



# $T > 0$ ensemble-state density functional theory via Legendre transform

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(Received 22 February 2010; revised manuscript received 6 September 2010; published 22 November 2010)

A logical foundation of equilibrium state density functional theory in a Kohn-Sham-type formulation is presented on the basis of Mermin's treatment of the grand canonical state by exploiting functional Legendre transforms. It is simpler and more satisfactory compared to the usual derivation of the ground-state theory and free of most remaining open points of the latter. The existence of the functional derivative of the corresponding density functional  $F[n]$  at all densities of grand canonical equilibrium states is proved even in the spin-density matrix version of the theory. It may, in particular, be relevant with respect to cases of spontaneous symmetry breaking such as noncollinear magnetism and orbital order.

 DOI: [10.1103/PhysRevB.82.205120](https://doi.org/10.1103/PhysRevB.82.205120)

PACS number(s): 31.15.ec, 05.30.Fk, 71.15.Mb

## I. INTRODUCTION

Modern ground-state (GS) density functional theory (DFT) for an inhomogeneous system of identical particles, having early roots in the work by Thomas and Fermi, was pioneered with the seminal papers by Hohenberg, Kohn, and Sham.<sup>1,2</sup> It was later generalized to the constrained search concept by Levy<sup>3</sup> and finally put on a mathematically rigorous basis of functional Legendre transforms by Lieb.<sup>4</sup> Meanwhile, DFT for the quasiparticle self-energy labeled by acronyms such as GW or local-density approximation (LDA) plus dynamic mean-field theory (DMFT), and time-dependent DFT for dynamical processes, related to Keldysh Green's functions, were developed, and all these theories laid the ground for enormously successful model approaches (by use of model functionals) to simulation of molecules and solids of any complexity.

A generalization of the ground-state DFT to thermodynamic equilibrium states by Mermin<sup>5</sup> appeared shortly after the work of Hohenberg, Kohn, and Sham. It has been considered from time to time (e.g., Refs. 6, 7, 9, and 10). Reference 8 presents a first claim of the existence of the functional derivative of Mermin's density functional for temperature  $T > 0$ . However, this paper does not specify the variational spaces for densities and potentials and hence does not even say what is meant with functional derivative. It also incorrectly bases the existence of the derivative on claims that a strictly concave and bounded above functional would always have a maximum. A simple counterexample is the function  $f(x) = -\exp(x)$  which is strictly concave and bounded above for all  $x$  and has no maximum and hence also no maximizing value of  $x$ . While strict concavity yields uniqueness of the maximum if it exists, it does not guarantee its existence on a noncompact domain. (In an infinite-dimensional space norm-compact neighborhoods do not exist, every  $\varepsilon$ -ball contains an infinite number of nowhere clustering vectors.) Below it is shown by complete functional analysis arguments that the Legendre transform approach for  $T > 0$  removes so far remaining weak points in the rigorous logical foundation of DFT.

As it sometimes happens,<sup>11</sup> a formalism for temperature  $T = 0$  need not be equivalent to that for  $T \downarrow 0$  which latter case is always the relevant case in physics. Although ground-state

DFT is largely settled now, some uneasy feeling remains in connection with the density functional failing to be differentiable in some cases (where  $n \mapsto v$  is not unique), notably in spin DFT.<sup>12,13</sup> As is well known, Lieb's Legendre transform approach readily extends to the spin density case, see, e.g., Refs. 14 and 15. However, since rather any practical application of DFT is based on equating the first variation in the density functional to zero, the existence and uniqueness of the first functional derivative of the density functional is *presupposed* in those applications. In Ref. 12 it is argued that these problems may reduce to the ordinary well-understood gap problem, now for the spin subsystems separately, if one restricts consideration to homogeneous external magnetic fields only. This might seem a reasonable restriction since static applied fields in laboratory can hardly vary over microscopic distances. However, in the very topical cases of spontaneous symmetry breaking with respect to the interplay of noncollinear magnetism with orbital order, in a statistical treatment one has to resort to the trick of Bogolubov's quasimeans by applying a suitable infinitesimal symmetry-breaking external field, otherwise statistical ensembles would not reproduce the broken symmetry. They would instead average over the energy-degenerate values of the order parameter. In the just mentioned cases this implies a microscopically inhomogeneous symmetry-breaking field and one would like to rely on a situation where everything is fine at least in an infinitesimal vicinity of such a field.

The good news is that the needed functional derivatives always exist for  $T > 0$ , although not necessarily in the common Kohn-Sham (KS) approach. This is shown with the help of Mermin's approach in the sequel. DFT is a rigorous theory for volume  $V < \infty$  and for temperature  $T > 0$ . For  $V = +\infty$  a ground-state wave function (WF) may not exist and for  $T = 0$  the functional derivative of the density functional may not exist. The theory then may be applied for  $V < +\infty$ ,  $T > 0$  and for the results the limits  $V \rightarrow \infty$  (as is routinely done with refinement of the grid in  $k$  space; a discrete regular  $k$  grid means periodic boundary conditions with a finite periodicity volume) and  $T \downarrow 0$  may be considered. (Contrary to the case of adiabatic molecular dynamics<sup>7</sup> the temperature of a finite system in an equilibrium state has a well-defined meaning in the average over states the system may be in after in had for a long time been in contact with a large thermal

bath.) Kohn-Sham theory, as shown below, further on rests on an assumption.

## II. SUBTLETIES OF HOHENBERG-KOHN-SHAM THEORY

Originally<sup>1</sup> DFT was built for systems in an (arbitrarily large) box of finite volume which conveniently can be replaced by periodic boundary conditions meaning to treat the position space of the particles as a three torus  $\mathbb{T}^3$  of finite volume  $|\mathbb{T}^3|$ , for instance  $x \equiv x+L$ ,  $y \equiv y+L$ ,  $z \equiv z+L$ , and  $|\mathbb{T}^3| = L^3$ .

Let the Hamiltonian be

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

$$\hat{T} = \frac{\hbar^2}{2m} \int \nabla \hat{\psi}^\dagger(x) \nabla \hat{\psi}(x) dx, \quad (2)$$

$$\hat{W} = \int \hat{\psi}^\dagger(x) \hat{\psi}^\dagger(x') w(\mathbf{r}, \mathbf{r}') \hat{\psi}(x') \hat{\psi}(x) dx' dx, \quad (3)$$

$$\hat{V} = \int \hat{\psi}^\dagger(\mathbf{r}, s) v(\mathbf{r}) \hat{\psi}(\mathbf{r}, s) dx, \quad (4)$$

where  $\hat{\psi}(x)$ ,  $x = (\mathbf{r}, s)$  with particle position  $\mathbf{r}$  and spin variable  $s$ , is the field operator of the particle field and  $\int dx = \sum_s \int d^3r$ .

Then, given any particle number  $N$ , a normalized GS WF  $\Psi(x_1, \dots, x_N)$  and a GS density  $n(\mathbf{r})$  exist for any reasonable external potential  $v(\mathbf{r})$  and for any non-negative pair interaction  $w(\mathbf{r}_i, \mathbf{r}_j)$ . In the infinite position space,  $\mathbf{r} \in \mathbb{R}^3$ , a GS would often not exist even for common potentials. For instance the potential  $v(\mathbf{r}) = -1/r$  created by a proton at the origin cannot bind three electrons interacting by Coulomb repulsion  $w$ ; for  $N \geq 3$  there are only scattering states for which there is no normalizable *stationary* WF. In a position space  $\mathbb{T}^3$  of finite volume even a repulsive potential, for instance  $v(\mathbf{r}) = 1/r$ , has a well-defined GS WF for any number  $N$  of mutually repulsive particles. One could think that anyhow only pairs  $(v, N)$  are of interest for which a GS WF exists, however, then the admissible densities  $n$  for which the density functional  $F[n]$  is defined and which form the domain of allowed density variations would not be known. Hence, the variational principle would even not be defined. This is why a box of finite volume was already introduced in the seminal paper by Hohenberg and Kohn (HK).

