

One-body reduced density-matrix functional theory for the canonical ensemble

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We establish one-body reduced density matrix (1RDM) functional theory for the canonical ensemble in a finite basis set at an elevated temperature. Including temperature guarantees the differentiability of the universal functional by occupying all states and additionally not fully occupying the states in a fermionic system. We use the convexity of the universal functional and invertibility of the potential-to-1RDM map to show that the subgradient contains only one element which is equivalent to differentiability. This allows us to show that all 1RDMs with a purely fractional occupation number spectrum ($0 < n_i < 1 \forall_i$) are uniquely v -representable up to a constant.

DOI: [10.1103/PhysRevA.107.022210](https://doi.org/10.1103/PhysRevA.107.022210)**I. INTRODUCTION**

Quantum chemistry and physics deal with the description of many interacting particles. Often we limit ourselves to a single-particle species. In quantum chemistry these are usually electrons, but in physics also bosonic particles are of interest. Though the many-body Schrödinger equation involves only linear operators, the daunting dimensionality of the many-body wave function renders a direct solution intractable, but for a few particles. This is one of the prime reasons to aim directly for reduced quantities.

In 1964 Hohenberg and Kohn presented their revolutionary work about density functional theory (DFT) [1]. They showed that any observable can be regarded as a functional of the density. Especially the Kohn-Sham (KS) formulation [2] has been important to the success of DFT. Their idea was to approximate the true kinetic energy by the kinetic energy of the KS system: a noninteracting system with the same density as the interacting system. The KS kinetic energy turns out to be a decent approximation to the true kinetic energy of the interacting system. The difference in the kinetic energy is then lumped together with the interaction beyond Hartree (classical Coulomb) in the exchange-correlation energy functional. Though formally exact, in practice KS-DFT has some weaknesses, since the exchange-correlation functional needs to be approximated. A famous example is the stretching of the H_2 bond [3–5].

One way to bypass some of these problems in constructing an approximate exchange-correlation energy functional is with one-body reduced density-matrix (1RDM) functional theory. One advantage over DFT is that we have also an explicit expression for the kinetic energy while still having the total energy as a functional of the 1RDM [6]. However, in a zero-temperature setting, mapping back from 1RDMs to (non-local) potentials is problematic, as already noted by Gilbert

[6] and others [7–10]. This is most clear in the case of non-interacting particles, since typically ground state 1RDMs are idempotent. It therefore seems that nonidempotent 1RDMs cannot be v -representable in the absence of interactions. There is the possibility for orbital energies to be degenerate, however, which allows fractionally occupied orbitals and hence nonidempotent 1RDMs [11,12]. But one quickly realizes that the scaled identity operator is the one-body Hamiltonian which has all 1RDMs as ground state 1RDM. It is clear that the interaction should play a crucial role in the back mapping, but there has been no progress in this direction.

An alternative to regularize the theory is to introduce entropy, i.e., work at finite temperature, as proposed more than a decade ago [8,9,13,14]. Though this is a theoretical motivation to introduce temperature, also physically this is a well justified choice, since most experiments are conducted at $T > 0$. Important examples where temperature plays an important role are metal-insulator transitions in transition metal oxides [15], high T_c superconductors [16], hot plasmas [17], etc.

In Ref. [10] 1RDM functional theory (1RDMFT) was presented for the grand canonical ensemble within a finite basis set. However, the use of a grand canonical ensemble is inappropriate if the number of particles is relatively low as in ultracold atom experiments [18], but also in the low-temperature limit the grand canonical ensemble can lead to unphysical results [19,20]. A canonical formulation of 1RDMFT is therefore desirable and will be the goal of this paper.

In classical thermodynamics the grand potential can be reached by a Legendre transformation of the Helmholtz free energy with respect to the number of particles. In the quantum mechanical setting we cannot do that. The reason is that the grand potential and the Helmholtz functional act on different spaces: the Fock space and the N -particle Hilbert spaces, respectively. Thus, we can not simply transform it back to obtain the canonical case. Another major difference with respect to the grand canonical ensemble is that in the noninteracting case the occupation numbers are not explicitly given by either the Fermi/Bose function for fermions/bosons.

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Instead, they need to be calculated recursively, using auxiliary partition functions [21]. In Ref. [14] it therefore remained an open question whether every thermal 1RDM (only fractional occupation numbers) would be noninteracting v -representable and not much progress could be made. However, we do not rely on such an explicit relation and are able to prove a one-to-one correspondence between thermal 1RDMs (all occupation numbers fractional) and (nonlocal) potentials for any interaction. The noninteracting system is just a particular case. This result justifies the existence of an algorithm which finds for any thermal 1RDM the corresponding noninteracting Hamiltonian as published recently by Kooi [22].

In this paper we present 1RDMFT in a rigorous way for a fixed number of particles, finite basis set, and elevated temperature. We show that the universal functional is differentiable and it holds

$$\frac{\partial F_{N,\pm}}{\partial \gamma} = -v, \quad (1)$$

where γ is the ground state 1RDM for the potential v . Here and in the following, $+$ and $-$ stand for the bosonic and the fermionic case, respectively. If we have a handy expression for $F_{N,\pm}[\gamma]$ then we can circumvent the handling of the density-matrix operator to compute the free energy and instead we only need to deal with the reduced quantity γ . The minimizer for the Helmholtz functional can then be determined through the above relation (1).

