

**Reduced-density-matrix-functional theory at finite temperature: Theoretical foundations**Tim Baldsiefen,<sup>1,2</sup> Attila Cangi,<sup>1</sup> and E. K. U. Gross<sup>1</sup><sup>1</sup>*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06112 Halle, Germany*<sup>2</sup>*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

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We present an *ab initio* approach for grand-canonical ensembles in thermal equilibrium (eq) with local or nonlocal external potentials based on the one-reduced density matrix (1RDM). We show that equilibrium properties of a grand-canonical ensemble are determined uniquely by the eq-1RDM and establish a variational principle for the grand potential with respect to its 1RDM. We further prove the existence of a Kohn-Sham system capable of reproducing the 1RDM of an interacting system at finite temperature. Utilizing this Kohn-Sham system as an unperturbed system, we deduce a many-body approach to iteratively construct approximations to the correlation contribution of the grand potential.

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**I. INTRODUCTION**

Based on the celebrated theorems of Hohenberg and Kohn [1], Kohn-Sham density-functional theory (KS-DFT) [2] is currently the method of choice for calculating ground-state (gs) properties of quantum systems.

There are, however, cases in which KS-DFT performs rather poorly. A prominent example is its failure in predicting the fundamental gap, in particular, of so-called Mott insulators [3,4]. KS-DFT with standard exchange-correlation approximations fails for this kind of strongly correlated system and typically yields a metallic ground state, while the true experimental low-temperature phase is that of an antiferromagnetic insulator. At finite temperature the description of strongly correlated systems is even more challenging. Genuine Mott insulators exhibit a characteristic feature: when heated up from their antiferromagnetic insulating gs, they stay insulating above the Néel temperature, i.e., in the absence of long-range magnetic order. Contrarily, weakly correlated insulators, so-called Slater insulators, become metallic at the Néel temperature.

A possible approach to tackle this challenge is to search for more accurate functionals in the framework of KS-DFT. Alternatively, one may look for other theoretical frameworks in which the treatment of strong correlation might be simpler. One candidate for such a framework is reduced-density-matrix-functional theory (RDMFT). Through its more direct treatment of many-particle correlations it has promising potential for calculations of finite [5–10] as well as infinite systems [11–13]. In particular, it was possible to predict insulating ground states for transition-metal oxides without breaking the spin symmetry [13].

Motivated by the success of RDMFT at zero temperature, the purpose of the present work is to lay the theoretical foundations for the finite-temperature version of RDMFT (FT-RDMFT). As a general *ab initio* theory its applicability is not restricted to Mott insulators. There is a variety of physical phenomena, in particular in the warm dense-matter regime [14], which requires an accurate description of quantum effects at finite temperature [15]. These phenomena include temperature-driven magnetic [16,17] or superconducting [18,19] phase transitions in solids, femtochemistry at surfaces of solids [20], properties of shock-compressed noble gases [21,22], the properties of plasmas [23–25], thermal

conductivities of inertial confinement fusion capsules [26], and planetary interiors and their formation processes [27–31].

This paper is divided as follows: In Sec. II we derive and present the formalism of FT-RDMFT. First, in Sec. II A we introduce our notation. Note that we work in atomic units throughout, where  $e^2 = \hbar = m_e = 1$ , so that lengths are expressed in Bohr radii and energies are in hartrees. Then, in Sec. II B we lay the foundations of FT-RDMFT by showing that the grand potential of systems with generally nonlocal external potentials can be written as a functional of the one-reduced density matrix (1RDM). Next, in Sec. II C we show the existence of a KS system in FT-RDMFT and demonstrate how the KS Hamiltonian is explicitly constructed. Subsequently, in Sec. II D we derive the adiabatic connection formula which forms the basis for the construction of approximations to the correlation functional in FT-RDMFT. Finally, in Sec. II E the existence of a KS system and the adiabatic connection formula enable us to derive a methodology for iteratively constructing correlation functionals based on finite-temperature many-body perturbation theory (FT-MBPT). Furthermore, in Appendix A we give a detailed analysis of occupation numbers in interacting systems, in Appendix B we investigate the one-to-one mapping between the external potential and the wave function at zero temperature, in Appendix C we show that our iterative procedure for constructing functionals from FT-MBPT yields the finite-temperature Hartree-Fock functional as the first-order contribution, and in Appendix D we present the formulation of FT-RDMFT for a canonical ensemble.

**II. FINITE-TEMPERATURE REDUCED-DENSITY-MATRIX-FUNCTIONAL THEORY****A. Background**

The main thermodynamic variable in a grand-canonical ensemble is the grand potential

$$\Omega[\hat{D}] = \text{tr}\{\hat{D}\hat{\Omega}\} \quad (1)$$

given as a statistical average over the grand-canonical operator

$$\hat{\Omega} = \hat{H} - \mu\hat{N} - \hat{S}/\beta, \quad (2)$$

where  $\hat{H}$ ,  $\hat{N}$ , and  $\hat{S}$  are the Hamiltonian, particle number, and entropy operators. In electronic structure theory the Hamiltonian is typically given by  $\hat{H} = \hat{T} + \hat{W} + \hat{V}$ , where  $\hat{T}$  denotes the kinetic-energy operator,  $\hat{W}$  is the interelectronic repulsion in a Coulombic system, and  $\hat{V}$  represents a scalar external potential. The coupling to particle and heat baths is achieved via the Lagrangian multipliers  $\mu$ , denoting the chemical potential, and  $1/\beta$ , denoting the temperature.

Statistical averages as in Eq. (1) are computed via the statistical density operator (SDO)  $\hat{D}$ , which is defined as a weighted sum of projection operators on the underlying Hilbert space. The appropriate Hilbert space for grand-canonical ensembles, where a change of particle number is allowed, is a direct sum of symmetrized tensor products of the one-particle Hilbert space, called the Fock space. Assuming that the system does not allow for mixing of states with different particle numbers, the set of all possible SDOs can be expressed just by projection operators on states with defined particle number  $N$ :

$$\hat{D} = \sum_{\alpha} w_{\alpha} |\Psi_{\alpha}\rangle \langle \Psi_{\alpha}|, \quad (3)$$

$$w_{\alpha} \geq 0, \quad \sum_{\alpha} w_{\alpha} = 1,$$

where  $|\Psi_{\alpha}\rangle$  and  $w_{\alpha}$  are orthonormal  $N$ -particle states and their corresponding weights.