As is now standard,<sup>4</sup> one allows for all potentials with the only condition that  $\int_{\mathbb{T}^3} |v|^{3/2} d^3r < \infty$ , that is,  $v \in \mathbf{L}^{3/2}(\mathbb{T}^3)$ . Potentials of arrays of finitely many point charges in the  $\mathbb{T}^3$  belong to this space,<sup>4,14</sup> and the Hamiltonian  $\hat{H}^0 = \hat{T} + \hat{V}$  of interaction-free fermions is bounded below for any such potential (another mandatory condition for the theory). Then, this also holds true for Hamiltonians (1), if  $w(\mathbf{r}, \mathbf{r}') \geq 0$ . Since the space  $\mathbb{T}^3$  has finite volume, all considered Hamiltonians have discrete spectra with at most finite degrees of level degeneracy. The functional space  $\mathbf{L}^{3/2}$  for admissible

potentials was introduced by Lieb<sup>4</sup> as the dual to the functional space  $\mathbf{L}^3$  for admissible densities  $n$  ( $\int |n|^3 d^3r < \infty$ ), so that  $\int n v d^3r$  is always finite due to Hölder's inequality. The condition  $n \in \mathbf{L}^3$  on the other hand comes from an inequality by Sobolev in three dimensions yielding  $(3/2)^3 (\pi/2)^4 \int |n|^3 d^3r \leq \langle \hat{T} \rangle^3$ , so that  $n \in \mathbf{L}^3$  for every WF with finite kinetic energy. (Lieb allowed the position space to be the real vector space  $\mathbb{R}^3$  of infinite volume which caused many problems with the continuous part of the spectrum of Hamiltonians, that is, scattering states toward the infimum of total energy. He then had to restrict  $n \in \mathbf{L}^3(\mathbb{R}^3) \cap \mathbf{L}^1(\mathbb{R}^3)$  since the density must integrate to a finite particle number  $N$  over the infinite space  $\mathbb{R}^3$ . This led him allow for potentials  $v \in \mathbf{L}^{3/2}(\mathbb{R}^3) + \mathbf{L}^\infty(\mathbb{R}^3)$ . In the three torus every function  $n \in \mathbf{L}^3(\mathbb{T}^3)$  may be normalized to integrate to a given  $N$ , that is,  $\mathbf{L}^3(\mathbb{T}^3) \subset \mathbf{L}^1(\mathbb{T}^3)$ .)

Recall that if  $X$  is a real normed functional space and  $F$  is a functional on  $X$ , that is, a real-valued function on  $X$ , the functional derivative (Fréchet derivative, total differential) at point  $n_0$ ,  $n_0, \delta n \in X$ , if it exists, is a continuous linear functional  $\langle (\delta F / \delta n)|_{n_0}, \delta n \rangle$  on  $X$  so that  $F(n_0 + \delta n) - F(n_0) = \langle (\delta F / \delta n)|_{n_0}, \delta n \rangle + o(\|\delta n\|)$ , where  $\|\delta n\|$  means the norm of  $\delta n$  and  $o(\cdot)$  means of higher than linear order in the argument. If  $X$  is the space  $\mathbf{L}^p(\Omega)$  of  $p$ -summable functions  $n(x)$ ,  $x \in \Omega$ ,  $1 \leq p < \infty$ , that is, of functions  $n$  for which  $\|n\|^p = \int_\Omega |n(x)|^p dx < \infty$ , then any continuous linear functional  $\langle u, n \rangle$  on  $X$  may be written as  $\int_\Omega u(x) n(x) dx$  with some  $q$ -summable function  $u(x)$ ,  $\|u\|^q = \int_\Omega |u(x)|^q dx < \infty$  where  $p^{-1} + q^{-1} = 1$ . In this sense, a function  $u(x) \in \mathbf{L}^q(\Omega)$ , the dual of  $\mathbf{L}^p(\Omega)$ , may be considered to be the functional derivative of a functional  $F$  on  $\mathbf{L}^p(\Omega)$ . (The in Physics well known special case is the real Hilbert space  $\mathbf{L}^2(\Omega)$  with scalar product  $(\psi | \varphi)$  for which the Riesz lemma says that every continuous linear functional is given as  $(\psi | \varphi)$  with some  $\psi \in \mathbf{L}^2(\Omega)$ . That is, the real Hilbert space is self-dual.)

The lemma by Hohenberg and Kohn<sup>1</sup> states the unique mapping  $n \mapsto (v \text{ mod const.})$  from GS densities (degenerate GSs allowed<sup>4</sup>) to external potentials, on which basis the Hohenberg-Kohn density functional

$$F_{\text{HK}}[n] = E[v[n], N] - \langle n, v[n] \rangle \quad (5)$$

is defined for any ground-state density  $n \in \mathcal{A}_N$ ,

$$\mathcal{A}_N = \{n \text{ coming from an } N\text{-particle GS-WF}\}. \quad (6)$$

In Eq. (5)  $v[n]$  means the potential causing a WF-GS density  $n$ , and henceforth we use the notation of linear functionals

$$\langle n, v \rangle = \int_{\mathbb{T}^3} n(\mathbf{r}) v(\mathbf{r}) d^3r. \quad (7)$$

As is easily seen,  $\langle n, v \rangle$  cancels an equal term in the GS energy  $E[v[n], N]$ , so that  $F_{\text{HK}}$  does not any more depend separately on  $v[n]$ . The functional  $F = F_{\text{HK}}$  might be used in the variational principle by Hohenberg and Kohn

$$E[v, N] = \min_n \{F[n] + \langle v, n \rangle | \langle 1, n \rangle = N\}, \quad (8)$$

where  $\{A|B\}$  means a set of elements  $A$  with property  $B$  and  $\langle 1, n \rangle$  abbreviates  $\int_{\mathbb{T}^3} n(\mathbf{r}) d^3r$ . The crucial point for the pos-

sibility to solve this problem with the help of Euler's equation is the knowledge of the variational domain for  $n$  and the existence of the functional derivative of  $F$ . Would the derivative of  $F$  at the minimizing density  $n_{\min}$  exist, it would be  $\delta F / \delta n|_{n_{\min}} = -v + \mu$ , where  $\mu$  is the Lagrange multiplier for the constraint in Eq. (8). For  $F_{\text{HK}}$ , unfortunately neither the domain of definition  $\mathcal{A}_N$  is explicitly known nor is anything known about the existence of the functional derivative. We know that  $\mathcal{A}_N \subset \mathcal{L}^3(\mathbb{T}^3)$  but Lieb has shown<sup>4</sup> that  $\mathcal{A}_N$  is not convex. There are densities  $n = \sum_i c_i n_i$ ,  $c_i \geq 0$ ,  $\sum_i c_i = 1$ , which are not in  $\mathcal{A}_N$  while the  $n_i$  all are in  $\mathcal{A}_N$ . This is, why nowadays more general definitions of  $F[n]$  are used.