This paper is constructed in the following way. In Sec. II we introduce all the relevant spaces, then, in Sec. III, we present the Helmholtz functional, its minimizing density-matrix operator, and the general approach for 1RDMFT. For this task we make use of the universal functional $F_{N,\pm}$. To show differentiability of $F_{N,\pm}$ we utilize results from convex analysis. In Sec. IV we show that all the relevant functionals are convex. Additionally, we show that two potentials differing by more than a constant cannot generate the same density-matrix operator. The proof of differentiability of $F_{N,\pm}$ is finalized in Sec. V.

II. SETTING

We build our N -particle space from a finite number of single-particle states $|i\rangle$, for $i \in \{1, \dots, N_b\}$ and $N_b < \infty$. We require the states to be orthonormal. The one-particle Hilbert space \mathcal{H} is now the \mathbb{C} -vector space generated by the states $|i\rangle$, i.e., $\mathcal{H} := \text{span}\{|1\rangle, \dots, |N_b\rangle\} \cong \mathbb{C}^{N_b}$. To build the N -particle space we need to distinguish between bosons and fermions.

Bosons. A system with N bosons is described by a symmetric wave function. Therefore, the bosonic N -particle Hilbert state, denoted by \mathcal{H}_+^N , consists of all symmetric tensors of order N , i.e., $\mathcal{H}_+^N := \text{Sym}^N(\mathcal{H})$. The dimension of \mathcal{H}_+^N is $\binom{N_b+N-1}{N}$.

Fermions. Fermionic systems are described by antisymmetric wave functions. Thus, we consider the space of antisymmetric tensors of order N , i.e., $\mathcal{H}_-^N := \wedge^N \mathcal{H}$. The dimension is given by $\binom{N_b}{N}$. Note that we need to have $N_b \geq N$. The case $N_b = N$ is trivial since we have only one possible state. Thus, we will only consider $N_b > N$.

The set of density-matrix operators on the N -particle space \mathcal{H}_\pm^N is defined as

$$\overline{\mathcal{P}}_{N,\pm} := \{ \hat{\rho} : \mathcal{H}_\pm^N \rightarrow \mathcal{H}_\pm^N \mid \hat{\rho} = \hat{\rho}^\dagger, \hat{\rho} \geq 0, \text{Tr}\{\hat{\rho}\} = 1 \}, \quad (2)$$

which we endow with the norm

$$\|\hat{\rho}\|_2 = (\text{Tr}\{|\hat{\rho}|^2\})^{1/2}. \quad (3)$$

A density-matrix operator $\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm}$ has a spectral decomposition

$$\hat{\rho} = \sum_l \lambda_l |\psi_l\rangle \langle \psi_l|, \quad (4)$$

and its kernel is given by

$$\begin{aligned} \rho(x_1, \dots, x_N; y_1, \dots, y_N) \\ = \sum_l \lambda_l \psi_l(x_1, \dots, x_N) \psi_l^*(y_1, \dots, y_N). \end{aligned} \quad (5)$$

We can define the 1RDM γ by [23]

$$\gamma_{ij}[\hat{\rho}] = \text{Tr}\{\hat{\rho} \hat{a}_i^\dagger \hat{a}_j\}.$$

It turns out (see the Appendix) that the relevant spaces for the 1RDMs are subsets of the space of all Hermitian $N_b \times N_b$ matrices denoted by $\mathbb{H}(N_b)$,

$$\overline{\mathcal{N}}_{N,+} := \{ \gamma \in \mathbb{H}(N_b) \mid \gamma \geq 0, \text{tr}\{\gamma\} = N \}, \quad (6a)$$

$$\overline{\mathcal{N}}_{N,-} := \{ \gamma \in \mathbb{H}(N_b) \mid \gamma \geq 0, \gamma^2 \leq \gamma, \text{tr}\{\gamma\} = N \}. \quad (6b)$$

We have used $\text{tr}\{\cdot\}$ to emphasize that the trace is over the one-particle Hilbert space \mathcal{H} as opposed to the $\text{Tr}\{\cdot\}$ which is over a \mathcal{H}_\pm^N Hilbert space. By convention, the eigenvalues and eigenstates of the 1RDM γ are called natural occupation numbers and natural orbitals (NOs), respectively. Coleman has shown that all elements of $\overline{\mathcal{N}}_{N,\pm}$ can be obtained from a density-matrix operator in $\overline{\mathcal{P}}_{N,\pm}$, so it is a true 1RDM [24].

Theorem II.1 (Coleman). For any $\gamma \in \overline{\mathcal{N}}_{N,\pm}$ there is a density matrix $\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm}$ which generates γ .

The proof can be found in the Appendix.

III. GENERAL APPROACH

The Helmholtz functional for the canonical ensemble is defined as

$$\Omega_v[\hat{\rho}] := E_v[\hat{\rho}] - \beta^{-1} S[\hat{\rho}], \quad (7)$$

where

$$E_v[\hat{\rho}] := \text{Tr}[\hat{\rho} \hat{H}_v] \quad (8)$$

is the energy of a system with the Hamiltonian $\hat{H}_v := \hat{H}_0 + \hat{V}_v$ [\hat{H}_0 contains the kinetic and interaction part and \hat{V}_v is the potential with kernel $v(x, x')$]. The second term contains the entropy

$$S[\hat{\rho}] := -\text{Tr}\{\hat{\rho} \ln(\hat{\rho})\} \quad (9)$$

and the inverse temperature $\beta = 1/T$. The minimizer $\hat{\rho}_v$ of the Helmholtz functional can be found by variations in the

density-matrix operator which yields the equation

$$\text{Tr}\{\delta\hat{\rho}[\hat{H}_v + \beta^{-1} \ln(\hat{\rho}_v)]\} + \beta^{-1} \text{Tr}\{\delta\hat{\rho}\} = 0. \quad (10)$$

From the unit trace condition and (10) it follows that

$$\hat{\rho}_v = e^{-\beta\hat{H}_v} / Z[v], \quad \text{where } Z[v] := \text{Tr}\{e^{-\beta\hat{H}_v}\}. \quad (11)$$

The minimizer $\hat{\rho}_v$ is called the Gibbs state of our system. Note that we only have a proper solution for $0 < Z[v] < \infty$. This is always the case since we work in a finite basis setting with a fixed number of particles, so the trace only runs over a finite number of elements.