The thermal equilibrium (eq) of a grand-canonical ensemble is then defined as that SDO for which the grand potential  $\Omega[\hat{D}]$  is minimal. This definition leads to the finite-temperature Rayleigh-Ritz variational principle [32], which states that

$$\Omega[\hat{D}] > \Omega[\hat{D}_{\text{eq}}], \quad \hat{D} \neq \hat{D}_{\text{eq}}, \quad (4)$$

with

$$\hat{D}_{\text{eq}} = e^{-\beta(\hat{H} - \mu\hat{N})} / \text{tr}\{e^{-\beta(\hat{H} - \mu\hat{N})}\}. \quad (5)$$

The 1RDM is defined by the SDO and the help of the common fermionic field operators  $\hat{\psi}$  as

$$\begin{aligned} \gamma(x, x') &= \text{tr}\{\hat{D}\hat{\psi}^+(x')\hat{\psi}(x)\} \\ &= \sum_{\alpha} w_{\alpha} \langle \Psi_{\alpha} | \hat{\psi}^+(x')\hat{\psi}(x) | \Psi_{\alpha} \rangle, \end{aligned} \quad (6)$$

where the variable  $x$  denotes a combination of spin index  $\sigma$  and spatial coordinate  $\mathbf{r}$ , where  $x = (\mathbf{r}, \sigma)$ . An integration over  $x$  is therefore to be interpreted as an integration over  $\mathbf{r}$  and a summation over  $\sigma$ . Since the 1RDM is Hermitian by construction, it is commonly written in spectral representation as

$$\gamma(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x), \quad (7)$$

with real-valued eigenvalues  $\{n_i\}$  and eigenfunctions  $\{\phi_i(x)\}$ , which are called occupation numbers and natural orbitals [33]. The necessary and sufficient conditions for  $N$ -representability [34] of  $\gamma(x, x')$  are that  $\{\phi_i\}$  is a complete set and

$$0 \leq n_i \leq 1, \quad \sum_i n_i = N. \quad (8)$$

In Appendix A the relationship between the 1RDM expressed as in Eq. (6) and in terms of its spectral representation in Eq. (7) is further discussed.

It is sometimes desirable to treat spin and spatial variables separately. To this end we introduce a two-component (Pauli) spinor notation:

$$\Phi_i(\mathbf{r}) = \begin{pmatrix} \phi_{i1}(\mathbf{r}) \\ \phi_{i2}(\mathbf{r}) \end{pmatrix}, \quad (9)$$

where  $\phi_{i\sigma}(\mathbf{r}) = \phi_i(x) = \phi_i(\sigma, \mathbf{r})$  ( $\sigma = 1, 2$ ) are the orbitals of Eq. (7). The 1RDM can then be written as a matrix in spin space as

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \sum_i n_i \Phi_i^{\dagger}(\mathbf{r}') \otimes \Phi_i(\mathbf{r}) \\ &= \sum_i n_i \begin{pmatrix} \phi_{i1}^*(\mathbf{r}')\phi_{i1}(\mathbf{r}) & \phi_{i2}^*(\mathbf{r}')\phi_{i1}(\mathbf{r}) \\ \phi_{i1}^*(\mathbf{r}')\phi_{i2}(\mathbf{r}) & \phi_{i2}^*(\mathbf{r}')\phi_{i2}(\mathbf{r}) \end{pmatrix}. \end{aligned} \quad (10)$$

In the special case of collinear spin configuration different spin channels can be treated separately. For these systems, the natural orbitals are so-called spin orbitals, i.e., spinors containing only one spin component, where

$$\Phi_{i1}(\mathbf{r}) = \begin{pmatrix} \phi_{i1}(\mathbf{r}) \\ 0 \end{pmatrix}, \quad \Phi_{i2}(\mathbf{r}) = \begin{pmatrix} 0 \\ \phi_{i2}(\mathbf{r}) \end{pmatrix}. \quad (12)$$

This leads to a 1RDM which has only one nonvanishing entry in every  $2 \times 2$  matrix of Eq. (11), either the 11 or the 22 element. Hence the complete 1RDM is diagonal with respect to the spin coordinate

$$\gamma_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \delta_{\sigma\sigma'} \sum_i n_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}), \quad (13)$$

where  $n_{i\sigma}$  are the occupation numbers of the special spinors  $\Phi_{i\sigma}(\mathbf{r})$  in Eq. (12). Spin-spiral states are another special case where this separation also applies [35].

## B. Hohenberg-Kohn theorems for finite-temperature reduced-density-matrix-functional theory

We lay the foundations of FT-RDMFT by formulating its Hohenberg-Kohn (HK) theorems. We divide this up into three steps, namely, showing (i) that the map between the eq-SDO and the eq-1RDM is invertible, i.e.,

$$\hat{D}_{\text{eq}} \xleftrightarrow{1-1} \mu(x, x') \xleftrightarrow{1-1} \gamma_{\text{eq}}(x, x'), \quad (14)$$

implying the existence of a grand potential functional  $\Omega[\gamma]$ , (ii) the existence of a universal functional  $F[\gamma]$ , and (iii) that the minimization of  $\Omega[\gamma]$  leads to the eq-1RDM. Note that we consider only eq-1RDMs for the proof in step (i). However, we can relax this restriction in step (ii).

(i) *Proof of  $\hat{D}_{\text{eq}} \xleftrightarrow{1-1} \gamma_{\text{eq}}(x, x')$  (one-to-one mapping between eq-SDO and eq-1RDM).* Note that Mermin's extension of the HK theorems to finite temperature [36] immediately implies the one-to-one mappings

$$\gamma(\mathbf{r}, \mathbf{r}') \longrightarrow \rho(\mathbf{r}) \xleftrightarrow{HK} v(\mathbf{r}), \quad (15a)$$

$$v(\mathbf{r}) \longrightarrow \Psi(\hat{D}) \longrightarrow \gamma(\mathbf{r}, \mathbf{r}'), \quad (15b)$$

i.e., between the 1RDM, the density, the eq-SDO, and the *local* external potential [37]. However, in FT-RDMFT we need to go further than this and consider *nonlocal* external potentials, in which case the ground state is not uniquely determined by the

density anymore but by the 1RDM [38]. Going beyond local external potentials is necessary because the KS potentials in FT-RDMFT are *nonlocal* in general, as we show in Sec. II C.

We divide proving the existence of a one-to-one mapping in Eq. (14) into two parts. We prove first (i.i) the one-to-one mapping between  $\hat{D}_{\text{eq}}$  and the nonlocal chemical potential  $\mu(x, x') = v(x, x') - \mu$  and then (i.ii) the one-to-one mapping between  $\mu(x, x')$  and  $\gamma_{\text{eq}}(x, x')$ .

(i.i) *Proof of  $\hat{D}_{\text{eq}} \xleftrightarrow{1-1} \mu(x, x')$  (one-to-one mapping between eq-SDO and nonlocal chemical potential).* We show this with a *proof by contradiction*. Let  $\hat{H}$  and  $\hat{H}'$  be two different Hamiltonians with corresponding eq-SDOs  $\hat{D}_{\text{eq}}$  and  $\hat{D}'_{\text{eq}}$ .  $\hat{H}'$  shall differ from  $\hat{H}$  only by a one-particle potential contribution  $\Delta\hat{V}$ . Now assume that both Hamiltonians lead to the same SDO, i.e.,  $\hat{D}_{\text{eq}} = \hat{D}'_{\text{eq}}$ . With Eq. (5) this reads

$$e^{-\beta(\hat{H}-\mu\hat{N})}/Z = e^{-\beta(\hat{H}+\Delta\hat{V}-\mu\hat{N})}/Z', \quad (16)$$

where  $Z$  and  $Z'$  are the partition functions, e.g.,  $Z = \text{tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}$ . Solving Eq. (16) for  $\Delta\hat{V}$  yields

$$\Delta\hat{V} = \int dx dx' \Delta v(x', x) \hat{\psi}^\dagger(x') \hat{\psi}(x) = \frac{1}{\beta} \ln \frac{Z}{Z'}. \quad (17)$$