As the theory can be build for any reasonable pair interaction  $w$ , the interaction-free case  $w=0$  is of some help. Further on this case will be denoted by a superscript 0 but the corresponding density functionals  $F^0$  will as usually be denoted by  $T$  since they obviously reduce to the kinetic energy of an interaction-free system with GS density  $n$ . In this case, an alternative to Eq. (5) is the density matrix (DM), that is, ensemble state functional

$$T_{\text{DM}}[n] = \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1 \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \sum_k p_k (\varphi_k | \hat{t} | \varphi_k) \left| \sum_k p_k |\varphi_k|^2 = n \right. \right\} \quad (9)$$

with  $\hat{t} = -\hbar^2 \Delta / 2m$ . For any  $N$ -particle DM state (not only GS),

$$\begin{aligned} \mathcal{T}[\{p_k, \varphi_k\}] &= \sum_k p_k (\varphi_k | \hat{t} | \varphi_k), \\ 0 \leq p_k \leq 1, \quad \sum_k p_k &= N, \quad (\varphi_k | \varphi_{k'}) = \delta_{kk'}, \end{aligned} \quad (10)$$

is the general expression of the kinetic energy (with the set of orthonormal orbitals  $\varphi_k$  depending on the state). Given a potential  $v$ , the orbitals with  $(\hat{t} + v)\varphi_k = \varphi_k \varepsilon_k$  and occupation numbers  $p_k = 1$  for  $\varepsilon_k < \varepsilon_N$ ,  $p_k = 0$  for  $\varepsilon_k > \varepsilon_N$  minimize Eq. (9) for the corresponding GS density  $n \in \mathcal{A}_{\text{DM},N}^0$  since the potential energy is fixed for fixed  $n$ . The GS is unique if the highest occupied level  $\varepsilon_N$  is not degenerate. The GSs and their energies are obtained from the KS variational principle

$$E^0[v, N] = \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1, \sum p_k = N \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \mathcal{T}[\{p_k, \varphi_k\}] + \sum_{k=1}^N (\varphi_k | v | \varphi_k) \right\} \quad (11)$$

while Eq. (9) is defined for the density  $n$  integrating to any real  $N \geq 0$  (in a quantum ensemble sense), that is,<sup>4</sup> on the domain

$$\mathcal{J}_N = \{n | n(\mathbf{r}) \geq 0, \nabla(n^{1/2}) \in \mathcal{L}^2(\mathbb{T}^3), \langle 1, n \rangle = N\} \quad (12)$$

which is a convex subset of  $\mathcal{L}^3(\mathbb{T}^3)$ . [The inequality  $(1/2) \int [\nabla(n^{1/2})]^2 d^3r \leq \langle \hat{T} \rangle$  is another estimate for the kinetic energy demonstrated in Ref. 4 together with the fact that a minimum, Eq. (9) exists for every  $n \in \mathcal{J}_N$ .]

Let for the sake of simplicity  $v$  have a nondegenerate  $N$ -particle ( $N$  integer) GS (which is a single determinant of orbitals in this case) with density  $n$ . Any admissible variation must keep the orbitals orthonormal. It is easily seen from general properties of a determinant that the most general variation around this  $n$  permitted by Eq. (10) is a linear combination of  $\{\delta\varphi_k = \lambda_k \tilde{\varphi}_k\}$ ,  $\varepsilon_k \leq \varepsilon_N$ ,  $(\tilde{\varphi}_k | \varphi_{k'}) = 0$ , and  $\lambda_k \rightarrow 0$ . To lowest order in the  $\lambda_k$  it yields  $\delta T_{\text{DM}} = 2 \text{Re} \sum_k \lambda_k \tilde{\varphi}_k | \hat{t} | \varphi_k = -2 \text{Re} \sum_k \lambda_k \tilde{\varphi}_k | v | \varphi_k = -2 \text{Re} \sum_k (\delta\varphi_k | v | \varphi_k) = -\langle v, \delta n \rangle$ , where  $(\hat{t} + v)\varphi_k = \varepsilon_k \varphi_k$  and  $(\tilde{\varphi}_k | \varepsilon_k | \varphi_k) = \varepsilon_k (\tilde{\varphi}_k | \varphi_k) = 0$  was used. Linear combinations of these variations reach every  $N$ -particle single determinant state in a neighborhood of the considered GS (with respect to the  $\mathbf{H}^1(\mathbb{T}^{3N})$ -norm  $\|\Psi\|^2 = \int (|\Psi|^2 + |\nabla\Psi|^2) d^{3N}r$ ). Since<sup>4</sup> single determinant states map continuously onto  $\mathcal{J}_N$ , the corresponding  $\delta n$  is a general variation in a neighborhood  $\|\delta n\| < \varepsilon$  of  $n$  in  $\mathcal{J}_N$  (relative to the  $\mathcal{L}^3(\mathbb{T}^3)$  norm), and hence the functional derivative of the convex functional  $T_{\text{DM}}$  exists at  $n$  as a (Fréchet) derivative in  $\mathcal{J}_N$  and equals  $-v$ . The argument can be generalized to the case of a degenerate GS, that is, for all  $n \in \mathcal{A}_{\text{DM},N}^0 \subset \mathcal{J}_N$ . It even extends to noninteger  $N$  since a minimum energy ensemble state with noninteger  $N$  is always a linear combination of GSs with neighboring integer  $N$ . This is true since Hamiltonian (1) commutes with the particle number operator  $\hat{N} = \int \hat{\psi}^\dagger(\mathbf{r}, s) \hat{\psi}(\mathbf{r}, s) dx$  and hence energy eigenstates may be chosen as eigenstate of the particle number operator  $\hat{N}$  which has integer eigenvalues.

Since  $N = \langle 1, n \rangle$  is fixed in  $\mathcal{J}_N$ , any spatially constant potential term  $\mu$  annihilates every density variation in  $\mathcal{J}_N$ ,  $\langle \mu, \delta n \rangle = \mu \langle 1, \delta n \rangle = 0$ ; hence it does not contribute to a derivative in  $\mathcal{J}_N$  although it contributes to a derivative in  $\mathcal{L}^3(\mathbb{T}^3)$  in directions leading out of  $\mathcal{J}_N$  by changing  $N$ .

Now, let  $n \in \mathcal{J}_N \setminus \mathcal{A}_{\text{DM},N}^0$ . Such densities exist, for instance densities having zeros cannot be in  $\mathcal{A}_{\text{DM},N}^0$ . (In any ground state with  $N > 0$  at least the orbital lowest in energy is occupied whose density contribution is nowhere zero.) Assume that the derivative of  $T_{\text{DM}}$  (with respect to the  $\mathcal{L}^3(\mathbb{T}^3)$  norm exists at that  $n$ . Since derivatives of functionals of  $n \in \mathcal{L}^3(\mathbb{T}^3)$  are given through functions  $u \in \mathcal{L}^{3/2}(\mathbb{T}^3)$  this means that there is some  $u \in \mathcal{L}^{3/2}(\mathbb{T}^3)$  with  $\delta T_{\text{DM}} = \langle u, \delta n \rangle$  for all permitted  $\delta n$ . For a convex function  $f(x)$  which has a derivative  $f'$  at  $x_0$  it holds that  $f(x_0) - f' \cdot x_0 = \min_x \{f(x) - f' \cdot x\}$ . Since  $T_{\text{DM}}$  was shown<sup>4</sup> to be a convex function, the assumption implies that  $n$  minimizes  $T_{\text{DM}}[n'] - \langle u, n' \rangle$  and hence is a GS density to the potential  $-u$  in contradiction to the presupposition.  $T_{\text{DM}}$  has nowhere outside of  $\mathcal{A}_{\text{DM},N}^0$  a functional derivative.

KS theory in the interacting case  $w > 0$  now uses the splitting

$$F[n] = T_{\text{DM}}[n] + E_{\text{H}}[n] + E_{\text{XC}}[n], \quad (13)$$

which defines the density functional  $E_{\text{XC}}[n]$  through the preceding ones. [The term  $E_{\text{H}}[n]$  is explicitly given by  $(1/2) \int n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d^3r d^3r'$ .] While this definition is correct, nothing can be said on the existence of the functional derivative of  $E_{\text{XC}}[n]$  for GS densities  $n \in \mathcal{A}_{\text{DM},N}$  of the interacting system since we do not know the sets  $\mathcal{A}_{\text{DM},N}^0$  and  $\mathcal{A}_{\text{DM},N}$  and cannot assume  $\mathcal{A}_{\text{DM},N} \subset \mathcal{A}_{\text{DM},N}^0$ . (Recall that there

exist densities  $n \in \mathcal{J}_N$  which are not in  $\mathcal{A}_{\text{DM},N}^0$ .) Even though  $F$  has a functional derivative for  $n \in \mathcal{A}_{\text{DM},N}$  (see below),  $E_{\text{XC}}[n]$  can only have one there if  $T_{\text{DM}}$  has one which as shown above is only the case in  $\mathcal{A}_{\text{DM},N}^0$ .

