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Thermal properties of many-electron systems: An integral formulation of density-functional theory

Weitao Yang*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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A new approach for the calculation of thermal properties of many-electron systems is proposed via an integral formulation of the Mermin-Kohn-Sham finite-temperature density-functional theory. The electron density of a thermal-equilibrium state can be determined by solving self-consistently equations for the electron density without using orbitals. Exchange and correlation effects are incorporated. In place of the set of the single-electron equations, the total electron density is explicitly expressed in terms of the Kohn-Sham effective local potential through multidimensional integrations. The development is based on the first-order density matrix as obtained from the one-body Green's function in polygonal and Fourier path-integral representations. The formulation can also be applied to general fermions.

I. INTRODUCTION

In place of the full density matrix in Fock space, the equilibrium state of a many-electron system in a grand-canonical ensemble at finite temperatures can be uniquely determined by its total electron density; further, such an equilibrium electron density minimizes a grand-canonical-potential density functional. This is the essence of the Mermin generalization of the Hohenberg-Kohn density-functional theory (DFT) to finite-temperature systems.[1-3] It provides the most economical way to describe a many-electron equilibrium state. However, the cost is that the universal grand-canonical potential as functional of electron density is not exactly known.

For the approximation of the exchange-correlation contribution to the free energy, the local density approximation (LDA) and its spin-polarized version local spin density (LSD) approximation have been suggested.[2,3] They became available for a wide range of temperatures only recently.[4]

There are two classes of approximations to the kinetic energy and entropy components: the finite-temperature Thomas-Fermi (TF) and related theories, and the finite-temperature Kohn-Sham (KS) theory. In TF and related theories, a direct but crude approach is taken so that extreme simplicity is manifested in the grand-canonical potential as a functional of electron density.[5] Gradient corrections to finite-temperature TF theory have been recently devised, completing the so-called extended-Thomas-Fermi (ETF) theory.[6] Applications of the ETF theory have been made in condensed matter, nuclei, plasma, astronomy, and other fields of physics involving many fermions [see the references in Refs. 6(c) and 6(d)].

On the other hand, finite-temperature KS theory rigorously uses a reference system of noninteracting electrons and a corresponding set of single-electron equations.[2] This reduces the solution of a many-electron problem to the self-consistent solution of the set of many one-electron orbital equations.

Although the Mermin-Kohn-Sham (MKS) finite-temperature density-functional theory was given long ago, only a few applications have been reported.[2] This is due partially to the lack of availability until recently of finite-temperature approximate exchange-correlation functionals, and partially to the fact that even though the many-electron problem is reduced, one still has in principle an *infinite* number of one-electron equations, including the continuum states.

The present work is directed toward the construction of an integral formulation of the Mermin-Kohn-Sham density-functional theory, as the generalization of the integral formulation of Hohenberg-Kohn-Sham (HKS) theory for ground states,[7] which was developed from the works of Handler for linear and harmonic potentials,[8] and in particular from the work of Harris and Pratt for many-electron ground-state Hartree theory.[9] Only equations for total electron density are involved, and orbitals are not needed. The proposed method preserves the simplicity of the finite-temperature TF or ETF theory and includes exchange and correlation effects like the KS theory.

II. ELECTRON DENSITY AS A FUNCTIONAL OF THE KOHN-SHAM LOCAL POTENTIAL

Consider a grand-canonical ensemble characterized by temperature θ, chemical potential μ, and external field $v(\mathbf{r})$. The grand-canonical potential as functional of the total electron density $\rho'(\mathbf{r})$ can be written as[2,3]

$$\Omega[\rho'(\mathbf{r})]=G_s[\rho'(\mathbf{r})]+\int[v(\mathbf{r})-\mu]\rho'(\mathbf{r})d\mathbf{r}+\frac{e^2}{2}\int\int\frac{\rho'(\mathbf{r})\rho'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+F_{\mathrm{xc}}[\rho'(\mathbf{r})]\ , \tag{1}$$

where G_s is the Helmholtz free energy of the noninteracting reference system with density $\rho'(\mathbf{r})$ at temperature θ,

$$G_s[\rho'(\mathbf{r})]=T_s[\rho'(\mathbf{r})]-\theta S_s[\rho'(\mathbf{r})]\ , \tag{2}$$

where $T_s[\rho'(\mathbf{r})]$ and $S_s[\rho'(\mathbf{r})]$ are the corresponding kinetic energy and entropy; $F_{\mathrm{xc}}[\rho'(\mathbf{r})]$ is the exchange-correlation contribution to the free energy,

$$F[\rho'(\mathbf{r})]=\frac{e^2}{2}\int\int\frac{\rho'(\mathbf{r})\rho'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+G_s[\rho'(\mathbf{r})]+F_{\mathrm{xc}}[\rho'(\mathbf{r})]\ . \tag{3}$$

The total electron density $\rho(\mathbf{r})$ for the equilibrium state minimizes the grand-canonical-potential functional, and therefore can be determined by the Euler equation

$$\frac{\delta G_s[\rho]}{\delta\rho(\mathbf{r})}+v_{\mathrm{eff}}(\mathbf{r})=\mu\ , \tag{4}$$

where $v_{\mathrm{eff}}(\mathbf{r})$, the KS local potential, includes the external field, electrostatic, and exchange-correlation contributions,

$$v_{\mathrm{eff}}(\mathbf{r})=v(\mathbf{r})+e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\frac{\delta F_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}\ . \tag{5}$$