We now need to show that a one-particle potential  $\Delta v(x, x') \neq 0$  fulfilling this equality cannot exist, thereby contradicting our initial assumption. To proceed we calculate the expectation value  $\Delta V$  of Eq. (17) using both  $\hat{D}_{\text{eq}}$  and  $\hat{D}'_{\text{eq}}$ :

$$\begin{aligned} \Delta V &= \frac{1}{\beta} \ln \frac{Z}{Z'} = \text{tr}\{\hat{D}_{\text{eq}} \Delta\hat{V}\} \\ &= \text{tr}\{\hat{D}'_{\text{eq}} \Delta\hat{V}\}. \end{aligned} \quad (18)$$

We evaluate the trace by expanding the  $N$ -particle states  $\Psi_\alpha$  in terms of Slater determinants  $\chi_j$ , which form a basis of the Hilbert space and are constructed from the natural orbitals  $\phi_i$  introduced in Eq. (7):

$$|\Psi_\alpha\rangle = \sum_j c_{j\alpha} |\chi_j\rangle, \quad c_{j\alpha} = \langle \chi_j | \Psi_\alpha \rangle. \quad (19)$$

We also express the fermionic field operators in the basis of the natural orbitals:

$$\hat{\Psi}(x) = \sum_i \hat{c}_i \phi_i(x), \quad \hat{\Psi}^\dagger(x) = \sum_i \hat{c}_i^\dagger \phi_i(x), \quad (20)$$

where  $\hat{c}_i^\dagger$  and  $\hat{c}_i$  are the common creation and annihilation operators defining the particle number operator  $\hat{N} = \sum_i \hat{n}_i$ , with  $\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$ . Using these expansions in Eq. (18) for  $\hat{D}_{\text{eq}}$  yields

$$\frac{1}{\beta} \ln \frac{Z}{Z'} = \sum_{\alpha ij} \frac{\Delta v_{jj}}{Z} |c_{j\alpha}|^2 \langle \chi_j | e^{-\beta(\hat{H}-\mu\hat{N})} \hat{n}_j | \chi_j \rangle, \quad (21)$$

whereas for  $\hat{D}'_{\text{eq}}$  it yields

$$\frac{1}{\beta} \ln \frac{Z}{Z'} = \sum_{\alpha ij} \frac{\Delta v_{jj}}{Z'} |c_{j\alpha}|^2 \langle \chi_j | e^{-\beta(\hat{H}-\mu\hat{N}+\Delta\hat{V})} \hat{n}_j | \chi_j \rangle, \quad (22)$$

where  $\Delta v_{jj} = \int dx dx' \Delta v(x', x) \phi_j^*(x') \phi_j(x)$ . Equations (21) and (22) imply that Eq. (18) can be simultaneously fulfilled by

$\hat{D}_{\text{eq}}$  and  $\hat{D}'_{\text{eq}}$  only if  $\Delta\hat{V} = 0$ . This in turn proves the one-to-one correspondence between  $\hat{D}_{\text{eq}}$  and  $v(x, x')$  and hence the one-to-one correspondence between  $\hat{D}_{\text{eq}}$  and  $\mu(x, x')$ .

This proof is valid for any finite temperature. It is based on the bijectivity of the exponential function, which allows us to invert Eq. (16), leading to Eq. (18). At zero temperature, however, this bijectivity breaks down. Further elaborations on zero-temperature mappings between external potentials and wave functions are given in Appendix B.

(i.ii) *Proof of  $\mu(x, x') \xleftrightarrow{1-1} \gamma_{\text{eq}}(x, x')$  (one-to-one mapping between nonlocal chemical potential and eq-1RDM).* In order to prove the one-to-one correspondence between  $\mu(x, x')$  and  $\gamma_{\text{eq}}(x, x')$  we use a *proof by contradiction* again. Consider two Hamiltonians  $\hat{H}$  and  $\hat{H}'$  differing only in their external and chemical potentials. The corresponding grand potentials are given by

$$\Omega[\hat{D}_{\text{eq}}] = \text{tr}\{\hat{D}_{\text{eq}}(\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D}_{\text{eq}})\}, \quad (23)$$

$$\Omega'[\hat{D}'_{\text{eq}}] = \text{tr}\{\hat{D}'_{\text{eq}}(\hat{H}' - \mu'\hat{N} + 1/\beta \ln \hat{D}'_{\text{eq}})\}, \quad (24)$$

where  $\hat{D}_{\text{eq}}$  and  $\hat{D}'_{\text{eq}}$  are defined by Eq. (5). Using  $\hat{D}_{\text{eq}} \neq \hat{D}'_{\text{eq}}$  as we have proven in (i.i), the variational principle in Eq. (4) then leads to

$$\Omega[\hat{D}_{\text{eq}}] < \Omega[\hat{D}'_{\text{eq}}] \quad (25)$$

$$= \text{tr}\{\hat{D}'_{\text{eq}}(\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D}'_{\text{eq}})\} \quad (26)$$

$$= \Omega'[\hat{D}'_{\text{eq}}] + \text{tr}\{\hat{D}'_{\text{eq}}[(\hat{H} - \mu\hat{N}) - (\hat{H}' - \mu'\hat{N})]\}. \quad (27)$$

By exchanging primed and unprimed quantities we obtain

$$\Omega[\hat{D}_{\text{eq}}] < \Omega'[\hat{D}'_{\text{eq}}] + \int dx dx' [\mu(x', x) - \mu'(x', x)] \gamma'(x, x'), \quad (28)$$

$$\Omega'[\hat{D}'_{\text{eq}}] < \Omega[\hat{D}_{\text{eq}}] + \int dx dx' [\mu'(x', x) - \mu(x', x)] \gamma(x, x'). \quad (29)$$

Adding these two equations leads to

$$\int dx dx' [\mu'(x', x) - \mu(x', x)] [\gamma(x, x') - \gamma'(x, x')] > 0. \quad (30)$$

The existence of two different sets of external and chemical potentials yielding the same eq-1RDM lets the integral in Eq. (30) vanish, which leads to a contradiction. Hence the initial assumption is falsified. This concludes our proof of Eq. (14).