One aim is to show that the map from the potential v to the density-matrix operator $\hat{\rho}_v$ is invertible. However, this is only doable up to a constant since adding a constant to the potential does not change the density-matrix operator. To achieve a one-to-one correspondence we allow only potentials from the following set,

$$\mathcal{V} := \{v \in \mathbb{H}(N_b) \mid \text{tr}\{v\} = 0\}. \quad (12)$$

We can also think of $v \in \mathcal{V}$ being a representative of the equivalence class containing potentials differing by a constant.

In Theorem II.1 we have seen that all $\gamma \in \overline{\mathcal{N}}_{N,\pm}$ are N -representable. However, physically relevant are only the 1RDMs that are associated with a Gibbs state $\hat{\rho}_v$. Thus, we denote the set of all v -representable 1RDM by

$$\mathcal{V}_{N,\pm} := \{\gamma \in \overline{\mathcal{N}}_{N,\pm} \mid \exists v \in \mathcal{V} \mapsto \gamma\}. \quad (13)$$

The approach is to partition the minimization in the Helmholtz functional as

$$\Omega_{N,\pm}[v] := \inf_{\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm}} \Omega_v[\hat{\rho}] = \inf_{\gamma \in \overline{\mathcal{N}}_{N,\pm}} (F_{N,\pm}[\gamma] + \text{tr}\{v\gamma\}), \quad (14)$$

where

$$\begin{aligned} F_{N,\pm}[\gamma] &:= \inf_{\substack{\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm} \\ \hat{\rho} \rightarrow \gamma}} \Omega_0[\hat{\rho}] \\ &= \inf_{\substack{\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm} \\ \hat{\rho} \rightarrow \gamma}} \text{Tr}\{\hat{\rho}[\hat{H}_0 + \beta^{-1} \ln(\hat{\rho})]\} \end{aligned} \quad (15)$$

is called the universal functional which takes the value ∞ in case no $\hat{\rho} \rightarrow \gamma$ exists. Here and in the following, $\Omega_0[\hat{\rho}] = \Omega_{v=0}[\hat{\rho}]$. The aim is to show that $F_{N,\pm}$ is differentiable. Then the minimizer can be found through the relation

$$\frac{\partial F_{N,\pm}}{\partial \gamma} = -v,$$

and we know that γ is a canonical eq-1RDM (equilibrium 1-RDM) which was an open question in Ref. [14].

IV. GENERAL PROPERTIES OF THE HELMHOLTZ FUNCTIONAL AND IMPLICATIONS ON THE UNIVERSAL FUNCTIONAL

Theorem IV.1. The mapping $\hat{H}_v \mapsto \hat{\rho}_v$ with $v \in \mathcal{V}$ is invertible up to a constant in the Hamiltonian.

Proof. Assume that two Hamiltonians \hat{H}_v and \hat{H}'_v differing in their potential yield the same density-matrix operator $\hat{\rho}_v$. From (10) it follows that $\hat{\rho}_v$ fulfills

$$\begin{aligned} \frac{1}{\beta} \ln(\hat{\rho}_v) + \hat{H}_v &= C, \\ \frac{1}{\beta} \ln(\hat{\rho}_v) + \hat{H}'_v &= C'. \end{aligned}$$

Subtracting these equations gives $\hat{H}_v - \hat{H}'_v = C - C'$. ■

Remark 1. Since we have a fixed number of particles in the Hilbert space, the constant in Theorem IV.1 can be of the form $f(\hat{N})$ where $f: \mathbb{R} \rightarrow \mathbb{R}$, so this includes the arbitrary constant shift in the potential.

Corollary 1. The map $v \mapsto \hat{\rho}_v$ with $v \in \mathcal{V}$ is invertible.

Note that we only have a one-to-one correspondence because we require $\text{tr}\{v\} = 0$. Otherwise a constant shift in the potential would lead to the same density-matrix operator.

At this point we want to mention that the density-matrix operator $\hat{\rho}_v$ is positive definite, $\hat{\rho}_v > 0$, and lies in the following subspace of $\overline{\mathcal{P}}_{N,\pm}$,

$$\mathcal{P}_{N,\pm} := \{\hat{\rho} : \mathcal{H}_{\pm}^N \rightarrow \mathcal{H}_{\pm}^N \mid \hat{\rho} = \hat{\rho}^\dagger, \hat{\rho} > 0, \text{Tr}\{\hat{\rho}\} = 1\}. \quad (16)$$

