetic correlation energy [13–16]. Such formulas were written down and collected explicitly in Ref. [12], and even used to construct accurate and approximate adiabatic connection curves.

This paper reports both the thermal connection formula and the derivation and many results for these formulas at nonzero temperatures, with examples from the uniform gas. Atomic units are used throughout, with energies in hartrees and distances in Bohr radii.

To begin, we review only those thermal DFT concepts needed to proceed, beginning with the Mermin-Kohn-Sham (MKS) equations. For a full introduction to thermal DFT, please see Ref. [9], and see Ref. [17] for an alternative perspective presented via Legendre transforms. The MKS equations closely resemble those at zero temperature, though they are complicated by temperature-dependent eigenvalues and chemical potential [7]:

$$\left[-\frac{1}{2}\nabla^2 + v_{\rm s}^{\tau}(\mathbf{r})\right]\phi_i^{\tau}(\mathbf{r}) = \epsilon_i^{\tau}\phi_i^{\tau}(\mathbf{r}) \tag{3}$$

where $v_{\rm s}^{\tau}(\mathbf{r})$ is *defined* by requiring that the resulting thermal density

$$n^{\tau}(\mathbf{r}) = \sum_i f_i^{\tau}|\phi_i(\mathbf{r})|^2 \tag{4}$$

matches that of the physical problem, where

$$f_i^{\tau} = (1 + e^{(\epsilon_i^{\tau}-\mu)/\tau})^{-1} \tag{5}$$

are Fermi occupation factors at temperature τ. The chemical potential μ is chosen to yield the desired average number of electrons, N. In the usual way [18], the free energy of the physical system is

$$A = T + V_{\rm ee} + V - \tau S \tag{6}$$

where T is the kinetic energy, $V_{\rm ee}$ is the interelectron repulsion, V is the one-body potential, and S is the entropy. In terms of the corresponding KS quantities,

$$A = T_{\rm s} + U + V - \tau S_{\rm s} + A_{\rm xc}, \tag{7}$$

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where the subscript s denotes evaluation for the KS system, U is the Hartree energy, and $A_{\rm XC}$ is the XC free energy, defined by this relation. All quantities can be considered as density functionals, in which the chemical potential has already been eliminated in terms of the mean particle number, since that is determined by the density. Most are also explicitly temperature dependent. Others, such as the Hartree and one-body energies, are not, but their values for a fixed potential vary with temperature via the temperature-dependent density. Because the density minimizes the free energy, one finds

$$v_{\rm s}^{\tau}[n](\mathbf{r}) = v(\mathbf{r}) + v_{\rm H}[n^{\tau}](\mathbf{r}) + v_{\rm XC}^{\tau}[n^{\tau}](\mathbf{r}) \tag{8}$$

where $v_{\rm H}[n](\mathbf{r})$ is the traditionally defined Hartree potential [19,20] and

$$v_{\rm XC}^{\tau}[n](\mathbf{r}) = \delta A_{\rm XC}^{\tau}/\delta n(\mathbf{r}). \tag{9}$$

Unlike the ground-state XC energy, $A_{\rm XC}$ includes entropic contributions. Here our focus is on the correlation effects, so we subtract off the exchange contribution [which can be isolated by scaling to the high-density (weakly coupled) limit [10]]. Then the kinetic correlation energy is

$$T_{\rm C}^{\tau}[n] = T^{\tau}[n] - T_{\rm s}^{\tau}[n], \tag{10}$$

while the potential correlation energy is

$$U_{\rm C}^{\tau}[n] = V_{\rm ee}^{\tau}[n] - U[n] - E_{\rm X}^{\tau}[n]. \tag{11}$$

Both these are exact analogs of their ground-state counterparts. But we also have correlation entropy:

$$S_{\rm C}^{\tau}[n] = S^{\tau}[n] - S_{\rm s}^{\tau}[n]. \tag{12}$$

We write $A_{\rm C}^{\tau}$ as a sum of two contributions:

$$A_{\rm C}^{\tau}[n] = K_{\rm C}^{\tau}[n] + U_{\rm C}^{\tau}[n], \tag{13}$$

where the kentropic component is

$$K_{\rm C}^{\tau}[n] = T_{\rm C}^{\tau}[n] - \tau\, S_{\rm C}^{\tau}[n] \tag{14}$$

and this combination plays a role mimicking that of the kinetic correlation alone in the ground-state case [10].