Having established the existence of a one-to-one mapping between  $\hat{D}_{\text{eq}}$  and  $\gamma_{\text{eq}}$ , we can now proceed and properly define the grand potential as a functional of the 1RDM as

$$\Omega[\gamma_{\text{eq}}] = \text{tr}\{\hat{D}[\gamma_{\text{eq}}][\hat{H} - \mu\hat{N} + 1/\beta \ln(\hat{D}[\gamma_{\text{eq}}])]\}. \quad (31)$$

(ii) *Existence of a universal functional  $F[\gamma_{\text{eq}}]$ .* In analogy to DFT, we define a universal functional by separating the external and chemical potential contributions from

Eq. (31):

$$F[\gamma_{\text{eq}}] = \text{tr}\{\hat{D}[\gamma_{\text{eq}}](\hat{T} + \hat{W} + 1/\beta \ln \hat{D}[\gamma_{\text{eq}}])\}, \quad (32)$$

such that

$$\Omega[\gamma_{\text{eq}}] = \int dx dx' \mu(x, x') \gamma_{\text{eq}}(x, x') + \mathcal{F}[\gamma_{\text{eq}}]. \quad (33)$$

Notice a subtlety involved with defining the universal functional in Eq. (32). In our proof we considered a restricted set of 1RDMs, namely, those coming from eq-SDOs given by Eq. (5). However, the conditions to ensure that an arbitrary 1RDM comes from such a SDO are unknown. Nevertheless, following ideas of Valone [39] and Lieb [40], we can resolve this subtle point and extend the domain of  $\Omega[\gamma]$  to the whole set of ensemble- $N$ -representable 1RDMs. Accordingly, we can now define the universal functional as

$$\mathfrak{F}[\gamma] = \inf_{\hat{D} \rightarrow \gamma} \text{tr}\{\hat{D}(\hat{T} + \hat{W} + 1/\beta \ln \hat{D})\}, \quad (34)$$

such that

$$\Omega[\gamma] = \int dx dx' \mu(x, x') \gamma(x, x') + \mathfrak{F}[\gamma]. \quad (35)$$

(iii) *Minimization of  $\Omega[\gamma]$ .* The variational principle in Eq. (4) now allows us to determine the equilibrium grand potential by

$$\Omega_{\text{eq}} = \min_{\gamma \in \Gamma^N} \Omega[\gamma], \quad (36)$$

a minimization over  $\Gamma^N$  which is the set of all ensemble- $N$ -representable 1RDMs. Additionally, we postulate

$$\left. \frac{\delta \mathfrak{F}[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{\text{eq}}} + v(x, x') = \mu, \quad (37)$$

the Euler-Lagrange equation for the eq-1RDM in FT-RDMFT [41].

### C. Kohn-Sham system for finite-temperature reduced-density-matrix-functional theory

We have established the theoretical framework of FT-RDMFT by proving Hohenberg-Kohn-like theorems. The central problem for turning this theory into a practical scheme is finding approximations as a functional of the 1RDM. In analogy to DFT, one possible route for constructing such approximations requires us to introduce the KS scheme. Then we can exploit the existence of a KS system to derive a methodology for the iterative construction of functionals using methods from FT-MBPT.

Our starting point is an auxiliary system of noninteracting fermions described by the Hamiltonian

$$\hat{H}_S^{(1)} = \hat{T} + \hat{V}_S, \quad \hat{H}_S^{(1)} = \sum_i \varepsilon_i |\phi_i\rangle \langle \phi_i|, \quad (38)$$

with eigenvalues  $\{\varepsilon_i\}$  and eigenfunctions  $\{\phi_i(x)\}$  and  $\hat{V}_S$  denoting the operator of the KS potential. Then we assume the existence of a nonlocal potential, the KS potential  $v_S(x, x')$ , which yields a ground-state or eq-1RDM that equals the true

ground state or eq-1RDM,

$$\gamma_{\text{eq}}(x, x') = \gamma_{S, \text{eq}}(x, x'). \quad (39)$$

Note that a KS system does not exist in RDMFT for Coulombic matter at zero temperature. The reason behind this is the presence of the electron-electron cusp emerging from the interelectronic repulsion [42]. Capturing this cusp requires a superposition of infinitely many Slater determinants [43]. Hence, the gs 1RDM for Coulombic systems has an infinite number of occupied orbitals, i.e., natural orbitals with occupation numbers  $n_i > 0$ .

In the following we show that in FT-RDMFT, however, such a KS system *does indeed exist*. From the spectral decomposition of the eq-1RDM in Eq. (39) it follows that

$$\gamma_{S, \text{eq}}(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x), \quad (40)$$

with  $\{n_i\}$  and  $\{\phi_i(x)\}$  being the same occupation numbers and natural orbitals as those of the interacting 1RDM given in Eq. (7). The eigenvalues  $\{\varepsilon_i\}$  and the chemical potential  $\mu$  completely determine the occupation numbers  $\{n_i\}$  by the relation

$$n_i = \frac{1}{1 + e^{\beta(\varepsilon_i - \mu)}}, \quad (41)$$

which can be inverted to yield

$$\varepsilon_i - \mu = \frac{1}{\beta} \ln \left( \frac{1 - n_i}{n_i} \right). \quad (42)$$

In contrast to the zero-temperature case, it is now possible to construct the KS Hamiltonian in the following way: The KS Hamiltonian is obtained via its spectral representation in Eq. (38), where its eigenvalues are determined from Eq. (42), while its eigenfunctions are given by the natural orbitals of the given 1RDM in Eq. (40). The occupation numbers of a KS system in thermal equilibrium at finite temperature cannot be 0 or 1, as can be seen from Eq. (41). This is also true for the interacting 1RDM of a grand-canonical ensemble, as we show in Appendix A. Hence, it is ensured that the domain of the KS system includes the interacting system.

Furthermore, due to the variational principle the KS potential is generally nonlocal [38]. Its uniqueness follows from the Hohenberg-Kohn-like theorems shown in Sec. II B. It can be expressed explicitly as

$$v_S(x, x') = \sum_{i, j} (\delta_{ij} \varepsilon_i - t_{ij}) \phi_i^*(x') \phi_j(x), \quad (43)$$

where  $t_{ij} = \langle \phi_i | \hat{T} | \phi_j \rangle$  is the kinetic operator in the basis of natural orbitals. The requirement of locality can be imposed on the KS potential. This is computationally advantageous but leaves the domain of an exact theory because this requirement results in approximate natural orbitals that cannot be equal to the true natural orbitals [44].

Having established the KS scheme, we can express the grand potential of the interacting system as

$$\Omega[\gamma] = F[\gamma] + V[\gamma] - \mu N[\gamma], \quad (44)$$



where we express the universal functional in terms of common KS quantities as

$$F[\gamma] = \Omega_k[\gamma] - \frac{S_0[\gamma]}{\beta} + \Omega_H[\gamma] + \Omega_X[\gamma] + \Omega_C[\gamma]. \quad (45)$$

Here,

$$\Omega_k[\gamma] = \int dx' \lim_{x \rightarrow x'} \left( -\frac{\nabla^2}{2} \right) \gamma(x, x'), \quad (46)$$

$$V[\gamma] = \int dx dx' v(x, x') \gamma(x', x), \quad (47)$$

$$N[\gamma] = \int dx \gamma(x, x), \quad (48)$$

$$S_S[\gamma] = - \sum_i [n_i \ln n_i + (1 - n_i) \ln(1 - n_i)], \quad (49)$$

$$\Omega_H[\gamma] = \frac{1}{2} \int dx dx' w(x, x') \gamma(x, x) \gamma(x', x'), \quad (50)$$

$$\Omega_X[\gamma] = -\frac{1}{2} \int dx dx' w(x, x') \gamma(x, x') \gamma(x', x) \quad (51)$$

denote the functionals of kinetic energy, external potential, particle number, KS entropy, Hartree energy, and exchange energy, which are known explicitly [45]. The remaining term,  $\Omega_C[\gamma]$ , is the correlation contribution, but its exact form is not known explicitly.