Like in Eq. (11), with  $n = \sum_k p_k |\varphi_k|^2$  a KS variational principle is set out with the KS equation as the corresponding Euler equation. Now one *assumes* that there is a representation

$$T_{\text{DM}}[n] + E_{\text{XC}}[n] = \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1 \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \sum_{k=1}^N p_k (\varphi_k | \hat{t} | \varphi_k) + \mathcal{E}_{\text{XC}}[\{p_k, \varphi_k\}] \left| \sum_{k=1}^N p_k |\varphi_k|^2 = n \right. \right\}. \quad (14)$$

This leads to a KS equation with a (nonlinear) exchange and correlation (XC) potential operator

$$\frac{1}{p_k} \frac{\delta \mathcal{E}_{\text{XC}}}{\delta \varphi_k^*(\mathbf{r})} = \hat{v}_{\text{XC}} \varphi_k(\mathbf{r}), \quad (\hat{v}_{\text{XC}} \varphi_k)^* = \hat{v}_{\text{XC}} \varphi_k^*, \quad (15)$$

if one further assumes that  $\mathcal{E}_{\text{XC}}$  depends on  $p_k$  and on a Hermitian form of the  $\varphi_k$  only. A trivial candidate for  $\mathcal{E}_{\text{XC}}$  is  $\mathcal{E}_{\text{XC}}[\{p_k, \varphi_k\}] = E_{\text{XC}}[n[\{p_k, \varphi_k\}]]$  which as a constant for constant  $n$  can be taken out of the variation in Eq. (14) and which is mostly considered in literature. The disadvantage of this choice is that the derivative with respect to  $p_k$  and  $\varphi_k$  does not exist where the derivative with respect to  $n$  does not exist while this need not be the case in the more general setting, Eq. (14). (For instance the derivative of  $\mathcal{T}$  with respect to  $p_k$ , one-sided derivative at the interval ends  $p_k=0$  and  $p_k=1$ , respectively, and with respect to  $\varphi_k$  exists everywhere while that of  $T_{\text{DM}}[n[\{p_k, \varphi_k\}]]$  of course exists only for  $\{p_k, \varphi_k\}$  yielding  $n \in \mathcal{A}_{\text{DM},N}^0$ .) However, the existence with an everywhere differentiable  $\mathcal{E}_{\text{XC}}[\{p_k, \varphi_k\}]$  which can figure in Eq. (14) is not proven so far, only  $\mathcal{E}_X[\{p_k, \varphi_k\}]$  is a simple explicitly known expression. Anyhow, as the example  $\mathcal{T}$  shows, the setting of the right-hand side of Eq. (14) has more potential for the derivatives with respect to  $p_k, \varphi_k$  to exist. Moreover, as will be shown below and in the next section, there is an  $F[n]$  which has functional derivatives (in  $\mathcal{J}_N$ ) for all such GS densities  $n \in \mathcal{A}_{\text{DM},N}$  which uniquely determine the external potential  $v$  mod const. (see lemma by Hohenberg and Kohn). Then, of course,  $F[n[\{p_k, \varphi_k\}]]$  has derivatives with respect to  $p_k, \varphi_k$  there, and, as shows Eq. (13),  $\mathcal{E}_{\text{XC}}$ , if it exists, has them also since all other terms corresponding to the right-hand side of Eq. (13) have them.

Hence,  $\hat{v}_{\text{XC}}$  need in general not be a local potential function, it may, in particular, be orbital dependent ( $\hat{v}_X$  is nonlocal, its orbital dependence is canceled by inclusion of the orbital-dependent self-interaction in both  $v_H$  and  $v_X$ ; the model XC potentials with partial self-interaction correction or in LDA+ $U$  models are nonlocal and orbital dependent). Would  $v_{\text{XC}}$  exist as a local potential, then this would be the functional derivative of  $E_{\text{XC}}[n]$  at  $n \in \mathcal{A}_{\text{DM},N}$  ( $\mathcal{E}[\{p_k, \varphi_k\}] = E_{\text{XC}}[n[\{p_k, \varphi_k\}]]$  would be enough). The KS equation

would, however, always yield a solution  $n \in \mathcal{A}_{\text{DM},N}^0$  (GS of an interaction-free system with external potential  $v' = v + v_H + v_{\text{XC}}$ ) and hence there would be  $\mathcal{A}_{\text{DM},N} \subset \mathcal{A}_{\text{DM},N}^0$  which can by no means be taken for granted. Even though the existence of the more general right-hand side of Eq. (14) is not yet proven, it provides a more general frame for modeling functionals than the assumption of the existence of the functional derivative of  $E_{\text{XC}}[n]$ .

Who considers the necessity of the determination of the variational space with its topology and of the proof of existence of the functional derivative to be just a mathematical sophistry may for instance consider the minimum of the seemingly harmless ‘‘action integral’’

$$S = \int_0^1 L(x, \dot{x}, t) dt, \quad L = \frac{1}{1 + \dot{x}^2}$$

for  $x(0)=0=x(1)$ . The Euler-Lagrange equation would yield

$$\frac{d}{dt} \frac{\dot{x}}{(1 + \dot{x}^2)^2} = 0$$

and hence  $\dot{x} = c$  with a first integration constant  $c$ . The boundary conditions now demand  $c=0$  and hence  $x(t) \equiv 0$  yielding  $S_0=1$  as a candidate for the minimum of  $S$ . However, consider the sequence of trajectories  $x_n(t) = n^{-1/4} \sin(n\pi t)$ ,  $n \rightarrow \infty$  which uniformly converges to  $x(t) \equiv 0$  and where each of the  $x_n$  obeys the boundary conditions. The integral  $S$  is easily estimated from above by estimating the integrand from above by 1 for  $\dot{x}^2 \leq \pi^2 n^{1/2}$  and by  $\pi^{-2} n^{-1/2}$  for  $\dot{x}^2 > \pi^2 n^{1/2}$  which yields

$$S < 2c_n n^{-1/2} + (1 - 2c_n n^{-1/2}) \pi^{-2} n^{-1/2}, \quad c_n \rightarrow 1,$$

so that in fact  $\inf S=0$ . Now you may correctly say that you saw without any calculation that  $S_0=1$  was an extremum in this case, namely, the maximum of  $S$ . Right but the infimum  $S=0$  is not at all provided by the Euler-Lagrange equation and worse, it is approached by trajectories uniformly converging to the maximal trajectory. There, the functional derivative of  $S[x]$  does not exist in any naive understanding.

The only density functional  $F$  for which the issue of the existence of the functional derivative can be addressed in general is the Legendre transform<sup>4</sup> (see next section for the meaning of  $X^*$ )

$$F_N[n] = \sup_{v \in X^*} \{E[v, N] - \langle n, v \rangle\} \quad (16)$$

for both cases,  $w=0$  and  $w \neq 0$ . It is convex and defined on the whole functional space  $X$  (it takes on the value  $+\infty$  in part of  $X$ , in particular, if  $n$  is negative on some domain of non-zero measure, and also if  $\langle 1, n \rangle \neq N$ ), and if, given  $n$ , there exists a unique maximizing  $v$ , then  $-v$  is the functional derivative of  $F_N[n]$  in the hyperplane  $\langle 1, n \rangle = N$ . Since  $v$  is indeed up to a constant uniquely determined by any GS  $n$ , the functional derivative of  $F_N$  exists at least for  $n \in \mathcal{A}_{\text{DM},N}$  as a derivative (gradient, more precisely Fréchet derivative) in the hyperplane  $\{n \in X | \langle 1, n \rangle = N\}$  containing  $\mathcal{J}_N$ .