For the description of the equilibrium state, electron density is all that is needed, but $G_s[\rho]$ and $F_{\mathrm{xc}}[\rho]$ remain unknown. To resolve the difficulty of $G_s[\rho]$ Kohn and Sham[3] proposed the following: Eq. (4) has the same form as the stationary condition for a noninteracting system in an external field $v(\mathbf{r})=v_{\mathrm{eff}}(\mathbf{r})$. Since the solution of the noninteracting problem is known in terms of the eigenfunctions and eigenvalues of the single-particle Hamiltonian, the solution of Eq. (4) can be obtained through the KS equations

$$\hat{H}\psi_i(\mathbf{r})=\left[-\frac{\hbar^2}{2m}\nabla^2+v_{\mathrm{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})\ , \tag{6}$$

$$\rho(\mathbf{r})=2\sum_i|\psi_i(\mathbf{r})|^2 f(\mu-\varepsilon_i)\ , \tag{7}$$

where $f(\mu-\varepsilon_i)$ is the Fermi function

$$f(\mu-\varepsilon_i)=\{1+\exp[(\varepsilon_i-\mu)/\theta]\}^{-1}\ , \tag{8}$$

with temperature θ measured in energy units (Boltzmann constant $k_B=1$), and $v_{\mathrm{eff}}(\mathbf{r})$ given by Eq. (5). Double occupancy for each orbital is assumed here; the general case allowing a different orbital for a different spin is discussed in Sec. V.

The grand-canonical potential of the equilibrium state can be calculated from Eq. (1); the entropy is given by

$$S_s=-2\sum_i[f_i\ln f_i+(1-f_i)\ln(1-f_i)]\ , \tag{9}$$

where $f_i=f(\mu-\varepsilon_i)$, and the kinetic energy is obtained in one of the two following ways. The direct way makes use of

$$\begin{aligned}&T_s[\rho]=\int t(\mathbf{r})d\mathbf{r}\ ,\\&t(\mathbf{r})=\lim_{\mathbf{r}'\to\mathbf{r}}\frac{\hbar^2}{2m}[-\nabla_{\mathbf{r}}^2\rho^{(\theta)}(\mathbf{r},\mathbf{r}')]\ ,\end{aligned} \tag{10}$$

where $\rho^{(\theta)}(\mathbf{r},\mathbf{r}')$ is the first-order reduced density matrix for the noninteracting system

$$\rho^{(\theta)}(\mathbf{r},\mathbf{r}')=2\sum_i f_i\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')=2\langle\mathbf{r}|f(\mu-\hat{H})|\mathbf{r}'\rangle\ , \tag{11}$$

where f is the Fermi function, but with an operator argument. The indirect way makes use of

$$\begin{aligned}&\tilde{T}_s[\rho]=\int d\mathbf{r}\,\tilde{t}(\mathbf{r})\ ,\\&\tilde{t}(\mathbf{r})=2\sum_i\varepsilon_i f_i|\psi_i(\mathbf{r})|^2-\int v_{\mathrm{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\ ,\end{aligned} \tag{12}$$

where the electron density has been determined so as to satisfy the exact KS equations (6) and (7). In an actual calculation, the difference between $t(r)$ and $\tilde{t}(\mathbf{r})$, or $T_s[\rho]$ and $\tilde{T}_s[\rho]$, can be used as a crierion for the accuracy of the solution $\rho(\mathbf{r})$ in satisfying the exact KS equations.

The situation here is in parallel to the ground-state case.[7] The infinite number of KS equations are introduced only as auxiliaries for facilitating the solution of Eq. (4). Through Eq. (4) alone, the electron density is *implicitly* a functional of $v_{\mathrm{eff}}(\mathbf{r})$, denoted as

$$\rho(\mathbf{r})=\rho^{(\theta)}[\mu-v_{\mathrm{eff}}(\mathbf{r});\mathbf{r}]\ . \tag{13}$$

The present work is devoted to the *explicit* construction of the functional relation in Eq. (13). The self-consistent relations (5) and (13) constitute the essentials of the present integral formulation of DFT at finite temperature.

The primitive form of Eq. (13) is the finite-temperature Thomas-Fermi theory.[5] Even when potential gradients are included in the extended-Thomas-Fermi theory,[6] there is still no quantum detail in the theory; this is to be recovered in the present work.

The formulation is based on the relation between the density matrix (11) and the one-particle Green's function,[5] namely,

$$\rho^{(\theta)}(\mathbf{r},\mathbf{r}')=2\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi\theta}{\sin(\pi\theta\beta)}e^{\beta\mu}G(\mathbf{r},\mathbf{r}';\beta)\ , \tag{14}$$

where the Green's function is

$$G(\mathbf{r},\mathbf{r}';\beta)=\langle\mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\ , \tag{15}$$

and $\hat{H}$ is the one-particle Hamiltonian defined by Eq. (6). In Eq. (14), the complex integration is the inverse bilateral Laplacian transfer of the quantity $2\pi\theta G/\sin(\pi\theta\beta)$, and γ satisfies $0<\gamma<1/\theta$. To prove Eq. (14), one only needs to verify the corresponding equality for the function f, namely,

$$\frac{1}{1+e^{(\varepsilon_i-\mu)/\theta}}=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi\theta}{\sin(\pi\theta\beta)}e^{\beta\mu}e^{-\beta\varepsilon_i}\ . \tag{16}$$

One way to prove Eq. (16) is to do the β integration by the calculus of residues. The contour can be closed on the left-hand side of the complex β plane for $\mu-\varepsilon_i>0$ and on the right-hand side for $\mu-\varepsilon_i<0$. In both cases, the sum of contributions from all residues is identical to the representation of the left-hand side as a convergent power series of $\exp[(\varepsilon_i-\mu)/\theta]$.