#### D. Adiabatic connection formula in finite-temperature reduced-density-matrix-functional theory

We derive the adiabatic connection formula in FT-RDMFT, which allows us to connect the interacting system to the KS system with the same eq-1RDM and forms the basis for systematically constructing approximations to the correlation functional  $\Omega_C[\gamma]$  via FT-MBPT.

Closely following the standard zero-temperature DFT approach [46,47], we begin by introducing a coupling constant  $\lambda$  into the electronic Hamiltonian

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{W} + \hat{V}^\lambda, \quad (52)$$

where  $0 \leq \lambda \leq 1$ . The potential  $\hat{V}^\lambda$  is chosen such that for any  $\lambda$  there is an associated eq-SDO  $\hat{D}^\lambda[\gamma]$  that leaves the eq-1RDM invariant under a change of  $\lambda$ . Along with that we define an auxiliary Hamiltonian

$$\hat{H}_a^\lambda = \hat{T} + \lambda \hat{W} + \hat{V}, \quad (53)$$

such that it agrees with Eq. (52) at full coupling strength when  $\lambda = 1$ , i.e.,  $\hat{H}_a^1 = \hat{H}^1$ . Additionally, we also introduce an auxiliary potential  $\hat{V}_a^\lambda = \hat{V}^\lambda - \hat{V}$  such that  $\hat{H}_a^\lambda + \hat{V}_a^\lambda = \hat{H}^\lambda$ . The grand potential for the auxiliary Hamiltonian becomes

$$\Omega_a^\lambda[\gamma] = \min_{\hat{D} \rightarrow \gamma} \text{Tr} \{ \hat{D} (\hat{H}_a^\lambda - \mu \hat{N} + \ln \hat{D} / \beta) \}. \quad (54)$$

With the aid of the auxiliary potential we obtain

$$\begin{aligned} \Omega_a^\lambda[\gamma] &= \min_{\hat{D} \rightarrow \gamma} (\text{Tr} \{ \hat{D} (\hat{H}_a^\lambda + \hat{V}_a^\lambda - \mu \hat{N} + \ln \hat{D} / \beta) \} \\ &\quad - \text{Tr} \{ \hat{D} \hat{V}_a^\lambda \}). \end{aligned} \quad (55)$$

Since  $\hat{V}_a^\lambda$  is a one-particle operator, we can take the last term out of the minimization and replace  $\hat{D}$  in this term by any

$\hat{D} \rightarrow \gamma$ . Then, the minimization in Eq. (55) yields the eq-SDO  $\hat{D}^\lambda = \exp \hat{H}^\lambda - \mu \hat{N} / \text{Tr} \{ \exp \hat{H}^\lambda \}$  that is associated with  $\hat{H}^\lambda$ , yielding the eq-1RDM of the true interacting system that is invariant under a change of  $\lambda$ . Hence the grand potential becomes

$$\Omega_a^\lambda[\gamma] = \text{Tr} \{ \hat{D}^\lambda (\hat{H}_a^\lambda + \hat{V}_a^\lambda - \mu \hat{N} + \ln \hat{D}^\lambda / \beta) \} - \text{Tr} \{ \hat{D}^\lambda \hat{V}_a^\lambda \}. \quad (56)$$

By definition  $\Omega_a^1[\gamma] = \Omega[\gamma]$ , i.e., the auxiliary grand potential at full coupling strength is identical to the true interacting grand potential; therefore

$$\Omega[\gamma] = \Omega_a^0 + \int_0^1 d\lambda \frac{d\Omega_a^\lambda[\gamma]}{d\lambda}. \quad (57)$$

Taking the derivative with respect to the coupling constant is simplified by the fact that we consider a system in thermal equilibrium. Hence, only  $\lambda \hat{W}$  and  $\hat{V}_a^\lambda$  contribute to the coupling-constant derivative in Eq. (57), yielding

$$\Omega[\gamma] = \Omega_a^0 + \int_0^1 d\lambda \text{Tr} \{ \hat{D}^\lambda \hat{W} \}. \quad (58)$$

Consider the grand potentials

$$\Omega[\gamma] = \text{Tr} \{ \hat{D} (\hat{T} + \hat{V} + \hat{W} - \mu \hat{N} + \ln \hat{D} / \beta) \}, \quad (59)$$

$$\Omega_a^0[\gamma] = \text{Tr} \{ \hat{D}^0 (\hat{T} + \hat{V} - \mu \hat{N} + \ln \hat{D}^0 / \beta) \} \quad (60)$$

and take into account that  $\hat{D}$  and  $\hat{D}^0$  yield the same eq-1RDM, hence the same expectation values of one-particle operators, such as  $\text{Tr} \{ \hat{D} \hat{T} \} = \text{Tr} \{ \hat{D}^0 \hat{T} \}$ ,  $\text{Tr} \{ \hat{D} \hat{V} \} = \text{Tr} \{ \hat{D}^0 \hat{V} \}$ , and  $\text{Tr} \{ \hat{D} \hat{N} \} = \text{Tr} \{ \hat{D}^0 \hat{N} \}$ .

Then, we can further reduce Eq. (58) and obtain the adiabatic connection formula for the entire interaction as

$$\Omega_W[\gamma] = \int_0^1 d\lambda W^\lambda[\gamma], \quad (61)$$

where we define  $\Omega_W = W - S_C / \beta$ ,  $W^\lambda = \text{Tr} \{ \hat{D}^\lambda \hat{W} \}$ ,  $W = \text{Tr} \{ \hat{D} \hat{W} \}$ , and  $S_C = \text{Tr} \{ \hat{D}^0 \ln \hat{D}^0 \} - \text{Tr} \{ \hat{D} - \ln \hat{D} \}$  as the entropic correlation contribution.

Finally, by subtracting the Hartree and exchange contributions defined as  $W_{\text{HX}} = \text{Tr} \{ \hat{D}^0 \hat{W} \}$  we obtain the adiabatic connection formula for the correlation contribution

$$\Omega_C[\gamma] = \int_0^1 \frac{d\lambda}{\lambda} W_C^\lambda[\gamma], \quad (62)$$

where we define  $\Omega_C = W_C - S_C / \beta$ ,  $W_C = W - W_{\text{HX}}$ , and  $W_C^\lambda = \text{Tr} \{ \lambda (\hat{D}^\lambda - \hat{D}^0) \hat{W} \}$ .

In analogy to DFT, Eq. (62) allows us to express the correlation contribution to the KS system in FT-RDMFT as a contribution coming solely from the interaction potential. It is interesting to note another similarity between DFT and FT-RDMFT. In DFT, the adiabatic connection formula includes the kinetic correlation contribution, i.e., the difference between the kinetic energy of the interacting system and the KS system via the coupling constant integration. In FT-RDMFT, where there is no kinetic correlation contribution, the coupling-constant integral instead incorporates the entropic correlation contribution  $S_C$ .

The adiabatic connection formulas derived in Eqs. (61) and (62) are central results because they are our key for developing systematic approximations to  $\Omega_W[\gamma]$  and its correlation contribution  $\Omega_C[\gamma]$  based on FT-MBPT.