As just stated, for every given  $N$  there is a separate functional  $F_N[n]$  given by Eq. (16) which is  $+\infty$  for  $\langle 1, n \rangle \neq N$ . As was shown in Ref. 14, one may use

$$H[n] = \inf_N F_N[n] \quad (17)$$

instead of  $F[n]$  in the variational principle, Eq. (8) and obtain the convex hull of all  $E[v, N]$ ,  $N$  integer. The undetermined potential constant of the theory with  $N$  fixed takes now on the role of the chemical potential  $\mu(T=0)$ . The derivative of  $H[n]$  for  $n \in L^3(T^3)$  in a direction which changes  $N$  is discontinuous at integer  $N$ . This is the reason for the failure of model functionals which do not correctly model this discontinuity to reproduce ionization potentials and electron affinities of molecules and semiconductor gaps of solids.

Less clear is the situation in spin DFT.<sup>12</sup> Now, also  $F$  need not have a derivative for GS densities even when  $N$  is kept fixed.

### III. A FEW ESSENTIALS ON LEGENDRE TRANSFORMS

Let  $X = X^{**}$  and  $X^*$  be two mutually dual functional spaces, that is,  $X^*$  comprises all norm-continuous linear functions on  $X$  and vice versa.  $[(\mathbb{R}^M)^* = \mathbb{R}^M$  is the space of all gradient vectors to real functions on  $\mathbb{R}^M$ ;  $[L^3(T^3)]^* = L^{3/2}(T^3)$  is the space of all norm-continuous linear functionals  $\langle u, n \rangle$  of  $n \in L^3(T^3)$ , and vice versa.] Consider real functions on  $X$  or  $X^*$  which may take on the “value”  $+\infty$  but not  $-\infty$ , however, with at least one finite value in their range. The Legendre transform  $f^*(n)$ ,  $n \in X$  of such a function  $f(u)$ ,  $u \in X^*$  is defined as

$$f^*(n) = \sup_{u \in X^*} \{ \langle n, u \rangle - f(u) \}. \quad (18)$$

A second Legendre transformation yields

$$f^{**}(u) = \sup_{n \in X} \{ \langle u, n \rangle - f^*(n) \}. \quad (19)$$

All we need is (1)  $f^*(n)$  is a convex function of  $n$ , no matter what  $f(u)$  is; if  $f(u)$  is convex, then  $f^{**}(u) = f(u)$ ; in general  $f^{**}(u) \leq f(u)$ . (2)  $f(u) + f^*(n) \geq \langle u, n \rangle$ ; if, for convex  $f$  and some  $u$  and  $n$ ,  $f(u) + f^*(n) = \langle u, n \rangle$ , then  $u \in \partial f^*(n)$  and  $n \in \partial f(u)$ .

In the second statement  $\partial f^*(n)$  is the subdifferential of the convex function  $f^*$  at point  $n$ : the set of all linear functions  $\langle u, n' \rangle$  so that  $f^*(n') \geq f^*(n) + \langle u, n' - n \rangle$  for all  $n' \in X$ . If this set consists of a single linear function only, then this linear function is the (total) differential  $df^*(n)$ , that is,  $u$  is the derivative (generalized gradient) of  $f^*$  at  $n$ .

To elucidate these properties one may consider convex functions of one real variable,  $f(N)$  and  $f^*(\mu)$  [see, e.g., Fig. 11 of Ref. 14 with  $f(N) = E(N)$ ,  $f^*(\mu) = G(\mu)$ ]. Put a supporting tangent to the graph of  $f$  at point  $N$  (a line having the common point  $[N, f(N)]$  with the graph of the function and being nowhere above). The tangent has a slope  $\mu$ . The sign carrying distance from the intersection point of this line with the  $f$  axis to the coordinate origin is  $f^*(\mu)$ . If  $f$  has a derivative at  $N$ , then its value is  $\mu$ . It is easily seen that, if the derivative of  $f$  jumps at  $N$ , then there is a (closed if finite) interval  $[\mu_1, \mu_2]$  from the left derivative  $\mu_1$  to the right derivative  $\mu_2$  ( $\mu_1$  may be  $-\infty$  or  $\mu_2$  may be  $+\infty$ ), and  $f^*(\mu)$  is linear on this interval, the interval being the subdifferential  $\partial f(N)$ . Inversely, if the convex function  $f$  is not strictly con-

vex but has a linear dependence on some interval with slope  $\mu$ , then the derivative of  $f^*$  jumps at that  $\mu$ .

This simple geometric picture readily transfers to the general case: let  $f^*(n)$  be convex and take a tangent hyperplane  $f^*(n_0) + \langle u, (n - n_0) \rangle$  supporting the graph of  $f^*(n)$  at some  $n_0$ . The distance from its intersection point with the  $f^*$  axis to the origin is  $f^{**}(u) = f(u)$ . If the derivative of  $f^*$  jumps at some  $n$  (and hence does not exist there), then there is a convex domain (including its boundary) in  $u$  space on which  $f(u)$  is linearly depending on  $u$ , and vice versa.

If the GS density  $n$  uniquely determines the external potential  $v$  mod const. as it does by virtue of the lemma by Hohenberg and Kohn in the spin independent theory, then the derivative of  $F_N[n]$  exists for those  $n$  on the hyperplane  $\langle 1, n \rangle = N$ , that is, for  $\delta n$  with  $\langle 1, \delta n \rangle = 0$ . If, however, the GS wave function is independent of some potential change  $\delta v$  called a “phantom” potential perturbation in Ref. 13, then the GS density  $n$  does also not change and the GS energy has a linear dependence  $E[v + \delta v] = E[v] + \langle \delta v, n \rangle$ . Consequently, the functional derivative of  $F_N[n]$  defined by Eq. (16) does not exist at that  $n$ . This is precisely the role of phantom potential perturbations in DFT.

### IV. UNIQUE MAPPINGS FOR $T > 0$

We now move to temperature  $T > 0$  and to grand canonical states. We also generalize to spin DFT and allow for external magnetic fields coupling to the particle spin but not to its charge (diamagnetic couplings as usually in spin DFT are neglected). Consider a system of identical particles in an external field  $v_{ss'}(\mathbf{r})$ . Let the system be confined to a large box, or, placed in a large three torus equivalent to periodic boundary conditions (regular  $\mathbf{k}$  grid). Let the Hamiltonian be that of Eqs. (1)–(3) but Eq. (4) generalized to

$$\hat{V} = \sum_{ss'} \int \hat{\psi}^\dagger(\mathbf{r}, s) v_{ss'}(\mathbf{r}) \hat{\psi}(\mathbf{r}, s') d^3 r. \quad (20)$$

The particle number operator is  $\hat{N} = \int \hat{\psi}^\dagger(x) \hat{\psi}(x) dx$  so that  $\hat{H} - \mu \hat{N}$  depends on the combination  $v - \mu = v_{ss'}(\mathbf{r}) - \mu \delta_{ss'}$ , only.

Fix the temperature  $\beta = 1/kT$ , the chemical potential  $\mu$  and the external potential  $v$ . Then, the grand canonical state is

$$\rho_\beta[v - \mu] = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\text{tr } e^{-\beta(\hat{H} - \mu \hat{N})}}. \quad (21)$$

If  $\rho > 0$ ,  $\text{tr } \rho = 1$ , is any state (density matrix), then  $\text{tr } \rho(\hat{V} - \mu \hat{N}) = \int (v - \mu) n[\rho] dx$  with the particle (spin) density

$$n[\rho] = n_{s's}(\mathbf{r}) = \text{tr } \rho \hat{\psi}^\dagger(\mathbf{r}, s) \hat{\psi}(\mathbf{r}, s'). \quad (22)$$

In the following  $\text{tr}$  will always mean the trace in the Fock space of the  $\hat{\psi}$ . Also, the natural abbreviation

$$\sum_{ss'} \int (v_{ss'}(\mathbf{r}) - \mu \delta_{ss'}) n_{s's}(\mathbf{r}) d^3 r = \langle (v - \mu), n \rangle \quad (23)$$

will be used.