Reference [10] introduced two important results. The first is the relation between coupling constant and scaling at finite temperature. Introduce a coupling constant λ in front of $V_{\rm ee}$, which is a positive number, and consider varying λ keeping $n(\mathbf{r})$ fixed. The physical system has $\lambda = 1$, while $\lambda = 0$ reduces to the KS system. In a method similar to that used in the ground state [21], combining Eq. (31) of Ref. [10] with finite-temperature density scaling and the relationship between coordinate- and interaction-scaled statistical operators yields

$$A_{\rm XC}^{\tau,\lambda}[n] = \lambda^2\, A_{\rm XC}^{\tau/\lambda^2}[n_{1/\lambda}], \tag{15}$$

where $A_{\rm XC}^{\tau,\lambda}$ is the value at coupling constant λ, and on the right the density has been coordinate scaled. This relates changes in the coupling constant to coordinate scaling of the density, just as in the ground-state theory [11]. All components of the energy, such as the exchange, kentropic, and potential contributions, scale in the fashion of Eq. (15). Because exchange is evaluated on the KS thermal density matrix of noninteracting electrons, it scales simply with λ [10]:

$$A_{\rm X}^{\tau,\lambda}[n] = \lambda\, A_{\rm X}^{\tau/\lambda^2}[n]. \tag{16}$$

A second important result of Ref. [10] is the conventional adiabatic connection formula. Write this in terms of correlation alone by using the above lambda scaling of exchange:

$$A_{\rm C}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda}\, U_{\rm C}^{\tau,\lambda}[n]. \tag{17}$$

This extracts the full C free energy from its potential contribution alone, but at the price of having to integrate over the coupling constant. This is a generalization of the formula that has proven so useful at zero temperature [2].

But one can go further than this, and convert all coordinate scaling into temperature scaling, yielding very different formulas. Begin with the exchange-correlation version of Eq. (17) and insert Eq. (15). Define $\tau' = \tau/\lambda^2$, and change variables to find Eq. (1). This is one of the central results of this paper: The XC free energy can be extracted from the potential-only contribution, as a temperature integral, not a coupling-constant integral. This integral runs from the given temperature *upwards*, and so does not include information from the ground-state functional, but rather from the high-temperature limit.

We can also generalize the adiabatic connection formula for $A_{\rm C}^{\tau}$ to an arbitrary coupling constant. This follows precisely the derivation in ground-state DFT [11]. Apply Eq. (15) to Eq. (17), insert the adiabatic connection, and identify the potential-only piece inside the integral to find

$$A_{\rm C}^{\tau,\lambda}[n] = \int_0^{\lambda} \frac{d\lambda'}{\lambda'}\, U_{\rm C}^{\tau,\lambda'}[n]. \tag{18}$$

We can then generalize the thermal connection to arbitrary coupling constants:

$$A_{\rm C}^{\tau,\lambda}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau/\lambda^2}^{\tau''} \frac{d\tau'}{\tau'^2}\, U_{\rm C}^{\tau'}[n_{\sqrt{\tau'/\tau}/\lambda}]. \tag{19}$$

This shows that we can trivially generate the coupling-constant dependence of $A_{\rm XC}$ by changing the limits of the thermal integration and scaling the density argument. This completes our formulas for extracting $A_{\rm C}^{\tau}$ from $U_{\rm C}^{\tau}$. These are useful when an expression (exact or approximate) is derived for $U_{\rm C}^{\tau}$, to get an expression for $A_{\rm C}^{\tau}$. Our thermal connection formula negates the need for a coupling-constant dependence when τ is finite.

However, it can also happen that, e.g., by calculation, $A_{\rm C}^{\tau}$ is known, but it is desired to extract $U_{\rm C}^{\tau}$, i.e., the reverse process. This is used in ground-state DFT when plotting the integrand in the adiabatic connection formula [22–24]. It is now straightforward to find this relation, by differentiating Eq. (19) with respect to λ, yielding

$$U_{\rm C}^{\tau,\lambda}[n] = \lambda\, \frac{dA_{\rm C}^{\tau,\lambda}[n]}{d\lambda}. \tag{20}$$

In the special case where $\lambda = 1$, we find the compact result

$$U_{\rm C}^{\tau}[n] = \left.\frac{dA_{\rm C}^{\tau,\lambda}[n]}{d\lambda}\right|_{\lambda=1}, \tag{21}$$

which is exactly analogous to the ground-state formula. This cannot be simply rewritten without the coupling-constant dependence, as derivatives with respect to scaling yield terms that depend on the potential.