It follows that the natural occupation numbers n_i are positive and in the fermionic case additionally $n_i < 1$. To see this let $\phi_1, \dots, \phi_{N_b}$ be the NO basis and $\hat{\rho}_v = \sum_j \lambda_j |\psi_j\rangle \langle \psi_j|$ be the spectral decomposition of the density-matrix operator. Then, as the ψ_j 's build a basis of \mathcal{H}_{\pm}^N , each NO ϕ_i contributes to at least one of the eigenstates. So,

$$\begin{aligned} n_i &= \sum_j \lambda_j \int dx dy dx_2 \dots dx_N \phi_i^*(x) \phi_i(y) \\ &\quad \times \psi_j(x, x_2, \dots, x_N) \psi_j^*(y, x_2, \dots, x_N) > 0, \end{aligned} \quad (17)$$

where we used the fact that all weights $\lambda_j = e^{-\beta E_j} / Z$ are positive. In the case of fermions we have already showed that $n_i \leq 1$. The i th NO cannot be present in all ψ_j 's (in the case $N \neq N_b$), so

$$\begin{aligned} n_i &= \sum_j \lambda_j \int dx dy dx_2 \dots dx_N \phi_i^*(x) \phi_i(y) \\ &\quad \times \psi_j(x, x_2, \dots, x_N) \psi_j^*(y, x_2, \dots, x_N) < 1, \end{aligned} \quad (18)$$

because the integral is at least for one j not equal to 1. Summarized, the 1RDMs produced by a potential are contained in

$$\mathcal{N}_{N,+} := \{\gamma \in \mathbb{H}(N_b) \mid \gamma > 0\}, \quad (19)$$

$$\mathcal{N}_{N,-} := \{\gamma \in \mathbb{H}(N_b) \mid \gamma > 0, \gamma^2 < \gamma\}. \quad (20)$$

We want to show that the most important functionals are either convex or concave to be able to use results from convex analysis. We start with the functional $\Omega_{N,\pm}[v]$ which is achieved through a minimization and thus turns out to be concave [25].

Theorem IV.2. The functional $\Omega_{N,\pm}[v] = \min_{\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm}} \Omega_v[\hat{\rho}] = \min_{\hat{\rho} \in \mathcal{P}_{N,\pm}} \Omega_v[\hat{\rho}] = -\beta^{-1} \ln(Z[v])$ is strictly concave in v .

Proof. Let $v_1 \neq v_2$ be two potentials in \mathcal{V} and let $0 < t < 1$. Then we have

$$\begin{aligned}\Omega_{N,\pm}[tv_1 + (1-t)v_2] &= \min_{\hat{\rho} \in \mathcal{P}_{N,\pm}} \text{Tr} \left\{ \hat{\rho} \left[t\hat{H}_{v_1} + t\frac{1}{\beta} \ln(\hat{\rho}) \right] \right\} + \text{Tr} \left\{ \hat{\rho} \left[(1-t)\hat{H}_{v_2} + (1-t)\frac{1}{\beta} \ln(\hat{\rho}) \right] \right\} \\ &> t \min_{\hat{\rho}_1 \in \mathcal{P}_{N,\pm}} \text{Tr} \left\{ \hat{\rho}_1 \left[\hat{H}_{v_1} + \frac{1}{\beta} \ln(\hat{\rho}_1) \right] \right\} + (1-t) \min_{\hat{\rho}_2 \in \mathcal{P}_{N,\pm}} \text{Tr} \left\{ \hat{\rho}_2 \left[\hat{H}_{v_2} + \frac{1}{\beta} \ln(\hat{\rho}_2) \right] \right\} \\ &= t\Omega_{N,\pm}[v_1] + (1-t)\Omega_{N,\pm}[v_2],\end{aligned}$$

where the strict inequality follows from Corollary 1. \blacksquare

With Corollary 1 it is possible to show a generalization of the Hohenberg-Kohn theorem for 1RDMs and nonlocal potentials [26].

Theorem IV.3. The map $v \mapsto \gamma_v$ for $v \in \mathcal{V}$ is invertible.

Proof. Assume there are two potentials $v_1 \neq v_2 \in \mathcal{V}$ yielding different density-matrix operators $\hat{\rho}_1 \neq \hat{\rho}_2$ but the same 1RDM γ . Then we get

$$\begin{aligned}\Omega_{N,\pm}[v_1] &= \Omega_{v_1}[\hat{\rho}_1] = \Omega_{v_2}[\hat{\rho}_1] + \text{tr}\{\gamma(v_1 - v_2)\} \\ &> \Omega_{v_2}[\hat{\rho}_2] + \text{tr}\{\gamma(v_1 - v_2)\} \\ &= \Omega_{N,\pm}[v_2] + \text{tr}\{\gamma(v_1 - v_2)\}.\end{aligned}$$

Changing the role of v_1 and v_2 and adding the two inequalities gives

$$\Omega_{N,\pm}[v_1] + \Omega_{N,\pm}[v_2] < \Omega_{N,\pm}[v_2] + \Omega_{N,\pm}[v_1],$$

which is a contradiction. \blacksquare

One aim is to show that the universal functional is convex. For this purpose we first show that the entropy is strictly concave [27–29].

Theorem IV.4. The entropy is strictly concave, i.e., for any $\hat{\rho}_0, \hat{\rho}_1 \in \overline{\mathcal{P}}_{N,\pm}$ and $\lambda \in (0, 1)$ we have $S[\lambda\hat{\rho}_0 + (1-\lambda)\hat{\rho}_1] > \lambda S[\hat{\rho}_0] + (1-\lambda)S[\hat{\rho}_1]$.