Based on Eq. (14), all other properties are expressible in terms of G. The total electron density (13) is given by the diagonal part of Eq. (14), and the electron kinetic energy by the derivative of Eq. (14) according to Eq. (10). The entropy S_s defined by Eq. (9) can be calculated from[5]

$$S_S=\int d\mathbf{r}\,\sigma(\mathbf{r}),\quad \sigma(\mathbf{r})=2\frac{\partial}{\partial\theta}A^{(\theta)}(\mathbf{r},\mathbf{r})\ ,\tag{17}$$

where $\sigma(\mathbf{r})$ is the defined entropy density and

$$A^{(\theta)}(\mathbf{r},\mathbf{r}')=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi\theta}{\beta\sin(\pi\theta\beta)}e^{\beta\mu}\langle\mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\ .\tag{18}$$

A derivation of Eq. (17) is given in the Appendix A. In the indirect way of calculating kinetic energy by Eq. (12), use the identity

$$\begin{aligned}\sum_i \varepsilon_i f_i\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')&=\langle\mathbf{r}|\hat{H}f(\hat{H}-\mu)|\mathbf{r}'\rangle\\&=-\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi\theta}{\sin(\pi\theta\beta)}e^{\beta\mu}\frac{\partial}{\partial\beta}\langle\mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\\&=\mu\langle\mathbf{r}|f(\hat{H}-\mu)|\mathbf{r}'\rangle-\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{(\pi\theta)^2\cos(\pi\theta\beta)}{[\sin(\pi\theta\beta)]^2}e^{\beta\mu}\langle\mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\ ,\end{aligned}\tag{19}$$

where the second equality follows from Eq. (14), and the last equality from partial integration. Equation (19) is the finite temperature extension of Eq. (14) of Ref. 7(b). To simplify Eq. (19), differentiate Eq. (18),

$$\begin{aligned}\frac{\partial A^{(\theta)}(\mathbf{r},\mathbf{r}')}{\partial\theta}=&\frac{1}{\theta}A^{(\theta)}(\mathbf{r},\mathbf{r}')\\&-\frac{1}{\theta 2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{(\pi\theta)^2\cos(\pi\theta\beta)}{[\sin(\pi\theta\beta)]^2}\\&\times e^{\beta\mu}\langle\mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\ ,\end{aligned}\tag{20}$$

and substitute Eq. (20) into Eq. (19). One obtains

$$\begin{aligned}\langle\mathbf{r}|\hat{H}f(\hat{H}-\mu)|\mathbf{r}'\rangle=&\mu\langle\mathbf{r}|f(\hat{H}-\mu)|\mathbf{r}'\rangle\\&+\theta\frac{\partial}{\partial\theta}A^{(\theta)}(\mathbf{r},\mathbf{r}')-A^{(\theta)}(\mathbf{r},\mathbf{r}')\ .\end{aligned}\tag{21}$$

Therefore the kinetic energy can be computed indirectly by[5]

$$\begin{aligned}\tilde{t}(\mathbf{r})&=\tilde{t}[\mu-v_{\text{eff}};\mathbf{r}]\\&=[\mu-v_{\text{eff}}(\mathbf{r})]\rho(\mathbf{r})+2\theta\frac{\partial}{\partial\theta}A^{(\theta)}(\mathbf{r},\mathbf{r})-2A^{(\theta)}(\mathbf{r},\mathbf{r})\ .\end{aligned}\tag{22}$$

The free energy $G_s[\rho]$ is equal to

$$G_s[\rho]=\int d\mathbf{r}\,g_s(\mathbf{r}),\quad g_s(\mathbf{r})=t(\mathbf{r})-\theta\sigma(\mathbf{r})\ ,\tag{23}$$

If $\tilde{t}(\mathbf{r})$ is used instead,

$$\begin{aligned}\tilde{G}_s[\rho(\mathbf{r})]&=\int d\mathbf{r}\,\tilde{g}_s(\mathbf{r})\ ,\\\tilde{g}_s(\mathbf{r})&=\tilde{t}(\mathbf{r})-\theta\sigma(\mathbf{r})\\&=[\mu-v_{\text{eff}}(\mathbf{r})]\rho(\mathbf{r})-2A^{(\theta)}(\mathbf{r},\mathbf{r})\ .\end{aligned}\tag{24}$$

The foregoing establishes the determination of equilibrium properties from the one-particle Green's function, which is essentially from Ref. 5. In Secs. III and IV, the approach of the preceding paper[7(b)] is taken: the functional relation $\rho^{(\theta)}[\mu-v_{\text{eff}};\mathbf{r}]$ of Eq. (13) is constructed from the convergent-sequence representations of the Green's function in both polygonal and Fourier path integrals. The path-integral representations of the Green function are quoted in Secs. III and IV, directly from the preceding paper,[7(b)] to which and the references therein the reader is referred for detailed derivation.