Now, fix the particle interaction  $w$  and, following Mermin<sup>5</sup> (we try carefully to trace functional dependences and in doing so slightly deviate from Mermin's notation), consider for various external potentials  $v$  the functionals

$$\Omega_v[\rho] = \text{tr} \rho \left( \hat{H} - \mu \hat{N} + \frac{1}{\beta} \ln \rho \right). \quad (24)$$

As easily seen by direct substitution of Eq. (21), the grand canonical potential  $\Omega_\beta[v - \mu]$  is obtained as

$$\Omega_\beta[v - \mu] = -\frac{1}{\beta} \ln \text{tr} e^{-\beta(\hat{H} - \mu \hat{N})} = \Omega_v[\rho_\beta[v - \mu]]. \quad (25)$$

Moreover, as shown in Ref. 5, for any  $\rho > 0$ ,  $\text{tr} \rho = 1$ , it holds that

$$\Omega_v[\rho] > \Omega_v[\rho_\beta[v - \mu]] = \Omega_\beta[v - \mu] \quad \text{for} \quad \rho \neq \rho_\beta[v - \mu]. \quad (26)$$

In Mermin's approach, this inequality replaces the corresponding GS energy property. It immediately implies that  $\Omega_\beta[v - \mu] = \min_\rho \Omega_v[\rho]$  is concave in  $v$  by the simple reasoning (we write in short  $v_i$  for  $v_i - \mu_i$ )

$$\begin{aligned} \Omega_\beta[\alpha v_1 + (1 - \alpha)v_2] &= \min_\rho \text{tr} \rho \left( \alpha \hat{H}_1 + (1 - \alpha) \hat{H}_2 + \frac{1}{\beta} \ln \rho \right) \\ &\geq \alpha \min_{\rho_1} \text{tr} \rho_1 \left( \hat{H}_1 + \frac{1}{\beta} \ln \rho_1 \right) \\ &\quad + (1 - \alpha) \min_{\rho_2} \text{tr} \rho_2 \left( \hat{H}_2 + \frac{1}{\beta} \ln \rho_2 \right) \\ &= \alpha \Omega_\beta[v_1] + (1 - \alpha) \Omega_\beta[v_2], \\ &0 \leq \alpha \leq 1 \end{aligned} \quad (27)$$

because a joint minimum of a sum cannot be below the sum of the independent minima of the items.

As another advantage over the standard zero-temperature theory, it follows immediately from Eqs. (21) and (22) that the mappings  $(v - \mu) \mapsto \rho_\beta \mapsto n$  are unique. There is no problem with degenerate states since degenerate states automatically get equal statistical weight in  $\rho_\beta$  of Eq. (21). Also in contrast to the GS WF for given  $N$ , for fixed  $v$  different values of  $\mu$  yield different states  $\rho_\beta$ . However, as usual spontaneous symmetry breaking is not covered by this statistical approach; it has to be treated by an infinitesimal symmetry breaking external potential  $v$  in the spirit of Bogolubov's quasimeans in Statistical Physics. Nevertheless, by virtue of Eq. (26) which also holds in the spin case, in the standard way Mermin proved the analog of the Hohenberg-Kohn lemma:  $n \mapsto (v - \mu)$  is unique (even without mod const.,  $\mu$  is now the thermodynamic chemical potential and not just that of the noninteracting reference system of KS theory) for any  $n$  coming from a grand canonical ensemble at temperature  $1/k\beta$ . In summary, there are the unique mappings

$$\begin{array}{ccc} (v - \mu) & \leftarrow & n \\ \downarrow & & \uparrow \\ \text{grand canonical } & & \rho_\beta \end{array} \quad (28)$$

On the functional domain (which may depend on  $\hat{W}$ )

$$D_\beta = \{n \text{ coming from some } \rho_\beta, \beta \text{ fixed}\} \quad (29)$$

one can write  $(v - \mu)_\beta[n]$  and also  $\hat{H}_\beta[n]$  and  $\rho_\beta[n]$ , as well as  $n_\beta[v - \mu] = n[\rho_\beta[v - \mu]]$  on the domain of admissible potentials  $v$ . (Denoting the distinct functions  $\rho_\beta[n]$  and  $\rho_\beta[v]$  by the same symbol  $\rho_\beta$  will not cause confusion.)

Moreover, from the unique dependence of  $v - \mu$  on  $\rho_\beta$  it follows now also that  $\Omega_v[\rho]$  for different  $v_i - \mu_i$  is minimized by different  $\rho_i$ , and hence the inequality in Eq. (27) is sharpened into a strict inequality:  $\Omega_\beta[v]$  is strictly concave. If equality would hold in Eq. (27), this would imply that the minimizing  $\rho$  is also a minimizing  $\rho_1$  for  $v_1$  and a minimizing  $\rho_2$  for  $v_2$ . This is the principal difference from the  $T=0$  theory where  $E[v, N]$  is not always strictly concave in  $v_{ss'}$  and is never strictly convex in  $N$ .

## V. DENSITY FUNCTIONAL

As was already said, for electron systems it is well justified to allow for all potentials

$$v - \mu \in \mathbf{L}^{3/2}(\mathbb{T}^3) = X^* \quad (30)$$

for which the integral  $\int_{\mathbb{T}^3} |v - \mu|^{3/2} d^3r$  over the three torus (of finite volume) is finite. Recall that the Hamiltonian  $\hat{H}^0 = \hat{T} + \hat{V}$  of interaction-free fermions is bounded below for any such potential, that this also holds true for Hamiltonians (1)–(3) and (20), if  $w(\mathbf{r}, \mathbf{r}') \geq 0$ , and that since the space  $\mathbb{T}^3$  has finite volume, all considered Hamiltonians have discrete spectra with at most finite degrees of level degeneracy. Then,  $\Omega_\beta[v - \mu]$  of Eq. (25) is well defined on  $X^*$  and smooth in the norm topology.

In view of the concavity of  $\Omega_\beta[v]$ , introduce the Legendre transform<sup>4,14</sup> of  $-\Omega_\beta[v]$  as  $\tilde{F}_\beta[-n]$

$$F_\beta[n] = \tilde{F}_\beta[-n] = \sup_v \{-\langle n, v \rangle + \Omega_\beta[v]\} \quad (31)$$

which as a Legendre transform is a convex functional of  $-n$  (or likewise of  $n$ ), the dual variable to  $v: n \in X^{**} = X = \mathbf{L}^3(\mathbb{T}^3)$ .

Since the functional space  $X$  is reflexive,  $\mathbf{L}^3(\mathbb{T}^3) = (\mathbf{L}^3(\mathbb{T}^3))^{**}$ , the Legendre back transformation from Eq. (31),  $-\Omega_\beta[v] = \sup_n \{-\langle v, n \rangle - \tilde{F}_\beta[-n]\}$  or,

$$\Omega_\beta[v] = \inf_n \{F_\beta[n] + \langle v, n \rangle\} \quad (32)$$

represents the generalized Hohenberg-Kohn theorem (where equality holds since  $\Omega_\beta[v]$  is concave in  $v$ ). The chemical potential  $\mu$  is further on put to zero which simply means that single particle energies and potentials are measured from the chemical potential. Note that the constraint in Eq. (8) does not figure any more here, instead of the particle number  $N$  the chemical potential is fixed in a grand canonical state  $\rho$ .