Since none of the components of the correlation free energy are independent, we can also write the free energy in terms of the kentropic contribution alone. This is sometimes used in ground-state DFT (where the kentropy is just the kinetic energy) to create approximations starting from the strictly correlated limit [14]. In our case, we begin with Eq. (13), inserted into Eq. (20) to yield

$$K_{\rm c}^{\tau,\lambda}[n] = A_{\rm c}^{\tau,\lambda}[n] - \lambda \frac{dA_{\rm c}^{\tau,\lambda}[n]}{d\lambda}, \tag{22}$$

showing how to extract $K_{\rm c}^{\tau,\lambda}$ at any coupling strength from $A_{\rm c}^{\tau,\lambda}$. More specifically,

$$K_{\rm c}^{\tau}[n] = A_{\rm c}^{\tau}[n] - \left.\frac{dA_{\rm c}^{\tau,\lambda}[n]}{d\lambda}\right|_{\lambda=1}, \tag{23}$$

which means any approximation for $A_{\rm c}^{\tau}[n]$ uniquely determines an approximation for $K_{\rm c}^{\tau}[n]$. But we can also regard Eq. (22) as a differential equation in λ, and solve for $A_{\rm c}^{\tau,\lambda}$, to find

$$A_{\rm c}^{\tau,\lambda}[n] = -\lambda \int_0^{\lambda} \frac{d\lambda'}{\lambda'^2} K_{\rm c}^{\tau,\lambda'}[n], \tag{24}$$

which is the generalization of the ground-state adiabatic connection formula in terms of $K_{\rm c}^{\tau}$ to finite temperature [Eq. (18) of Ref. [12]]. For the physical system,

$$A_{\rm c}^{\tau}[n] = -\int_0^1 \frac{d\lambda}{\lambda^2} K_{\rm c}^{\tau,\lambda}[n]. \tag{25}$$

Finally, we can convert this into a thermal connection formula using the universal rule for scaling, and changing variables we find

$$A_{\rm c}^{\tau}[n] = -\frac{\sqrt{\tau}}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^{3/2}} K_{\rm c}^{\tau'}[n_{\sqrt{\tau'/\tau}}]. \tag{26}$$

This is the thermal connection formula in terms of the kentropic correlation energy.

It is straightforward to combine these various results to form relations between $K_{\rm c}^{\tau}$ and $U_{\rm c}^{\tau}$. We find

$$K_{\rm c}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda} U_{\rm c}^{\tau,\lambda}[n] - U_{\rm c}^{\tau}[n], \tag{27}$$

while the reverse relation is

$$U_{\rm c}^{\tau}[n] = -\int_0^1 \frac{d\lambda}{\lambda^2} K_{\rm c}^{\tau,\lambda}[n] - K_{\rm c}^{\tau}[n]. \tag{28}$$

We can turn these into thermal connection formulas. For Eq. (27), we simply use $A_{\rm c}^{\tau} = K_{\rm c}^{\tau} + U_{\rm c}^{\tau}$ in Eq. (1) to find

$$K_{\rm c}^{\tau}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2} (U_{\rm c}^{\tau'}[n_{\sqrt{\tau'/\tau}}] - 2U_{\rm c}^{\tau}[n]). \tag{29}$$

Lastly, we discuss how these results differ from many long-known results in the plasma physics community. In the standard approach to statistical mechanics, the potential is given and so held fixed, and energies and potentials are found for, e.g., fixed temperature dependence and chemical potential. The latter can be eliminated in favor of fixed mean particle number. But as the temperature varies, the one-body density also varies, and so such relations do not directly yield constraints on the exact density functionals that are independent of the specific system under study.

Our derivation yields direct relations among density functionals. Because the density fixes the average particle number, this is no longer a free variable, and so the only other dependence is on the temperature. Hence all derivatives with respect to temperature are total, not partial. By our methods, we are deriving relations that can, for example, be used to test or construct any thermal density functional correlation approximation, without reference to the given system. In fact, for inhomogeneous systems, both the chemical potential and the one-body external potential vary in complex ways as the temperature changes with fixed density. The beauty of this methodology, created by Levy and Perdew [11] for the ground-state problem, is that those dependencies need never be discussed.

In the special case of a homogeneous system, i.e., the uniform electron gas or the one-component plasma, none of these effects are relevant, since the potential and densities are constant at all temperatures. In this case, our formulas trivially match the long-known results [25–27], and so the uniform case serves as a useful consistency check. For example, in the uniform case, our formulas are trivially related to the standard coupling-constant integration [28,29]. Several of the relations for the uniform gas were used recently [30] to reparametrize quantum Monte Carlo results for the thermal uniform gas. On the other hand, since the coupling constant is defined in terms of parameters in some way averaged over the entire system, such a treatment differs utterly from ours for any inhomogeneous system. For example, in our high-temperature limit, the density retains all the inhomogeneity of the original system, and never becomes more uniform, by definition.