III. POLYGONAL PATH-INTEGRAL REPRESENTATION

The one-particle Green's function defined in Eq. (15) can be formulated in terms of path integrals. If the path integration is explicitly carried out by summing over all q-segment polygonal paths satisfying the proper boundary conditions, then the Green's function is represented as [Eq. (37) of Ref. 7(b)]

$$\begin{aligned}G_q^{(n)}(\mathbf{r},\mathbf{r}';\beta)=&\left[\frac{mq}{2\pi\beta\hbar^2}\right]^{3q/2}\int d\mathbf{r}_1\int\cdots\int d\mathbf{r}_{q-1}\exp\left[-\frac{1}{\beta}\frac{m}{2\hbar^2}l_q^2+\frac{\hbar^2}{2m}\beta k_q^2-\beta\mu\right]\\&\times\left[1+\sum_{\nu=2}^{n}(\beta/q)^\nu Q_q^{(\nu)}(\mathbf{r}_0,\mathbf{r}_1,\ldots,\mathbf{r}_q)\right]\ ,\end{aligned}\tag{25}$$

where

$$\begin{aligned}l_q^2&=q\sum_{j=0}^{q-1}(\mathbf{r}_{j+1}-\mathbf{r}_j)^2\ ,\\k_q^2&=\frac{2m}{\hbar^2}\left[\mu-\frac{1}{q}\sum_{j=0}^{q-1}u(\mathbf{r}_{j+1},\mathbf{r}_j)\right]\ ,\\u(\mathbf{r}_{j+1},\mathbf{r}_j)&=\int_0^1 v_{\text{eff}}(\mathbf{r}_j+(\mathbf{r}_{j+1}-\mathbf{r}_j)\tau)d\tau\ ,\\\mathbf{r}_0&=\mathbf{r}',\quad \mathbf{r}_q=\mathbf{r}\ ,\end{aligned}\tag{26}$$

q is any positive integer greater than 1, and the functions $Q_q^{(\nu)}$ are determined explicitly in terms of the gradients of v_{eff} [Eq. (38) of Ref. 7(b)]. As $q\rightarrow\infty$, $G_q^{(n)}$ converges to the exact Green's functions as

$$G_q^{(n)}(\mathbf{r},\mathbf{r}';\beta)=G(\mathbf{r},\mathbf{r}';\beta)+O(\beta^{n+1}/q^n)\ ,\tag{27}$$

where $O(x^n)$ represents terms of order equal to or higher than x^n. For $n=1, G_q^{(1)}$, or simply G_q, is the usual polygonal path integral using primitive, or the lowest-order, short-time approximation. A form similar to $G_q^{(1)}$ has been used by Handler for the ground state of many electrons in a linear and harmonic potentials,[8] and by Harris and Pratt for the ground-state Hartree theory.[9] The inclusion of the potential gradients through $Q_q^{(\nu)}$ functions is developed in the preceding paper[7(b)] based on the Fujiwara-Osborn-Wilk expansion of the Green's function[10] as a short-time approximation.

Now $G_q^{(n)}$ is used via Eq. (14) to construct the functional relation of Eq. (13); the result found is

$$\rho_q^{(\theta,n)}(\mathbf{r},\mathbf{r}')=2\left[\frac{m\theta q}{2\pi\hbar^2}\right]^{3q/2}\int d\mathbf{r}_1\int\cdots\int d\mathbf{r}_{q-1}\left[D_{3q/2}(\hbar^2k_q^2/2m\theta,m\theta l_q^2/2\hbar^2)+\sum_{\nu=1}^{n}(q\theta)^{-\nu}Q_q^{(\nu)}D_{3q/2-\nu}(\hbar^2k_q^2/2m\theta,m\theta l_q^2/2\hbar^2)\right], \tag{28}$$

where the function D_α is defined as

$$D_\alpha(x,y)=\frac{1}{2\pi i}\int_{\gamma'-i\infty}^{\gamma'+i\infty}d\beta\frac{\pi}{\sin(\pi\beta)}\frac{1}{\beta^\alpha}\exp\left[-\frac{1}{\beta}y+\beta x\right],\quad 0<\gamma'<1 \tag{29}$$

which can be transformed into a convenient form

$$\theta^\alpha D_\alpha(x,y)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi\theta}{\sin(\pi\theta\beta)}\frac{1}{\beta^\alpha}\exp\left[-\frac{1}{\beta}\frac{y}{\theta}+\beta\theta x\right],\quad 0<\gamma<\frac{1}{\theta}\ . \tag{30}$$

This function $D_\alpha(x,y)$ can be expressed in terms of the Fourier transform of the usual Fermi-Dirac function;[11] the detail is presented in the Appendix A.