### E. Constructing correlation functionals

With the aid of the adiabatic connection we can use methods from FT-MBPT [48] to systematically construct approximations to the functionals  $\Omega_W[\gamma]$  and  $\Omega_C[\gamma]$ , where the KS system, defined by the Hamiltonian  $\hat{H}^0$ , serves as our reference system in a perturbative expansion. Our starting point from the perspective of FT-MBPT is to relate the temperature Green's function  $\mathcal{G}^\lambda(x, \tau, x', \tau')$  to the adiabatic connection in Eq. (61). This relation is expressed as

$$\begin{aligned} \lambda W^\lambda = & \frac{1}{2} \int dx dx' \lim_{\tau' \rightarrow \tau^+} \left\{ -\delta(x - x') \frac{\partial}{\partial \tau} \right. \\ & \left. - \left[ -\delta(x - x') \frac{\nabla^2}{2} + v_S(x', x) \right] \right\} \mathcal{G}^\lambda(x, \tau, x', \tau') \\ & + \frac{1}{2} \int dx dx' [v_S(x', x) - v^\lambda(x', x)] \gamma(x, x'), \end{aligned} \quad (63)$$

where  $\tau = it$  denotes imaginary time and  $\tau^+ = \lim_{\eta \rightarrow 0^+} (\tau + \eta)$ . The use of FT-MBPT in Eq. (63) is facilitated by the existence of the adiabatic connection which connects the true interacting system with the KS system and hence allows us to express the resulting Feynman diagrams in terms of occupation numbers and natural orbitals of the 1RDM.

Well-known methods of FT-MBPT can now be applied. The unperturbed Hamiltonian is  $\hat{H}^0$ , whereas the perturbation consists of a two-particle interaction  $\lambda \hat{W}$  and a nonlocal one-particle potential  $u^\lambda(x, x') = v^\lambda(x, x') - v_S(x, x')$ . The proof of Wicks theorem is still applicable for this kind of perturbation, and the same Feynman rules apply. We show our notation conventions in Table I.

TABLE I. Notation conventions for Feynman diagrams in FT-RDMFT, where  $w(x, x')$  denotes the interelectronic interaction,  $u^\lambda(x, x') = v^\lambda(x, x') - v_S(x, x')$  is the nonlocal one-particle potential,  $\mathcal{G}^0(x, \tau, x', \tau')$  is the Green's function of the unperturbed system, and  $\mathcal{G}^\lambda(x, \tau, x', \tau')$  are the temperature Green's functions.

	$\lambda w(x, x')$
	$u^\lambda(x, x')$
	$\mathcal{G}^0(x, \tau, x', \tau')$
	$\mathcal{G}^\lambda(x, \tau, x', \tau')$

In particular, if the Hamiltonian is temperature independent and the system is uniform, Eq. (58) can be written entirely in terms of Feynman diagrams as

$$\lambda W_{unif}^\lambda = \frac{1}{2} \left( \text{Diagram 1} - \text{Diagram 2} \right), \quad (64)$$

where  $\Sigma^*$  denotes the irreducible self-energy. However, in general, the irreducible self-energy  $\Sigma^*$  for the first-order contribution becomes

$$\Sigma^* = \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5}. \quad (65)$$

Combining Eqs. (61), (58), and (65), we arrive at the first-order contribution to the interaction-induced grand potential functional in FT-RDMFT, which is

$$\Omega_W^{(1)}[\gamma] = \Omega_H[\gamma] + \Omega_X[\gamma], \quad (66)$$

$$\Omega_H[\gamma] = \frac{1}{2} \int dx dx' w(x, x') \gamma(x, x) \gamma(x', x'), \quad (67)$$

$$\Omega_X[\gamma] = -\frac{1}{2} \int dx dx' w(x, x') \gamma(x, x') \gamma(x', x). \quad (68)$$

This justifies the definitions of the Hartree and exchange energies which we postulated in Eqs. (50) and (51). Note that the functional form of the first-order contributions are equivalent to the Hartree and exchange functionals in zero-temperature RDMFT [49].

Approximations for the correlation functional  $\Omega_C = \Omega_W - \Omega_W^{(1)}$  can now be derived by expanding the Green's function to higher orders and then solving Eqs. (61) and (63).

### III. SUMMARY AND CONCLUSIONS

In this work, we have derived and presented the foundations of FT-RDMFT. We have proven Hohenberg-Kohn-like theorems and shown that the equilibrium properties of a grand-canonical ensemble with nonlocal external potential are determined uniquely by the eq-1RDM. This allows us to establish a functional theory for the grand potential in terms of the 1RDM and, in analogy to DFT, to define a universal functional. A minimization of that grand potential functional then yields the eq-1RDM.

Furthermore, we have shown that there exists a KS system in FT-RDMFT, in contrast to the zero-temperature case, and derived the adiabatic connection formula. Based on this, we have established an iterative procedure for constructing approximations to the correlation functional in FT-RDMFT by utilizing methods from FT-MBPT. We have further demonstrated that the minimization of the first-order functional in this perturbative scheme is equivalent to the solution of the finite-temperature Hartree-Fock equations.

The present work sparks the hope that FT-RDMFT might become the method of choice for quantum problems at finite temperature where the standard DFT approach fails and the thermal DFT approach has not been developed to satisfaction [50].

The main task for the future is the development of correlation functionals for the grand potential and free energy in FT-RDMFT and the application to real systems. Some further developments, such as an exchange-only functional for collinear and noncollinear spins, as well as correlation functionals, momentum distributions, and phase diagrams in the framework of FT-RDMFT, will be presented in Ref. [35].

### APPENDIX A: EQUILIBRIUM OCCUPATION NUMBERS IN GENERAL SYSTEMS

As we have pointed out in Sec. II C, the eq-1RDM of a noninteracting system has occupation numbers strictly between 0 and 1. We now show that this is also true for the occupation numbers of eq-1RDMs of arbitrary systems, including interacting ones.

We start from the spectral representation of the eq-1RDM given by

$$\gamma(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x). \quad (\text{A1})$$

The occupation number operator  $\hat{n}_i$  is now defined as

$$\hat{n}_i = \hat{c}_i^+ \hat{c}_i, \quad (\text{A2})$$

where  $c_i^+$  creates and  $c_i$  annihilates the natural orbital  $\phi_i$ . An arbitrary occupation number of the eq-1RDM in grand canonical equilibrium can then be written as

$$n_i = \text{tr}\{\hat{D}\hat{n}_i\} = \sum_e w_e \langle \Psi_e | \hat{n}_i | \Psi_e \rangle. \quad (\text{A3})$$

$\{\Psi_e\}$  are eigenfunctions of the Hamiltonian and form a basis of the underlying Hilbert space. Another basis is formed by the Slater determinants  $\{\chi_\alpha\}$ , which are constructed by the natural orbitals  $\{\phi_i\}$  of the eq-1RDM. The transformation between these bases is governed by the expansion coefficients  $c_{e\alpha}$  via

$$\Psi_e = \sum_\alpha c_{e\alpha} \chi_\alpha. \quad (\text{A4})$$

Due to completeness and normalization of the  $\{\Psi_e\}$  and  $\{\chi_\alpha\}$ , the coefficients fulfill

$$\sum_e |c_{e\alpha}|^2 = \sum_\alpha |c_{e\alpha}|^2 = 1. \quad (\text{A5})$$

Expanding  $\{\Psi_e\}$  in Eq. (A3) in terms of  $\{\chi_\alpha\}$  then leads to

$$n_i = \sum_e w_e \sum_{\alpha\beta} c_{e\alpha}^* c_{e\beta} \langle \chi_\alpha | \hat{n}_i | \chi_\beta \rangle. \quad (\text{A6})$$