In Fig. 1, we plot the correlation free energy for the uniform gas, based on the recent parametrization of Ref. [30], for several values of $r_{\rm s}$. In every case, the free energy initially increases in magnitude with temperature, and then slowly shrinks for temperatures beyond the Fermi temperature. We

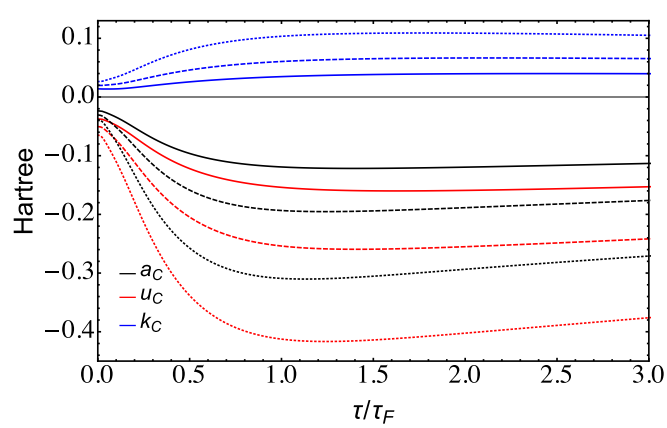

FIG. 1. The correlation free energy and correlation components per particle for the uniform electron gas with $r_{\rm s} = 2$ (solid), $r_{\rm s} = 1$ (dashed), and $r_{\rm s} = 0.5$ (dotted), as a function of the temperature in units of the Fermi temperature. The parametrization in Ref. [30] is used as a starting point, from which the correlation free energy per particle (black), the potential correlation (red), and the kentropic correlation (blue) are extracted.

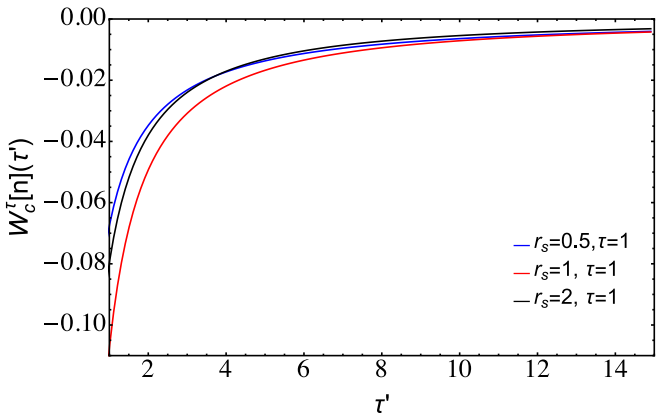

FIG. 2. The integrand of the thermal connection formula for the uniform gas at various r_s values with $\tau = 1$.

write the connection formula

$$A_c^\tau[n] = \lim_{\tau''\to\infty} \int_\tau^{\tau''} d\tau' W_c^\tau[n](\tau') \tag{30}$$

where

$$W_c^\tau[n](\tau') = \frac{\tau}{2\tau'^2} U_c^{\tau'}[n_{\sqrt{\tau'/\tau}}]. \tag{31}$$

For the uniform gas, we divide by the volume and plot energy densities. In Fig. 2, we plot the integrand for $\tau = 1$ for various values of r_s. Clearly, the curves themselves do not yield much insight directly into the thermal correlation free energy (at least, plotted in this way). But we have carefully checked that integrating the curves from $\tau' = \tau$ to infinity yields the $a_c^\tau = A_c^\tau/V$ values plotted in Fig. 1. The smaller τ is, the more carefully the integrand must be approximated, especially since there is a delicate balance between the divergence in the integrand and the prefactor of τ. But obviously approximations that expand $W_c^\tau(\tau')$ about the high-temperature, high-density limit yield approximations to $A_c^\tau[n]$ via Eq. (30).

To conclude, we have found a temperature integral representation of the XC free energy of thermal DFT, which we call the thermal connection formula. Unlike the ground-state adiabatic connection formula, it relates the XC free energy to the potential contribution at higher temperatures. We have also derived many other relations among the different correlation components. We have used these to plot the various contributions to the uniform gas. We anticipate these relations playing a key role in the development of thermal density functional approximations beyond the local approximation.