From Eq. (28), the total electron density can also be expressed explicitly in terms of the KS effective potential, namely,

$$\rho_q^{(n)}=\rho_q^{(\theta,n)}[\mu-v_{\text{eff}}(\mathbf{r});\mathbf{r}]=\rho_q^{(\theta,n)}(\mathbf{r},\mathbf{r})\ . \tag{31}$$

Unlike the ground-state case, to assess the convergence of $\rho_q^{(n)}$ here is not a simple matter. However, the present formulation is supported by the convergence of $G_q^{(n)}$ as in Eq. (27), the convergence of the zero-temperature limit of $\rho_q^{(n)}$,[7(b)] and the fact that in the lowest order in q, $\rho_{q=1}(r)$ contains essentially the finite-temperature ETF theory.[6]

The self-consistent solution of Eqs. (5) and (31) gives the total electron density as the (q,n)-level approximation to the Euler equation (4). From this $\rho_q^{(n)}$, all the properties of the equilibrium state can be determined. The function $A^{(\theta)}(\mathbf{r},\mathbf{r}')$ is now given by inserting Eq. (25) into Eq. (18), leading to

$$A_q^{(\theta,n)}(\mathbf{r},\mathbf{r}')=\theta\left[\frac{m\theta q}{2\pi\hbar^2}\right]^{3q/2}\int d\mathbf{r}_1\int\cdots\int d\mathbf{r}_{q-1}\left[D_{3q/2+1}+\sum_{\nu=2}^{n}(q\theta)^{-\nu}Q_q^{(\nu)}D_{3q/2+1-\nu}\right], \tag{32}$$

where the arguments of D_α functions, not explicitly written, are the same as in Eq. (28). The derivative of $A_q^{(\theta,n)}$ is

$$\frac{\partial A_q^{(\theta,n)}(r,r')}{\partial\theta}=\left[\frac{m\theta q}{2\pi\hbar^2}\right]^{3q/2}\int d\mathbf{r}_1\int\cdots\int d\mathbf{r}_{q-1}\left[(3q/2+1)D_{3q/2+1}-\frac{\hbar^2k_q^2}{2m\theta}D_{3q/2}-\frac{m\theta l_q^2}{2\hbar^2}D_{3q/2+2}+\sum_{\nu=2}^{n}(q\theta)^{-\nu}Q_q^{(\nu)}\left[(3q/2+1-\nu)D_{3q/2+1-\nu}-\frac{\hbar^2k_q^2}{2m\theta}D_{3q/2-\nu}-\frac{m\theta l_q^2}{2\hbar^2}D_{3q/2+2-\nu}\right]\right], \tag{33}$$

where the following equalities have been used:

$$\frac{\partial D_\alpha(x,y)}{\partial x}=D_{\alpha-1}(x,y) \tag{34}$$

and

$$\frac{\partial D_\alpha(x,y)}{\partial y}=-D_{\alpha+1}(x,y)\ . \tag{35}$$

These preceding formulas can be easily derived from the definition given in Eq. (29). As presented in Sec. II, the entropy S_s, kinetic energy $\tilde{T}_s$, and the free energy $\tilde{G}_s$ are all simple functions of $\rho_q^{(\theta,n)}$, $A_q^{(\theta,n)}$, and $(\partial/\partial\theta)A^{(\theta,n)}$, given by Eqs. (28), (32), and (33), respectively. In the direct way of determining the kinetic energy, one uses Eqs. (10) and (28), leading to

$$
\begin{aligned}
t_q^{(\theta,1)}(\mathbf{r}) &= -\frac{\hbar^2}{2m}\lim_{\mathbf{r}'\to\mathbf{r}}[\nabla_{\mathbf{r}'}^2\rho_q^{(\theta,1)}(\mathbf{r},\mathbf{r}')] \\
&= -\frac{\hbar^2}{m}\left[\frac{m\theta q}{2\pi\hbar^2}\right]^{3q/2}\int d\mathbf{r}_1\int\cdots\int d\mathbf{r}_{q-1}\Bigg[D_{3q/2-2}\left[\frac{1}{q\theta}\nabla_{\mathbf{r}}u(\mathbf{r}_1,\mathbf{r})\right]^2 - D_{3q/2-1}\frac{1}{q\theta}\nabla_{\mathbf{r}}^2u(\mathbf{r}_1,\mathbf{r}) \\
&\qquad + D_{3q/2+2}\left[\frac{m\theta q}{\hbar^2}(\mathbf{r}_1-\mathbf{r})\right]^2 - D_{3q/2+1}\frac{3m\theta q}{\hbar^2} \\
&\qquad - 2D_{3q/2}\frac{m}{\hbar^2}\nabla_{\mathbf{r}}u(\mathbf{r}_1,\mathbf{r})\cdot(\mathbf{r}_1-\mathbf{r})\Bigg] ,
\end{aligned}
\tag{36}
$$

where the arguments of the D_α functions are the same as in Eq. (28) except that $\mathbf{r}'=\mathbf{r}$. For $n>1$, the expression for the kinetic energy in the direct way, not given here, is elementary, but cumbersome. This completes the construction of the integral formulation of the MKS density functional theory via the polygonal path integral.