For any density  $n \in D_\beta$  from Eq. (29), in analogy to the original Hohenberg-Kohn functional one may define

$$\Phi_\beta[n] = \Omega_v[\rho_\beta[n]] - \langle v, n \rangle, \quad n \in D_\beta \quad (33)$$

and, from Eq. (26), have

$$\Omega_\beta[v] = \min_{n \in D_\beta} \{ \Phi_\beta[n] + \langle v, n \rangle \} \quad (34)$$

since in view of Eq. (28) any  $n \neq n[v]$  refers to  $\rho_\beta[n] \neq \rho_\beta[n[v]]$ . From Eqs. (32) and (34) one infers that  $F_\beta[n] = \Phi_\beta[n]$  for all  $n \in D_\beta$ , and that the infimum of Eq. (32) is always a minimum with minimizing density  $n_\beta[v]$ ; indeed,  $\Phi_\beta[n_\beta[v]] + \langle v, n_\beta[v] \rangle = \Omega_\beta[v] \leq F_\beta[n_\beta[v]] + \langle v, n_\beta[v] \rangle$ , hence  $\Phi_\beta[n] \leq F_\beta[n]$  for  $n \in D_\beta$ , and by interchanging the role of Eqs. (32) and (34) in the argument the opposite inequality is obtained.

Moreover, for  $-\Omega_\beta[v]$  and  $\tilde{F}_\beta[-n]$  like in general for any pair of mutual Legendre transforms it holds that  $\tilde{F}_\beta[-n] - \Omega_\beta[v] = -\langle n, v \rangle$  implies  $v \in \partial \tilde{F}_\beta[-n]$  and  $-n \in \partial(-\Omega_\beta[v])$ , where  $\partial \tilde{F}_\beta[-n]$  means the subdifferential of  $\tilde{F}_\beta$  at point  $-n$  and  $\partial(-\Omega_\beta[v])$  means the subdifferential of  $-\Omega_\beta$  at point  $v$ . Since  $d\Omega_\beta[v] = \text{tr}(e^{-\beta \hat{H}} d\hat{V}) / \text{tr} e^{-\beta \hat{H}}$  as easily seen from the definition of  $\Omega_\beta[v]$ , the first (Fréchet) derivative (for finite volume  $|\mathbb{T}^3|$ ) always exists so that the subdifferential of  $\partial(-\Omega_\beta[v])$  contains only this one "gradient." Now, the reasoning after Eq. (34) yields  $F_\beta[n_\beta[v]] - \Omega_\beta[v] = -\langle n_\beta[v], v \rangle$  and hence

$$\frac{\delta \Omega_\beta}{\delta v} = n_\beta[v]. \quad (35)$$

As  $n_\beta[v]$  is a one-one mapping  $X^* \leftrightarrow D_\beta$ , for  $n \in D_\beta$  one has inversely  $v_\beta[n]$  and  $F_\beta[n] - \Omega_\beta[v_\beta[n]] = -\langle n, v_\beta[n] \rangle$  implying

$$\frac{\delta F_\beta}{\delta n} = -v_\beta[n], \quad n \in D_\beta. \quad (36)$$

Note that while Eq. (36) holds for  $n \in D_\beta \subset X$ , the derivative  $\delta / \delta n$  on the left-hand side is taken in  $X$ , that is, for any  $\delta n \in X$  with  $\|\delta n\|$  small enough.

From the strict concavity and continuous differentiability of  $\Omega_\beta[v]$  the differentiability of  $F_\beta[n]$  at every point  $n \in D_\beta$  follows, that is, at every density  $n$  thermodynamically corresponding to some  $v$  at temperature  $(k\beta)^{-1}$ . Like in the  $T=0$  theory,<sup>4,14</sup> Eq. (31) yields that  $F_\beta[n]$  jumps to  $+\infty$  if  $n < 0$  for an  $x$  domain of nonzero measure. Take  $v=c > 0$  for some domain where  $n < 0$  and  $v=0(=\mu)$  everywhere else. This  $v$  is admissible for arbitrary large  $c$  and  $\hat{H}[v]$  is bounded below for such a  $v$ . Hence,  $\Omega_\beta[v]$  is also bounded below and, as easily seen, the supremum Eq. (31) is obtained for  $c \rightarrow \infty$  to be  $+\infty$ . Assume now that  $n_\beta(x_0)=0$  for some  $x_0$ . Since any  $n_\beta \in D_\beta$  is continuous in  $x$  (any solution of the many-particle Schrödinger equation is continuous), there is always  $\delta n \in X$ ,  $\delta n(x_0) > 0$ , so that  $n_\beta(x) - \epsilon \delta n(x)$  would be negative in a neighborhood of  $x_0$  of nonzero measure for arbitrarily small  $|\epsilon|$  and the functional derivative Eq. (36) would not exist for that  $n_\beta$ . Thus, the result, Eq. (36) also implies  $n_\beta(x) > 0$  everywhere for  $T > 0$ . (See also next section.)

## VI. INTERACTION-FREE PARTICLES AND BEYOND

As is well known from Statistical Physics,<sup>16</sup> in a noninteracting particle system the particles in a single particle quantum state  $|\varphi_k\rangle$  may be treated as an independent subsystem even of a quantum ensemble with exchange symmetry. The corresponding statistical fermionic state is

$$\rho_k = | \rangle (1 - p_k) \langle | + |\varphi_k\rangle p_k \langle \varphi_k| \quad (37)$$

with occupation  $p_k \in [0, 1]$  of the orbital  $\varphi_k$  and  $| \rangle$  as the vacuum state. Accordingly we define<sup>7</sup>

$$\begin{aligned} \mathcal{T}_\beta[p_k, \varphi_k] &= \text{tr} \rho_k \left( \hat{T} + \frac{1}{\beta} \ln \rho_k \right) \\ &= p_k (\langle \varphi_k | \hat{T} | \varphi_k \rangle) \\ &\quad + \frac{1}{\beta} [p_k \ln p_k + (1 - p_k) \ln(1 - p_k)] \end{aligned} \quad (38)$$

and the density functional

$$T_\beta[n] = \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1 \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \sum_k \mathcal{T}_\beta[p_k, \varphi_k] \left| \sum_k p_k |\varphi_k|^2 = n \right. \right\}, \quad (39)$$

where the minimum taken over all orthonormal orbitals and orbital occupations which yield a given  $n$  exists like in the GS case.

Now, the grand canonical potential is

$$\begin{aligned} \Omega_\beta^0[v] &= \min_n \{ T_\beta[n] + \langle v, n \rangle \} \\ &= \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1 \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \sum_k \mathcal{T}_\beta[p_k, \varphi_k] + \langle v, n[p_k, \varphi_k] \rangle \right\}, \end{aligned} \quad (40)$$

where again the  $\varphi_k$  must be orthonormal.

Variation in the  $\varphi_k^*$  under the last constraint yields for the minimizing orbitals  $\varphi_k^0$

$$(\hat{t} + v) \varphi_k^0 = \varphi_k^0 \epsilon_k^0 \quad (41)$$

and variation in the  $p_k$  yields

$$p_k^0(\beta) = f_\beta(\epsilon_k^0) = \frac{1}{e^{\beta \epsilon_k^0} + 1} \quad (42)$$

which is the correct result in this physically trivial case. For any  $v \in X^*$  the minimum of Eq. (40) does indeed exist, and the minimizing density is

$$n_\beta^0[v] = n_{\beta s s'}^0(\mathbf{r}) = \sum_k f_\beta(\epsilon_k^0) \varphi_k^0(\mathbf{r}, s) \varphi_k^{0*}(\mathbf{r}, s') \quad (43)$$

so that  $N = \sum_k f_\beta(\epsilon_k^0)$  relates the average particle number  $N$  to the chemical potential  $\mu$ . Only the occupation numbers depend on temperature  $(k\beta)^{-1}$  and on the value of the chemical potential  $\mu$  from which  $v$  and the  $\epsilon_k^0$  are measured.