Proof. Let $\hat{\rho}_\lambda = \lambda\hat{\rho}_0 + (1-\lambda)\hat{\rho}_1 = \sum_k w_k |\psi_k\rangle \langle \psi_k|$. We use strict concavity of the function $s(x) = -x \ln(x)$ and we get

$$\begin{aligned}S(\hat{\rho}_\lambda) &= -\sum_k w_k \ln(w_k) = \sum_k s(\langle \psi_k | \hat{\rho}_\lambda | \psi_k \rangle) \\ &= \sum_k s(\lambda \langle \psi_k | \hat{\rho}_0 | \psi_k \rangle + (1-\lambda) \langle \psi_k | \hat{\rho}_1 | \psi_k \rangle) \\ &> \lambda \sum_k s(\langle \psi_k | \hat{\rho}_0 | \psi_k \rangle) + (1-\lambda) \sum_k s(\langle \psi_k | \hat{\rho}_1 | \psi_k \rangle) \\ &\geq \lambda \sum_k \langle \psi_k | s(\hat{\rho}_0) | \psi_k \rangle + (1-\lambda) \sum_k \langle \psi_k | s(\hat{\rho}_1) | \psi_k \rangle \\ &= \lambda S[\hat{\rho}_0] + (1-\lambda)S[\hat{\rho}_1],\end{aligned}$$

where we used Jensen's inequality for the last inequality. \blacksquare

Corollary 2. The Helmholtz functional $\Omega_v[\hat{\rho}]$ is strictly convex in the density operator $\hat{\rho}$.

Proof. It follows directly from the fact that the Helmholtz functional is the sum of a linear and a strictly convex functional. \blacksquare

Theorem IV.5. The universal functional $F_{N,\pm}[\gamma]$ is convex on $\overline{\mathcal{N}}_{N,\pm}$.

Proof. Let $\gamma_0, \gamma_1 \in \overline{\mathcal{N}}_{N,\pm}$, $\lambda \in [0, 1]$ and $\gamma_\lambda = \lambda\gamma_0 + (1-\lambda)\gamma_1$ and taking $\hat{\rho}, \hat{\rho}_0, \hat{\rho}_1 \in \overline{\mathcal{P}}_{N,\pm}$ we get

$$\begin{aligned}\lambda F_{N,\pm}[\gamma_0] + (1-\lambda)F_{N,\pm}[\gamma_1] &= \lambda \inf_{\hat{\rho}_0 \rightarrow \gamma_0} \Omega_0[\hat{\rho}_0] + (1-\lambda) \inf_{\hat{\rho}_1 \rightarrow \gamma_1} \Omega_0[\hat{\rho}_1] \\ &= \inf_{\hat{\rho}_0 \rightarrow \gamma_0} \inf_{\hat{\rho}_1 \rightarrow \gamma_1} \lambda \Omega_0[\hat{\rho}_0] + (1-\lambda) \Omega_0[\hat{\rho}_1] \\ &\geq \inf_{\hat{\rho}_0 \rightarrow \gamma_0} \inf_{\hat{\rho}_1 \rightarrow \gamma_1} \Omega_0[\lambda\hat{\rho}_0 + (1-\lambda)\hat{\rho}_1] \\ &= \inf_{\hat{\rho} \rightarrow \gamma_\lambda} \Omega_0[\hat{\rho}] = F_{N,\pm}[\gamma_\lambda].\end{aligned}$$

V. FINAL RESULT

Now we want to show that the universal functional $F_{N,\pm}$ is differentiable. Differentiability is only defined on an open set. However, the set $\overline{\mathcal{N}}_{N,\pm}$ has an empty interior in $\mathbb{H}(N_b)$. Thus, we need to embed $\overline{\mathcal{N}}_{N,\pm}$ in a topological space where $\overline{\mathcal{N}}_{N,\pm}$ is the interior of $\overline{\mathcal{N}}_{N,\pm}$. The idea is to use the following result about subgradients and subdifferentials.

Theorem V.1. Let X be a finite-dimensional vector space, and let $f : X \rightarrow \mathbb{R} \cup \{\infty\}$ be a convex function with domain M . Assume M is contained in $a + \mathcal{L}$ such that \mathcal{L} is a subspace with the lowest dimension such that there exists $a \in X$ with $M \subset a + \mathcal{L}$ [30]. Let $\partial_{\mathcal{L}} f(x) := \partial f(x) \cap \mathcal{L}$ where $\partial f(x)$ is the subdifferential of f at a point x in the set M . Then the following properties hold for $\partial_{\mathcal{L}} f(x)$: (i) The set $\partial_{\mathcal{L}} f(x)$ is nonempty. (ii) f is differentiable at x if and only if $\partial_{\mathcal{L}} f(x)$ contains only one element. In that case this element equals the usual gradient. [With differentiable we mean that there is a linear map $J : \mathcal{L} \rightarrow \mathbb{R}$ such that for all $h \in \mathcal{L}$ we have $\lim_{h \rightarrow 0} \frac{1}{\|h\|_{\mathcal{L}}} |f(x+h) - f(x) - J(h)| = 0$.]

The universal functional has domain $\overline{\mathcal{N}}_{N,\pm}$ which is contained in $\mathcal{L} + a$ with $\mathcal{L} = \{x \in \mathbb{H}(N_b) \mid \text{tr}\{x\} = 0\}$ and $a = N/N_b \cdot \mathbb{1}$ [31] and its (relative) interior is $\overline{\mathcal{N}}_{N,\pm}$. Figure 1 shows $\overline{\mathcal{N}}_{N,+}$ for two particles and three basis functions. This also justifies the choice of the potential gauge. The aim is to get the relation $\partial F_{N,\pm} / \partial \gamma = -v$. But as mentioned in Theorem V.1, the differential is a map $J : \mathcal{L} \rightarrow \mathbb{R}$, i.e., it is contained in \mathcal{V} . We can now apply the above theorem for all 1RDMs contained in $\overline{\mathcal{N}}_{N,\pm}$.

Theorem V.2. If the infimum in (15) is attained, then (i) $\overline{\mathcal{N}}_{N,\pm} = \mathcal{N}_{N,\pm}$, and (ii) the universal functional $F_{N,\pm}[\gamma]$ is differentiable on $\overline{\mathcal{N}}_{N,\pm}$.