To simplify the picture, consider the case $q=1$ and $n=1$. Then there is no spatial integration in the formulation; one finds from Eq. (28)

$$
\rho_{q=1}^{(\theta,1)}(\mathbf{r},\mathbf{r}')=2\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3/2}D_{3/2}(\hbar k_1^2/2m\theta,m\theta l_1^2/2\hbar^2) ,
\tag{37}
$$

and its diagonal part

$$
\rho_{q=1}^{(n=1)}(\mathbf{r})=2\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3/2}F_{3/2}([\mu-v_{\text{eff}}(\mathbf{r})]/\theta) ,
\tag{38}
$$

where the identity (proved in the Appendix) is used,

$$
D_\alpha(x,0)=F_\alpha(x) ,
\tag{39}
$$

where $F_\alpha(x)$ is the Fermi-Dirac function following the convention of Ref. 11;

$$
F_\alpha(x)=\frac{1}{\Gamma(\alpha)}\int_0^\infty\frac{t^{\alpha-1}}{1+e^{t-x}}dt .
\tag{40}
$$

Equation (38) is precisely the finite-temperature TF relation.[5] The TF density matrix of Eq. (37) does not seem to have been given before. The present formulation with $q=1$ and $n>1$ is essentially equivalent to the finite-temperature ETF theory.[6] Quantum details of the equilibrium state, not in ETF theory, can be described by using the formulation with $q>1$.

IV. FOURIER PATH-INTEGRAL REPRESENTATION

If the path integral representing the Green's function is carried out by integrating over the Fourier coefficients for the paths

$$
\mathbf{x}_p(\tau)=\mathbf{r}'+(\mathbf{r}-\mathbf{r}')\tau+\frac{\sqrt{2}}{\pi}\sum_{k=1}^{p=1}\mathbf{z}_k\frac{\sin(k\pi\tau)}{k} ,
\tag{41}
$$

then the Green's function can be represented as [Eq. (48) of Ref. 7(b)]

$$
G_p(\mathbf{r},\mathbf{r}';\beta)=\left[\frac{m}{2\pi\hbar^2\beta}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}\exp\left[-\frac{m}{2\hbar^2\beta}\left[(\mathbf{r}-\mathbf{r}')^2+\sum_{k=1}^{p-1}|\mathbf{z}_k|^2\right]-\beta\int_0^1 v_{\text{eff}}(\mathbf{x}_p(\tau))d\tau\right] .
\tag{42}
$$

The Fourier path-integral representation of the Green's function was originated by Feynman and has been applied in statistical mechanics and chemical dynamics. See the references listed in Ref. 7(b).

Now G_p is used in Eq. (14) to construct the corresponding functional relation of Eq. (13). One finds

$$
\rho_p^{(\theta)}(\mathbf{r},\mathbf{r}')=2\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}D_{3p/2}(\hbar^2k_p^2/2m\theta,m\theta l_p^2/2\hbar^2) ,
\tag{43}
$$

where Eq. (30) has been used and

$$
l_p^2=\left[(\mathbf{r}-\mathbf{r}')^2+\sum_{k=1}^{p-1}|\mathbf{z}_k|^2\right],\quad k_p^2=\frac{2m}{\hbar^2}\left[\mu-\int_0^1 v_{\text{eff}}(\mathbf{x}_p(\tau))d\tau\right] .
\tag{44}
$$

The total electron density is the diagonal part of Eq. (43); namely,

$$
\rho_p(\mathbf{r})=\rho_p^{(\theta)}[\mu-v_{\text{eff}};\mathbf{r}]=\rho_p^{(\theta)}(\mathbf{r},\mathbf{r})=2\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}D_{3p/2}(\hbar^2\tilde{k}_p^2/2m\theta,m\theta\tilde{l}_p^2/2\hbar^2) ,
\tag{45}
$$

where

$$
\tilde{l}_p^2=\sum_{k=1}^{p-1}|\mathbf{z}_k|^2,\quad \tilde{k}_p^2=\frac{2m}{\hbar^2}\left[\mu-\int_0^1 v_{\text{eff}}(\mathbf{y}_p(\tau))d\tau\right] ,
\tag{46}
$$

and

$$
\mathbf{y}_p(\tau)=\mathbf{r}+\frac{\sqrt{2}}{\pi}\sum_{k=1}^{p-1}\mathbf{z}_k\frac{\sin(k\pi\tau)}{k} .
\tag{47}
$$

The self-consistent solution of Eqs. (5) and (45) gives the total electron density as the p-level approximation to the Euler equation (4). From the solution $\rho_p(\mathbf{r})$ and $v_{\text{eff}}(\mathbf{r})$, all other properties of the equilibrium state can be determined. The function $A^{(\theta)}(\mathbf{r},\mathbf{r}')$ can be calculated by using G_p of Eq. (42) in Eq. (18), giving

$$A^{(\theta)}(\mathbf{r},\mathbf{r}')=\theta\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}D_{3p/2+1}(\hbar^2k_p^2/2m\theta,m\theta l_p^2/2\hbar^2)\ , \tag{48}$$

and its derivative

$$\frac{\partial}{\partial\theta}A^{(\theta)}(\mathbf{r},\mathbf{r}')=\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}\left[(3p/2+1)D_{3p/2+1}-\frac{\hbar^2k_p^2}{2m\theta}D_{3p/2}-\frac{m\theta l_p^2}{2\hbar^2}D_{3p/2+2}\right]\ , \tag{49}$$

where the arguments of the D_α functions are implied and Eqs. (34) and (35) have been used. According to Sec. II, the entropy S_s, kinetic energy $\widetilde{T}_s$, and the free energy $\widetilde{G}_s$ are all simply related to ρ_p, $A_p^{(\theta)}$, and $(\partial/\partial\theta)A_p^{(\theta)}$, all given above. To compute directly the kinetic energy, insert Eq. (43) into Eq. (10), leading to