Since the Slater determinants  $\{\chi_\alpha\}$  are, by definition, eigenfunctions of the occupation number operator  $\hat{n}_i$ , this reduces to

$$n_i = \sum_\alpha \underbrace{\left( \sum_e w_e |c_{e\alpha}|^2 \right)}_{f_\alpha} \underbrace{\langle \chi_\alpha | \hat{n}_i | \chi_\alpha \rangle}_{g_{i\alpha}}. \quad (\text{A7})$$

Using Eq. (A5) and the properties of the thermal weights,  $w_e > 0$  and  $\sum_e w_e = 1$ , we see that

$$f_\alpha > 0, \quad (\text{A8})$$

$$\sum_\alpha f_\alpha = 1. \quad (\text{A9})$$

The factors  $g_{i\alpha}$  are equal to 1 if the natural orbital  $\phi_i$  appears in the Slater determinant  $\chi_\alpha$ . Otherwise,  $g_{i\alpha}$  vanishes. The summation over  $\alpha$  corresponds to a summation over a basis of the Hilbert space, which is the Fock space in the case of a grand-canonical ensemble. Therefore, for a fixed  $i$ , there will be at least one  $\alpha$ , such that  $g_{i\alpha} = 1$  and at least one  $\alpha$  for which  $g_{i\alpha} = 0$ . Combining this fact with Eqs. (A8) and (A9), we can rewrite Eq. (A7) to yield the desired inequality

$$0 < n_i < 1. \quad (\text{A10})$$

### APPENDIX B: ZERO-TEMPERATURE MAPPING BETWEEN POTENTIALS AND WAVE FUNCTIONS

Due to Gilbert's theorem [38], the wave function can be written as a functional of the 1RDM allowing us to define an energy functional

$$E[\gamma] = \langle \Psi[\gamma] | \hat{H} | \Psi[\gamma] \rangle, \quad (\text{B1})$$

with a generic Hamiltonian  $\hat{H} = \hat{T} + \hat{V} + \hat{W}$  in electronic structure theory already given in Eq. (2). Due to the variational principle this energy functional is minimized by a gs-1RDM,

$$\gamma_{gs}(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x), \quad (\text{B2})$$

analogous to the eq-1RDM in Eq. (7). The minimization of Eq. (B1) is performed under the constraints ensuring  $N$ -representability of the 1RDM; that is, (i) the natural orbitals  $\{\phi_i\}$  form a complete set, (ii) the occupation numbers sum up the correct particle number ( $\sum_i n_i = N$ ), and (iii)  $0 \leq n_i \leq 1$ . These constraints are taken into account by defining the auxiliary functional

$$A[\gamma] = E[\gamma] - \sum_{ij} \int dx \phi_i^*(x) \phi_j(x') - \mu \sum_i \cos^2 \theta_i, \quad (\text{B3})$$

where the last constraint is accommodated by the substitution  $n_i = \cos^2 \theta_i$ . Minimizing with respect to variations in the natural orbitals  $\phi_k^*(x)$  and  $\phi_k(x)$  while keeping the occupation numbers fixed and variations in  $\theta_k$  while keeping the natural orbitals fixed leads to the following well-known set of equations [38]:

$$\frac{\delta A}{\delta \phi_k^*(x)} = n_k h \phi_k(x) - \sum_j \lambda_{kj} \phi_j(x) = 0, \quad (\text{B4})$$

$$\frac{\delta A}{\delta \phi_k(x)} = n_k h \phi_k^*(x) - \sum_i \lambda_{ik} \phi_i^*(x) = 0, \quad (\text{B5})$$

$$\frac{\partial A}{\partial \theta_k} = \sin(2\theta_k) \left( \left. \frac{\partial E[\gamma]}{\partial n_k} \right|_{\gamma_{gs}} - \mu \right) = 0, \quad (\text{B6})$$

where  $h = \delta E[\gamma] / \delta \gamma(x, x')$ . Equation (B6) implies that

$$\left. \frac{\partial E[\gamma]}{\partial n_k} \right|_{\gamma_{gs}} = \begin{cases} a_k > \mu & \text{and } \theta_k = \pi/2 \Leftrightarrow n_k = 0, \\ \mu & \text{and any } \theta_k \Leftrightarrow 0 < n_k < 1, \\ b_k < \mu & \text{and } \theta_k = 0 \Leftrightarrow n_k = 1. \end{cases} \quad (\text{B7})$$

If there are only unpinned states, i.e.,  $0 < n_k < 1$ , then Eq. (B7) equals the chemical potential  $\mu$ . If there are pinned

states, i.e.,  $n_k = 0$  or  $n_k = 1$ , Eq. (B7) is either greater or less than  $\mu$ , where  $a_k, b_k \in \mathbb{R}$ .

In the following we show that there is a one-to-one mapping between potential and gs-1RDM if and only if there are unpinned occupation numbers ( $0 < n_k < 1$ ). Contrarily, there is no one-to-one mapping between potential and gs-1RDM if there are pinned occupation numbers ( $n_k = 0$  or  $n_k = 1$ ). This is done in two steps: (i) For unpinned occupation numbers we show that the external potential is uniquely determined up to a constant; (ii) for gs-1RDMs with pinned occupation numbers we show explicitly that one can construct infinitely many potentials differing by more than a constant that lead to the same gs-1RDM.

(i) *Unpinned states.* For unpinned states Eqs. (B4), (B5), and (B6) imply that any 1RDM must fulfill

$$\left. \frac{\delta E[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \left. \frac{\delta N[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \delta(x, x'), \quad (\text{B8})$$

where  $\delta(x, x')$  denotes the Dirac delta function. Now assume an arbitrary potential contribution  $U[\gamma] = \int dx dx' \gamma(x, x') u(x, x')$ , which we add to the total energy by defining an energy functional  $E_u[\gamma] = E[\gamma] + U[\gamma]$ . Then Eq. (B8) yields

$$\left. \frac{\delta E_u[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \delta(x, x') + u(x, x'). \quad (\text{B9})$$

Due to Eq. (B8) the only choice for  $u(x, x')$  that leaves the gs-1RDM invariant is

$$u(x, x') = c \delta(x, x'), \quad (\text{B10})$$

with  $c$  being an arbitrary constant. Thus we have shown that the external potential is uniquely determined up to a constant.

(ii) *Pinned states.* For pinned occupation numbers the minimum of  $E[\gamma]$  is at the boundary of the domain, and hence Eqs. (B4), (B5), and (B6) do not imply Eq. (B8).

It is possible to adjust the Euler-Lagrange equation by incorporating Kuhn-Tucker multipliers [51], but there is a simpler way, as described in the following.