Here,  $n_\beta^0 > 0$  everywhere is intuitively clear because  $f_\beta(\varepsilon_k^0) > 0$  for all  $k$ . For densities minimizing Eq. (40) it obviously holds that

$$T_\beta[n] = \Phi_\beta^0[n] = F_\beta^0[n], \quad n \in D_\beta^0. \quad (44)$$

$\{T_\beta[n]\}$  replaces the density matrix functional  $T_{DM}[n]$  of the GS theory, Eq. (9).}

Accounting for the Coulomb interaction of the electrons in mean-field approximation simply means to replace  $v$  in the above Schrödinger equation by  $v + v_\beta^H$  where

$$v_\beta^H(\mathbf{r}) = \int \frac{n_{\beta s' s'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dx' \quad (45)$$

contains self-interaction. Since  $\nabla \varphi_k \in L^2(\mathbb{T}^3)$  implies  $|\varphi_k|^2 \in L^3(\mathbb{T}^3)$ , taken as a KS ansatz  $n = \sum_k p_k |\varphi_k|^2 \geq 0$  is sufficiently general for the density of an interacting system too. Densities of this type apparently form a convex domain  $D$  of the functional space  $X = L^3(\mathbb{T}^3)$  on which  $T_\beta[n]$  is also defined by Eq. (39). ( $\mathcal{J}_N \subset D$  for every real  $N$ ,  $0 < N < \infty$ .)

As  $D_\beta \subset D$  also for  $\hat{W} \neq 0$ , by

$$F_\beta[n] = T_\beta[n] + \frac{1}{2} \int \frac{n_{ss}(\mathbf{r}) n_{s's'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dx dx' + F_\beta^{\text{XC}}[n] \quad (46)$$

for  $n \in D$  an exchange and correlation density functional  $F_\beta^{\text{XC}}[n]$  is defined (since the other density functionals of this relation were previously defined or are explicitly given on  $D$ ). Inserting here  $n = \sum_k p_k |\varphi_k|^2$  transforms Eq. (32) into a minimum search by varying  $\varphi_k^*$  and  $p_k$  as above in the GS theory. The derivatives with respect to  $\varphi_k^*$  and  $p_k$  of  $F_\beta$  exist on the basis of Eq. (36) for  $\{p_k, \varphi_k\}$  yielding  $n \in D_\beta$ , and those of the second term on the right-hand side of Eq. (46) are explicitly known. Hence, the situation with  $T_\beta$  and  $F_\beta^{\text{XC}}$  is like in the GS theory. We cannot expect  $D_\beta \subset D_\beta^0$ .

Formally, like in Eq. (14) one may again assume

$$T_\beta[n] + F_\beta^{\text{XC}}[n] = \min_{\substack{\{p_k, \varphi_k\} \\ 0 \leq p_k \leq 1 \\ (\varphi_k | \varphi_{k'}) = \delta_{kk'}}} \left\{ \sum_k \mathcal{T}_\beta[p_k, \varphi_k] + F_\beta^{\text{XC}}[\{p_k, \varphi_k\}] \left| \sum_k p_k |\varphi_k|^2 = n \right. \right\} \quad (47)$$

which yields the KS equation

$$(\hat{t} + \hat{v}_\beta^{\text{eff}} - \varepsilon_k) \varphi_k = 0 \quad (48)$$

with

$$\hat{v}_\beta^{\text{eff}} \varphi_k = (v + v_\beta^H + \hat{v}_\beta^{\text{XC}}) \varphi_k, \quad \hat{v}_\beta^{\text{XC}} \varphi_k = \frac{1}{p_k} \frac{\delta \mathcal{F}_\beta^{\text{XC}}}{\delta \varphi_k^*} \quad (49)$$

and  $p_k(\beta) = f_\beta$  from Eq. (42) with  $\varepsilon_k^0$  replaced by  $\varepsilon_k$ . Compare also the previous discussion of the property, Eq. (15) of  $\hat{v}_\beta^{\text{XC}}$ . Note that we did again not prove the existence of  $\delta \mathcal{F}_\beta^{\text{XC}} / \delta n$  or of an everywhere differentiable  $\mathcal{F}_\beta^{\text{XC}}[\{p_k, \varphi_k\}]$ ; the effective KS potential  $\hat{v}_\beta^{\text{eff}}$ , if it exists at all, need not exist as an orbital independent local potential, it might be nonlocal and orbital dependent. In this respect the situation is the same as for the GS theory.

Under the assumption, Eq. (47), given the external potential  $v$ , the solutions of this KS equation determine, via the analogs of Eqs. (42) and (43) without superscripts, the density  $n_\beta[v] \in D_\beta$  minimizing the right-hand side of Eq. (32) and hence providing the grand canonical potential

$$\Omega_\beta[v - \mu] = F_\beta[n_\beta[v - \mu]] + \int (v - \mu) n_\beta[v - \mu] dx, \quad (50)$$

where we explicitly reinserted the chemical potential  $\mu$ . The latter is related to the particle number  $N$  by

$$- \frac{\partial \Omega}{\partial \mu} = N = \sum_k f_\beta(\varepsilon_k - \mu) \quad (51)$$

which is also confirmed by inserting Eq. (36) and the KS expression for  $n$  into Eq. (50).

## VII. SUMMARY

It is shown that the functional derivative of the density functional  $F_\beta[n]$  of Eq. (31) as Fréchet derivative (total differential) in the functional space  $L^3(\mathbb{T}^3)$  exists for all densities  $n = n_\beta[v]$ . These are all densities which relate to grand canonical states  $\rho_\beta[v]$  ( $v$  measured from the chemical potential  $\mu$ ) for some  $v \in L^{3/2}(\mathbb{T}^3)$ . These states minimize Mermin's generating functional  $\Omega_v[\rho]$  for the grand canonical potential  $\Omega_\beta[v]$ . Hence,  $\Omega_\beta[v]$  and  $n_\beta[v]$  can be obtained from determining the in view of strict convexity unique stationary point of  $F_\beta[n] + \langle v, n \rangle$ .

The whole  $T > 0$  theory, of course, as in the GS variant again depends on the knowledge of the density functional  $F_\beta[n]$  or of  $F_\beta^{\text{XC}}[n]$  and of  $\mathcal{F}_\beta^{\text{XC}}$  in the KS theory, all of which are hardly ever accessible (if the latter exists at all) and hence have to be modeled changing the exact theory into a model theory within a (nearly) rigorous frame. An early *ad hoc* application is Ref. 17. Since Eq. (51) rests on Eq. (36), it can be used as a check for the quality of a model  $F_\beta^{\text{XC}}[n]$ , for instance down to which temperature it can reasonably be used for a specific answer.

When using explicitly designed model density functionals one must keep in mind that most of those functionals while being convex locally in a neighborhood of a minimizing density, are often not convex globally. This is, in particular, the case for most orbital-dependent functionals in use. Hence, all stationary values must be found (for instance for different orbital configurations) and then their minimum selected. This is often overlooked in L(S)DA+ $U$  applications.

This is all valid when applying DFT with  $T > 0$  to molecular dynamics, although such an application has its own problems with the use of the grand canonical potential in a nonequilibrium situation. They are not related to the present text and are discussed in Ref. 7. If in such an application orbital dependent functionals are used, the above warning in view of lack of global convexity of such model potentials might be even more important.

The advantage of the  $T > 0$  theory against the GS theory is that the existence of the functional derivative of the exact

$F_{\beta}[n]$  is guaranteed for every grand canonical equilibrium state even in the spin dependent variant of the theory and as a derivative in  $L^3(\mathbb{T}^3)$ , not only on hyperplanes  $\langle 1, n \rangle = N$ . There is no gap problem left with a single (exact) functional  $F_{\beta}[n]$  and no problem with spin polarization while in the GS theory two different KS potentials are needed to obtain

the gap. (Strictly speaking, there is of course no gap for  $T > 0$ .)

#### ACKNOWLEDGMENT

I am grateful to K. Koepf for helpful discussions.

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