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[1] J. Harris and R. O. Jones, The surface energy of a bounded electron gas, J. Phys. F **4**, 1170 (1974).
[2] D. C. Langreth and J. P. Perdew, The exchange-correlation energy of a metallic surface, Solid State Commun. **17**, 1425 (1975).
[3] O. Gunnarsson and B. I. Lundqvist, Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism, Phys. Rev. B **13**, 4274 (1976).
[4] H. Hellmann, Z. Phys. **85**, 180 (1933).
[5] R. P. Feynman, Forces in molecules, Phys. Rev. **56**, 340 (1939).
[6] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, Phys. Rev. **136**, B864 (1964).
[7] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. **140**, A1133 (1965).
[8] N. D. Mermin, Thermal properties of the inhomogenous electron gas, Phys. Rev. **137**, A1441 (1965).
[9] *Frontiers and Challenges in Warm Dense Matter*, edited by Aurora Pribram-Jones, Stefano Pittalis, E. K. U. Gross, and Kieron Burke, Thermal density functional theory in context, In Frank Graziani, Michael P. Desjarlais, Ronald Redmer, and Samuel B. Trickey, *Lecture Notes in Computational Science and Engineering* Vol. 96 (Springer, New York, 2014), pp. 25–60.
[10] S. Pittalis, C. R. Proetto, A. Floris, A. Sanna, C. Bersier, K. Burke, and E. K. U. Gross, Exact Conditions in Finite-Temperature Density-Functional Theory, Phys. Rev. Lett. **107**, 163001 (2011).
[11] M. Levy and J. P. Perdew, Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. shape of the correlation potential and diamagnetic susceptibility for atoms, Phys. Rev. A **32**, 2010 (1985).
[12] D. Frydel, W. M. Terilla, and K. Burke, Adiabatic connection from accurate wave-function calculations, J. Chem. Phys. **112**, 5292 (2000).
[13] M. Seidl, P. Gori-Giorgi, and A. Savin, Strictly correlated electrons in density-functional theory: A general formulation with applications to spherical densities, Phys. Rev. A **75**, 042511 (2007).
[14] P. Gori-Giorgi, M. Seidl, and G. Vignale, Density-Functional Theory for Strongly Interacting Electrons, Phys. Rev. Lett. **103**, 166402 (2009).
[15] Z.-F. Liu and K. Burke, Adiabatic connection for strictly correlated electrons, J. Chem. Phys. **131**, 124124 (2009).
[16] F. Malet and P. Gori-Giorgi, Strong Correlation in Kohn-Sham Density Functional Theory, Phys. Rev. Lett. **109**, 246402 (2012).
[17] H. Eschrig, $T > 0$ ensemble-state density functional theory via Legendre transform, Phys. Rev. B **82**, 205120 (2010).
[18] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
[19] Á Nagy, Virial theorem in the density functional ensemble theory, Acta Phys. Chim. Debrecina **34–35**, 99 (2002).
[20] A. Pribram-Jones, Z.-H. Yang, J. R. Trail, K. Burke, R. J. Needs, and C. A. Ullrich, Excitations and benchmark ensemble density functional theory for two electrons, J. Chem. Phys. **140**, 18A541 (2014).
[21] K. Burke, The ABC of DFT, 2007, available online dft.uci.edu/doc/g1.pdf.
[22] M. K. Harbola, Differential virial theorem for the fractional electron number: Derivative discontinuity of the kohn-sham exchange-correlation energy, Phys. Rev. A **57**, 4253 (1998).

[23] A. Savin and F. Colonna, Correlation energies for some two- and four-elactron systems along the adiabatic connection in density functional theory, J. Chem. Phys. **110**, 2828 (1999).
[24] D. P. Joubert and G. P. Srivastava, Coupling-constant dependence of the density functional correlation energy, J. Chem. Phys. **109**, 5212 (1998).
[25] M. W. C. Dharma-Wardana and R. Taylor, Exchange and correlation potentials for finite temperature quantum calculations at intermediate degeneracies, J. Phys. C **14**, 629 (1981).
[26] S. Ichimaru, H. Iyetomi, and S. Tanaka, Statistical physics of dense plasmas: Thermodynamics, transport coefficients and dynamic correlations, Phys. Rep. **149**, 91 (1987).
[27] F. Perrot and M. W. C. Dharma-Wardana, Spin-polarized electron liquid at arbitrary temperatures: Exchange-correlation energies, electron-distribution functions, and the static response functions, Phys. Rev. B **62**, 16536 (2000).
[28] M. Baus and J.-P. Hansen, Statistical mechanics of simple coulomb systems, Phys. Rep. **59**, 1 (1980).
[29] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).
[30] V. V. Karasiev, T. Sjostrom, J. Dufty, and S. B. Trickey, Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for Local Spin-Density Calculations, Phys. Rev. Lett. **112**, 076403 (2014).