$$\begin{aligned}t_p^{(\theta)}(\mathbf{r})&=-\frac{\hbar^2}{2m}\lim_{\mathbf{r}'\to\mathbf{r}}\nabla_r^2\rho_p^{(\theta)}(\mathbf{r},\mathbf{r}')\\&=-\frac{\hbar^2}{m}\left[\frac{m\theta}{2\pi\hbar^2}\right]^{3p/2}\int d\mathbf{z}_1\int\cdots\int d\mathbf{z}_{p-1}\left[D_{3p/2-2}\left[\frac{1}{\theta}\int_0^1\tau\nabla v_{\text{eff}}(\mathbf{y}_p(\tau))d\tau\right]^2\right.\\&\qquad\left.-D_{3p/2-1}\frac{1}{\theta}\int_0^1\tau^2\nabla^2v_{\text{eff}}(\mathbf{y}_p(\tau))d\tau-D_{3p/2+1}\frac{3m\theta}{\hbar^2}\right]\ ,\end{aligned} \tag{50}$$

where the arguments of the D_α functions are the same as in Eq. (45). This completes the construction of the integral formulation of MKS density functional theory via the Fourier path integral.

An appealing feature of the functional relation in Eq. (45) is that the multidimensional integration involved is over the space of Fourier coefficients, rather than over the real space as in the polygonal path-integral approach. Therefore general computational algorithms can be designed regardless of the external potential $v(\mathbf{r})$. The functional relation in Eq. (45) is also reduced to the finite-temperature TF theory at the crudest level, $p=1$.

V. EXTENSION TO SPIN DFT AND SUMMARY

Extension of the foregoing integral formulation can be easily made to spin-polarized systems; namely,

$$\rho^{\pm}(\mathbf{r})=\tfrac{1}{2}\rho^{(\theta)}[\mu-v_{\text{eff}}^{\pm};\mathbf{r}]\ , \tag{51}$$

$$t^{\pm}(\mathbf{r})=\tfrac{1}{2}t[\mu-v_{\text{eff}}^{\pm};\mathbf{r}]\ , \tag{52}$$

and

$$\sigma^{\pm}(\mathbf{r})=\tfrac{1}{2}\sigma[\mu-v_{\text{eff}}^{\pm};\mathbf{r}]\ , \tag{53}$$

where the functionals ρ, t, and σ are defined in Sec. II and explicitly represented in Secs. III and IV. The symbol $+/-$ denotes spin up $(+)$ or spin down $(-)$, and the factor $\frac{1}{2}$ appears because each spin orbital is singly occupied, rather than doubly occupied as in Section II. The spin-dependent local effective potentials $v_{\text{eff}}^{\pm}$ are defined similarly to the case of ground state[2] [also see Sec. IV of Ref. 7(b)].

In summary, sequential representations of the exact functional relation $\rho^{(\theta)}[\mu-v_{\text{eff}},\mathbf{r}]$ have been developed via polygonal and Fourier path integrals (see Appendix B for an alternative family of representations). Coupled with the relation of $v_{\text{eff}}(\mathbf{r})$ to $\rho(\mathbf{r})$ [Eq. (5)], they constitute various schemes of self-consistent equations for the total electron density of the many-fermion equilibrium state, bypassing the set of infinite number of KS single-electron equations. In view of the difficulties associated with other approaches for many-electron systems, notably the cancellation due to electron exchange, the present integral formulation of the MKS density-functional theory, combined with the recent advances in exchange-correlation functionals[4] might provide one with an efficient approach to calculate the thermal properties of many-electron systems.

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APPENDIX A: FERMI-DIRAC FUNCTIONS AND THE $D_\alpha(x,y)$ FUNCTIONS

The Fermi-Dirac functions defined by Eq. (40) can also be represented via inverse bilateral Laplacian transform,[12]

$$F_\alpha(x)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}d\beta\frac{\pi}{\beta^\alpha\sin(\pi\beta)}e^{\beta x},\quad 0<\gamma<1 \tag{A1}$$

which can be put into a convenient form

$$\theta^\alpha F_\alpha(x)=\frac{1}{2\pi i}\int_{\gamma'-i\infty}^{\gamma'+i\infty}d\beta\frac{\theta\pi}{\beta^\alpha\sin(\pi\theta\beta)}e^{\beta\theta x},\quad 0<\gamma'<\frac{1}{\theta}\ . \tag{A2}$$

From Eq. (A1) follows the recurrence relation

$$\frac{\partial F_\alpha(x)}{\partial x}=F_{\alpha-1}(x)\ . \tag{A3}$$

For $\alpha = 1, 0$, these are elementary functions[6(c)]:

$$F_1(x) = \ln(1+e^{x}) , \tag{A4}$$

$$F_0(x) = (1+e^{-x})^{-1} . \tag{A5}$$

Letting $x = (\mu - \varepsilon_i)/\theta$, the representation of $F_0(x)$ via Eq. (A2) is just Eq. (16) of the text, providing another proof of Eq. (16). Comparing Eq. (A2) with Eq. (18) of the text, one finds

$$\begin{aligned} A^{(\theta)}(\mathbf{r},\mathbf{r}') &= \theta\langle \mathbf{r}|F_1((\mu-\hat{H})/\theta)|\mathbf{r}'\rangle \\ &= \theta\langle \mathbf{r}|\ln\{1+\exp[(\mu-\hat{H})/\theta]\}|\mathbf{r}'\rangle , \end{aligned} \tag{A6}$$

which, upon differentiation, leads to Eq. (17) in the text.