Proof. Convexity of $F_{N,\pm}$ implies that for any $\gamma \in \overline{\mathcal{N}}_{N,\pm}$ there exists at least one subgradient $h \in \mathcal{V}$. So for all

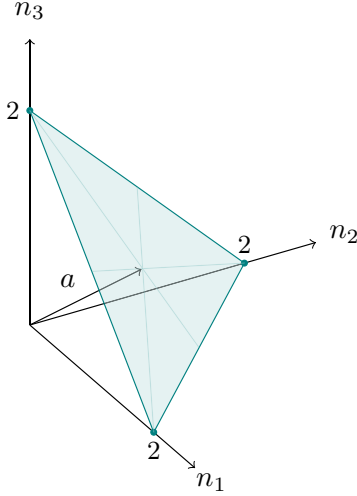


FIG. 1. Representation of $\overline{\mathcal{N}}_{N,+}$ in terms of the occupation numbers for $N_b = 3$ and $N = 2$ (see proof of Theorem II.1). The vector a shifts a two-dimensional subspace to an affine space which contains $\overline{\mathcal{N}}_{N,+}$.

$\tilde{\gamma} \in \overline{\mathcal{N}}_{N,\pm}$ it holds $F_{N,\pm}[\tilde{\gamma}] + \langle -h|\tilde{\gamma} \rangle \geq F_{N,\pm}[\gamma] + \langle -h|\gamma \rangle$, which implies

$$F_{N,\pm}[\gamma] + \langle -h|\gamma \rangle \leq \min_{\tilde{\gamma} \in \overline{\mathcal{N}}_{N,\pm}} F_{N,\pm}[\tilde{\gamma}] + \langle -h|\tilde{\gamma} \rangle = \Omega_{N,\pm}[-h].$$

Thus, the negative of the subgradient, $-h$, yields a potential generating γ and hence $\mathcal{N}_{N,\pm} = \mathcal{V}_{N,\pm}$. By Theorem IV.3, we get that there is only one such potential. Hence the subgradient is unique and $F_{N,\pm}[\gamma]$ is differentiable for all $\gamma \in \mathcal{N}_{N,\pm}$ by Theorem V.1. ■

We proved v -representability under the assumption that the minimum in (15) is attained. To finish the proof we still need to show that this is indeed the case. The idea is to show that the relevant functions are continuous and then use the fact that continuous functions attain their minima (and maxima) over compact sets.

Proposition V.3. The energy $E_v[\hat{\rho}]$ is Lipschitz continuous on $\overline{\mathcal{P}}_{N,\pm}$.

Proof. The Hamiltonian acts on a finite-dimensional space and thus it has a maximum eigenvalue, $\|\hat{H}_v\|_\infty < \infty$. For two density-matrix operators $\hat{\rho}_0, \hat{\rho}_1$ we have

$$|E_v[\hat{\rho}_0] - E_v[\hat{\rho}_1]| \leq \|\hat{H}_v\|_\infty \|\hat{\rho}_0 - \hat{\rho}_1\|.$$

Proposition V.4. The entropy is continuous on $\overline{\mathcal{P}}_{N,\pm}$. ■

Proof. The function $\hat{\rho} \mapsto (a_1, \dots, a_m)$ where (a_1, \dots, a_m) contains the eigenvalues of $\hat{\rho}$ in an ordered fashion and with multiplicity ($a_i \leq a_{i+1}$ for all $i = 1, \dots, m-1$) is continuous. The statement follows from continuity of the function $(a_1, \dots, a_m) \mapsto \sum_{j=1}^m a_j \ln(a_j)$. ■

To finish the proof we make use of the following theorem.

Theorem V.5. Let X be a compact metric space and let $f : X \rightarrow \mathbb{R}$ be a continuous function. Then f is bounded and it attains its maximum and minimum.

Compact sets in finite-dimensional affine spaces (with the usual metric) are fully characterized by closedness and

boundedness. Thus, $\overline{\mathcal{P}}_{N,\pm}$ and $\{\hat{\rho} \in \overline{\mathcal{P}}_{N,\pm} \mid \hat{\rho} \rightarrow \gamma\}$ are compact and we get the following corollary.

Corollary 3. The infima in the the Helmholtz functional $\Omega_{N,\pm}[v]$ and the universal functional $F_{N,\pm}[\gamma]$ are achieved in the fermionic and bosonic case, so the infima in (7) and (14) can be replaced by minima.

VI. CONCLUSION

For a fixed number of particles, finite numbers of basis functions, and elevated temperature the universal functional in 1RDM functional theory is differentiable with $\partial F_{N,\pm} / \partial \gamma = -v$ for all 1RDMs γ in $\mathcal{N}_{N,\pm}$. This relation holds for potential with $\text{tr}\{v\} = 0$. However, all potentials differing from v by only a constant lead to the same 1RDM. From this relation it follows directly that the map $v \mapsto \gamma$ is bijective up to a constant in the potential and it gives a characterization of the set of v -representable 1RDMs. Additionally, for every potential the Helmholtz functional and the universal functional attain a minimum. One might think of reaching the $T = 0$ case by taking the limit $T \rightarrow 0$. The Gibbs state will just be an equiensemble of the ground states, but a difficulty is that it changes discontinuously when the potential is varied such that other states become ground states. Additionally, we can no longer guarantee that the 1RDM will be in the (relative) interior of $\overline{\mathcal{N}}_{N,\pm}$ which prevents invertibility of $v \mapsto \gamma_v$ and also differentiability will probably no longer be in the cards.