To relate the D_α functions to Fermi-Dirac functions, use the identity[13]

$$\int_{-\infty}^{\infty} \exp(-p^2x^2 \pm qx)dx = \exp\left[\frac{q^2}{4p^2}\right]\frac{\sqrt{\pi}}{p}, \quad \mathrm{Re}(p) > 0 \tag{A7}$$

and change the variable of integration to get

$$\exp\left[-\frac{1}{\beta}y\right] = \sqrt{\beta/\pi}\int_{-\infty}^{\infty} e^{\pm i2\sqrt{y}t}e^{-\beta t^2}dt, \quad \mathrm{Re}(\beta) > 0 . \tag{A8}$$

Inserting Eq. (A8) into Eq. (29) in the text, and using Eq. (A1), one obtains

$$D_\alpha(x,y) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{\pm i2\sqrt{y}t}F_{\alpha-1/2}(x-t^2)dt . \tag{A9}$$

For $x < 0$, $F(x)$ has a convergent series expansion[11]

$$F_\alpha(x) = \sum_{n=1}^{\infty}(-1)^{n-1}\frac{e^{nx}}{n^\alpha}, \quad x < 0 . \tag{A10}$$

The corresponding expansion for D_α can be derived via Eq. (A9); namely,

$$D_\alpha(x,y) = \sum_{n=1}^{\infty}(-1)^{n-1}\frac{e^{nx-y/n}}{n^\alpha}, \quad x < 0 . \tag{A11}$$

Comparing Eq. (29) in the text with Eq. (A1) leads to the proof of Eq. (39) in the text. Finally, comparing Eq. (30) of the text with Eq. (26) of Ref. 7(b), one finds

$$\lim_{\theta\to 0}\theta^\alpha D_\alpha(x^2/\theta, y^2\theta)] = \left[\frac{x}{y}\right]^\alpha J_\alpha(2xy)\eta(x^2) , \tag{A12}$$

assuming that the θ→0 limiting is interchangeable with the complex β integration. Equation (A12) can be used as a transition of the finite-temperature formulation to the ground-state formulation.

APPENDIX B: ALTERNATIVE REPRESENTATIONS FOR THE DENSITY MATRIX

There is another way to relate the first-order reduced density matrix of the KS noninteracting system of Eq. (11) in the text to path integrals; namely,

$$\begin{aligned} \tfrac{1}{2}\rho^{(\theta)}(\mathbf{r},\mathbf{r}') &= \langle \mathbf{r}|f(\mu-\hat{H})|\mathbf{r}'\rangle \\ &= \int_{-\infty}^{\infty} dx\, f(\mu-x)\langle \mathbf{r}|\delta(x-\hat{H})|\mathbf{r}'\rangle , \end{aligned} \tag{B1}$$

where $f(x)$ is the Fermi function and $\delta(x)$ is the Dirac δ function. In turn, the δ operator can be derived from

$$\langle \mathbf{r}|\delta(x-\hat{H})|\mathbf{r}'\rangle = \frac{\partial}{\partial x}\langle \mathbf{r}|\eta(x-\hat{H})|\mathbf{r}'\rangle , \tag{B2}$$

where the step function operator is the ground-state density matrix discussed in detail in the preceding paper.[7(b)] See the following paper[14] for the explicit expressions of the δ-function operator in terms of $v_{\mathrm{eff}}(\mathbf{r})$ via path integrals.

Equation (B1), coupled with the Eq. (5) in the text, provides an alternative family of self-consistent equations for the determination of $\rho(\mathbf{r})$ and $v_{\mathrm{eff}}(\mathbf{r})$ for the equilibrium state. Other properties are determined from the self-consistent solution through

$$\begin{aligned} A^{(\theta)}(\mathbf{r},\mathbf{r}') &= \theta\left\langle \mathbf{r}\left|\ln\left[1+\exp\left[\frac{\mu-\hat{H}}{\theta}\right]\right]\right|\mathbf{r}'\right\rangle \\ &= \theta\int_{-\infty}^{\infty} dx\,\ln\left[1+\exp\left[\frac{\mu-x}{\theta}\right]\right] \\ &\qquad\times\langle \mathbf{r}|\delta(x-\hat{H})|\mathbf{r}'\rangle \end{aligned} \tag{B3}$$

and

$$\begin{aligned} \frac{\partial A^{(\theta)}(\mathbf{r},\mathbf{r}')}{\partial\theta} = \int_{-\infty}^{\infty} dx \Bigg\{ &\ln\left[1+\exp\left[\frac{\mu-x}{\theta}\right]\right] \\ &- \frac{(\mu-x)}{\theta\left[1+\exp\left[\frac{\mu-x}{\theta}\right]\right]}\Bigg\} \\ &\times\langle \mathbf{r}|\delta(x-\hat{H})|\mathbf{r}\rangle . \end{aligned} \tag{B4}$$

This formulation avoids the use of the special functions $D_\alpha(x,y)$ introduced in the text. With equivalent sequential path-integration representations to the δ-function operator and the exponential-function operator, Eq. (B1) and Eq. (14) in the text represent the first-order reduced density matrix in two ways.

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[*] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

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