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APPENDIX: PROPERTIES OF THE 1RDM

We are still left with showing that the set of 1RDMs is $\overline{\mathcal{N}}_{N,\pm}$. To show the properties (6a) and (6b) for the 1RDM we use the following equivalent definition.

The kernel of γ is given by tracing out $N - 1$ particles in the density-matrix operator,

$$\gamma(x, y) = N \int dx_2 \cdots dx_N \rho(x, x_2, \dots, x_N; y, x_2, \dots, x_N). \quad (\text{A1})$$

The 1RDM can be worked out in a one-particle orthonormal basis $\phi_1, \dots, \phi_{N_b}$ for a matrix representation with elements

$$\begin{aligned} \gamma_{ij} &= N \int dx dy dx_2 \cdots dx_N \phi_i^*(x) \phi_j(y) \\ &\quad \times \rho(x, x_2, \dots, x_N; y, x_2, \dots, x_N). \end{aligned} \quad (\text{A2})$$

Note that we have the following inequality,

$$\begin{aligned} \gamma_{ii} &= N \sum_l \lambda_l \int dx_2 \cdots dx_N \\ &\quad \times \left(\int dx \phi_i^*(x) \psi_l(x, x_2, \dots, x_N) \right)^2 \geq 0. \end{aligned} \quad (\text{A3})$$

Next we want to show that for the fermionic 1RDM the diagonal entries are bounded from above by 1. For this, note that the

entries of a statistical ensemble are bounded by the maximum value of the eigenstates of the corresponding density-matrix operator, i.e.,

$$\begin{aligned} \gamma_{ij} &= N \sum_l \lambda_l \int dx dy dx_2 \cdots dx_N \phi_l^*(x) \phi_j(y) \\ &\quad \times \psi_l(x, x_2, \dots, x_N) \psi_l^*(y, x_2, \dots, x_N) \\ &\leq \max_l N \int dx dy dx_2 \cdots dx_N \phi_l^*(x) \phi_j(y) \\ &\quad \times \psi_l(x, x_2, \dots, x_N) \psi_l^*(y, x_2, \dots, x_N) \\ &= \max_l (\gamma_{\psi_l})_{ij}, \end{aligned} \quad (\text{A4})$$

where γ_{ψ_l} means the 1RDM generated from the wave function ψ_l . Thus, we need to show the desired upper bound only for pure states. With a similar argument, it suffices to show the bound for Slater determinants built from one-particle orthonormal states f_1, \dots, f_N ,

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} (-1)^{\text{sgn}(\sigma)} f_{\sigma(1)}(x_1) \cdots f_{\sigma(N)}(x_N). \quad (\text{A5})$$

The kernel of the 1RDM can be worked out as

$$\gamma_{\psi}(x, y) = \sum_{j=1}^N f_j(x) f_j^*(y), \quad (\text{A6})$$

and its diagonal elements are

$$(\gamma_{\psi})_{ii} = \sum_{j=1}^N |\langle f_j | \phi_i \rangle|^2 \leq \langle \phi_i | \phi_i \rangle = 1. \quad (\text{A7})$$

It is easy to see that the 1RDM is Hermitian. Thus, it has a spectral decomposition

$$\gamma = \sum_{l=1}^{N_b} \lambda_l |\varphi_l\rangle \langle \varphi_l|. \quad (\text{A8})$$

Note that since the diagonal elements are non-negative for any basis, it follows that the eigenvalues λ_l are non-negative. Therefore, $\gamma \geq 0$ and for fermions we have additionally $\gamma \leq 1$. The trace of γ can be calculated through its integral

kernel (A1),

$$\begin{aligned} \text{tr}\{\gamma\} &= \int dx \gamma(x, x) \\ &= N \sum_l \lambda_l \int dx dx_2 \cdots dx_N |\psi_l(x, x_2, \dots, x_N)|^2 \\ &= N. \end{aligned} \quad (\text{A9})$$

All these properties together show that the set of 1RDMs is contained in $\mathcal{N}_{N,\pm}$.

Next, we want to prove Theorem II.1.

Proof. For $N = 1$ we can simply take $\hat{\rho} = \gamma$. So let us consider the case $N \geq 2$. We represent γ in the NO basis $\gamma = \sum_{j=1}^{N_b} \lambda_j |\varphi_j\rangle \langle \varphi_j|$. We need to distinguish between bosons and fermions.

Bosonic case. We define the N -particle wave function

$$\psi(x_1, \dots, x_N) := \frac{1}{\sqrt{N}} \sum_{j=1}^{N_b} \lambda_j^{1/2} \prod_{i=1}^N \varphi_j(x_i).$$

It is now easy to see that ψ is symmetric, normalized, and that it generates γ .

Fermionic case. We work with a polytope. The 1RDM γ can be expressed as a vector of length N_b containing its occupation numbers $\mathbf{n} = (\lambda_1, \dots, \lambda_{N_b})$. The extreme points of the polytope are all possible permutations of N occupation numbers set to one and all other set to zero,

$$\bar{\gamma}_I := \bar{\gamma}_{i_1 \dots i_N} := \mathbf{e}_{i_1} + \cdots + \mathbf{e}_{i_N},$$

for $1 \leq i_1 < \dots < i_N \leq N_b$ and where the \mathbf{e}_i 's are unit vectors. The index I is a reenumeration of $i_1 \dots i_N$ and can take $K = \binom{N_b}{N}$ values. The vector \mathbf{n} is an element of the polytope

$$\Gamma := \left\{ \sum_{I=1}^K \mu_I \bar{\gamma}_I \mid \mu_I \geq 0, \sum_{I=1}^K \mu_I = 1 \right\}.$$

The extreme points $\bar{\gamma}_{i_1 \dots i_N}$ can now be identified with $|\varphi_{i_1} \dots \varphi_{i_N}\rangle \langle \varphi_{i_1} \dots \varphi_{i_N}|$. Since the mapping $\hat{\rho} \rightarrow \gamma$ is linear we find that γ is generated from a linear combination of the Slater determinants $|\varphi_{i_1} \dots \varphi_{i_N}\rangle \langle \varphi_{i_1} \dots \varphi_{i_N}|$. ■

- [1] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [2] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [3] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Challenges for density functional theory, *Chem. Rev.* **112**, 289 (2012).
- [4] A. Becke, Perspective: Fifty years of density-functional theory in chemical physics, *J. Chem. Phys.* **140**, 18A301 (2014).
- [5] S. Vuckovic, L. O. Wagner, A. Mirschink, and P. Gori-Giorgi, Hydrogen molecule dissociation curve with functionals based on the strictly correlated regime, *J. Chem. Theory Comput.* **11**, 3153 (2015).
- [6] T. L. Gilbert, Hohenberg-Kohn theorem for nonlocal external potentials, *Phys. Rev. B* **12**, 2111 (1975).

- [7] K. Pernal, Effective Potential for Natural Spin Orbitals, *Phys. Rev. Lett.* **94**, 233002 (2005).
- [8] R. van Leeuwen, Functionals of the one-particle density matrix: Uniqueness theorems and v -representability in equilibrium and time-dependent systems (unpublished).
- [9] T. Baldsiefen, Reduced density matrix functional theory at finite temperature, Ph.D. thesis, Institut für Theoretische Physik, Freie Universität Berlin, 2012.
- [10] K. J. Giesbertz and M. Ruggenthaler, One-body reduced density-matrix functional theory in finite basis sets at elevated temperatures, *Phys. Rep.* **806**, 1 (2019).
- [11] R. Requist and O. Pankratov, Generalized Kohn-Sham system in one-matrix functional theory, *Phys. Rev. B* **77**, 235121 (2008).

- [12] K. J. H. Giesbertz and E. J. Baerends, Aufbau derived from a unified treatment of occupation numbers in Hartree–Fock, Kohn–Sham, and natural orbital theories with the Karush–Kuhn–Tucker conditions for the inequality constraints $n_i \leq 1$ and $n_i \geq 0$, *J. Chem. Phys.* **132**, 194108 (2010).
- [13] T. Baldsiefen and E. Gross, Minimization procedure in reduced density matrix functional theory by means of an effective non-interacting system, *Comput. Theor. Chem.* **1003**, 114 (2013).
- [14] T. Baldsiefen, A. Cangi, and E. K. U. Gross, Reduced-density-matrix-functional theory at finite temperature: Theoretical foundations, *Phys. Rev. A* **92**, 052514 (2015).
- [15] C. S. Yoo, B. Maddox, J. H. P. Klepeis, V. Iota, W. Evans, A. McMahan, M. Y. Hu, P. Chow, M. Somayazulu, D. Häusermann, R. T. Scalettar, and W. E. Pickett, First-Order Isostructural Mott Transition in Highly Compressed MnO, *Phys. Rev. Lett.* **94**, 115502 (2005).
- [16] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Superconductivity at 39 K in magnesium diboride, *Nature (London)* **410**, 63 (2001).
- [17] M. W. C. Dharma-wardana and F. Perrot, Density-functional theory of hydrogen plasmas, *Phys. Rev. A* **26**, 2096 (1982).
- [18] N. V. Ewald, T. Feldker, H. Hirzler, H. A. Fürst, and R. Gerritsma, Observation of Interactions between Trapped Ions and Ultracold Rydberg Atoms, *Phys. Rev. Lett.* **122**, 253401 (2019).
- [19] D. J. Bedingham, Bose-Einstein condensation in the canonical ensemble, *Phys. Rev. D* **68**, 105007 (2003).
- [20] W. J. Mullin and J. P. Fernández, Bose–Einstein condensation, fluctuations, and recurrence relations in statistical mechanics, *Am. J. Phys.* **71**, 661 (2003).
- [21] H. Barghathi, J. Yu, and A. Del Maestro, Theory of noninteracting fermions and bosons in the canonical ensemble, *Phys. Rev. Res.* **2**, 043206 (2020).
- [22] D. P. Kooi, Efficient bosonic and fermionic Sinkhorn algorithms for non-interacting ensembles in one-body reduced density matrix functional theory in the canonical ensemble, [arXiv:2205.15058](https://arxiv.org/abs/2205.15058).
- [23] Creation and annihilation operators are only defined pairwise for an N -particle space.
- [24] A. J. Coleman, Structure of fermion density matrices, *Rev. Mod. Phys.* **35**, 668 (1963).
- [25] H. Eschrig, $T > 0$ ensemble-state density functional theory via Legendre transform, *Phys. Rev. B* **82**, 205120 (2010).
- [26] N. D. Mermin, Thermal properties of the inhomogeneous electron gas, *Phys. Rev.* **137**, A1441 (1965).
- [27] D. Ruelle, *Statistical Mechanics*, Mathematical Physics Monograph Series (W. A. Benjamin, New York, 1969).
- [28] E. H. Lieb, Some convexity and subadditivity properties of entropy, *Bull. Am. Math. Soc.* **81**, 1 (1975).
- [29] A. Wehrl, General properties of entropy, *Rev. Mod. Phys.* **50**, 221 (1978).
- [30] This means M is contained in an affine space.
- [31] We could have taken a different point in $\mathcal{N}_{N,\pm}$, but the current choice is the most natural in this setting.