We exploit the fact that the derivatives in Eq. (B8) can be different from  $\mu$  for pinned states and construct a one-particle potential which leaves the gs-1RDM invariant. This potential shall be governed by the generally nonlocal kernel  $u(x, x')$ . By making it diagonal in the natural orbital basis of the gs-1RDM we ensure that the orbitals do not change upon addition of the potential. For simplicity, we choose only one component to be nonvanishing, namely,

$$u(x, x') = u \phi_\alpha^*(x') \phi_\alpha(x), \quad (\text{B11})$$

and define an energy functional

$$E_\alpha[\gamma] = E[\gamma] + \int dx dx' u(x, x') \gamma(x', x). \quad (\text{B12})$$

In analogy to Eq. (B7) the derivative with respect to the occupation numbers becomes

$$\left. \frac{\partial E_\alpha[\gamma]}{\partial n_k} \right|_{\gamma_{gs}} = \begin{cases} a_k + u \delta_{k\alpha} & \text{and } \theta_k = \pi/2 \Leftrightarrow n_k = 0, \\ \mu + u \delta_{k\alpha} & \text{and any } \theta_k \Leftrightarrow 0 < n_k < 1, \\ b_k + u \delta_{k\alpha} & \text{and } \theta_k = 0 \Leftrightarrow n_k = 1, \end{cases} \quad (\text{B13})$$

where  $\delta_{ij}$  denotes the Kronecker symbol.

These considerations can now be employed to show the ambiguity of the external potential in RDMFT for ground states with pinned occupation numbers. For simplicity we assume that there is exactly one pinned occupation number, e.g.,  $n_\beta = 0$ . We then construct an external potential as in Eq. (B11) with  $\alpha = \beta$ . We deduce from Eq. (B13) that every choice of  $u > \mu - a_\beta$  leads to a situation where the  $\beta$  orbital exhibits a derivative greater than  $\mu$ , but all choices yield the same gs-1RDM. Then we consider one pinned occupation number  $n_\beta = 1$ . Here we can choose  $u < \mu - b_\beta$  for which the derivative of the  $\beta$  orbital is always less than  $\mu$  but again leads to the same gs-1RDM as in the previous consideration. We can readily generalize these arguments to a gs-1RDM with several pinned states. Following this procedure, we can construct infinitely many external potentials in the form of Eq. (B11) that differ by more than a constant that all yield the same gs-1RDM. This proves the ambiguity of the one-particle potential for gs-1RDM with pinned occupation numbers.

### APPENDIX C: FINITE-TEMPERATURE HARTREE-FOCK THEORY

Consider Eq. (44) without the correlation contribution,

$$\begin{aligned} \Omega_{HF}[\gamma] = \Omega_k[\gamma] + V[\gamma] - \mu N[\gamma] - S_S[\gamma]/\beta \\ + \Omega_H[\gamma] + \Omega_x[\gamma]. \end{aligned} \quad (\text{C1})$$

In the following we show that Eq. (C1) is the Hartree-Fock functional and implies the finite-temperature Hartree-Fock equations given in Eq. (C4).

The derivative of the KS entropy  $S_S[\gamma]$  with respect to the occupation numbers diverges for  $n_i \rightarrow \{0, 1\}$ , whereas all other contributions are finite. Therefore, there are no pinned states at the minimum of  $\Omega_{HF}[\gamma]$ . Furthermore, Eq. (C1) is an explicit functional of the 1RDM. Therefore we conclude that the functional derivative with respect to the 1RDM exists and that  $\Omega_{HF}[\gamma]$  fulfills the Euler-Lagrange equation

$$\left. \frac{\delta \Omega_{HF}[\gamma]}{\delta \gamma(x', x)} \right|_{\gamma_{gs}} = 0 \quad (\text{C2})$$

at the minimum. Applying this condition on  $\Omega_{HF}[\gamma]$  and projecting the result on the  $i$ th natural orbital of the 1RDM leads to the FT-HF equations

$$0 = \int dx' \phi_i(x') \frac{\delta \Omega_{HF}[\gamma]}{\delta \gamma(x', x)} \quad (\text{C3})$$

$$\begin{aligned} &= \left( -\frac{\nabla^2}{2} \right) \phi_i(x) + \int dx' v(x, x') \phi_i(x') \\ &\quad - \int dx' w(x, x') \gamma(x, x') \phi_i(x') \\ &\quad + \int dx' w(x, x') \gamma(x', x') \phi_i(x) - \varepsilon_i \phi_i, \end{aligned} \quad (\text{C4})$$

where we used Eq. (42) in the last term.

### APPENDIX D: CANONICAL ENSEMBLES

Minimizing the grand potential implies coupling to a particle bath. There are, however, important physical problems



in which the particle number is intrinsically conserved and therefore the equilibrium is defined by the state which minimizes the free energy instead. An important example is a molecule in solution where the solvent is described by a bath of harmonic oscillators at finite temperature. In the following we present a concise formulation of FT-RDMFT for canonical ensembles and point out the most important differences from the grand-canonical formulation.

The appropriate Hilbert space for canonical ensembles of particle number  $N$  is given by the  $N$ -particle subspace

$$\mathcal{H}^N = \hat{S}h^{\otimes N} \quad (\text{D1})$$

of the Fock space

$$\mathcal{H} = \bigoplus_{n=0}^{\infty} \hat{S}h^{\otimes n}. \quad (\text{D2})$$

The associated SDOs are weighted sums of projection operators on  $\mathcal{H}^N$ :

$$\begin{aligned} \hat{D}^c &= \sum_{\alpha} w_{\alpha} |\Psi_{\alpha}\rangle \langle \Psi_{\alpha}|, \\ w_{\alpha} &\geq 0, \quad \sum_{\alpha} w_{\alpha} = 1. \end{aligned} \quad (\text{D3})$$

The variational principle now involves the free energy  $\mathcal{F} = \text{Tr}\{\hat{D}(\hat{H} + 1/\beta \ln \hat{D})\}$  rather than the grand potential, and the eq-SDO is given by

$$\hat{D}_{\text{eq}}^c = \frac{e^{-\beta \hat{H}}}{\text{tr}\{e^{-\beta \hat{H}}\}}, \quad (\text{D4})$$

where  $\hat{H}$  is now the  $N$ -particle Hamiltonian of the system. The one-to-one mapping between the eq-SDO and the eq-1RDM stays valid also in the case of canonical ensembles with the only difference being that the external potential is now determined only up to an additional constant. Following the construction by Lieb [40], we define a canonical universal functional  $\mathfrak{F}^c[\gamma]$  on the whole domain of ensemble- $N$ -representable 1RDMs as

$$\mathfrak{F}^c[\gamma] = \inf_{\hat{D} \in \mathcal{H}^N \rightarrow \gamma} \text{tr}\{\hat{D}(\hat{T} + \hat{W} + 1/\beta \ln \hat{D})\}. \quad (\text{D5})$$

The equilibrium of the system is then found by a minimization of the free-energy functional  $\mathcal{F}[\gamma] = \mathfrak{F}^c[\gamma] + V[\gamma]$ .

The main difference from the grand-canonical framework of FT-RDMFT lies in the canonical KS system. In the canonical ensemble a simple analytical relation between the eigenvalues of the KS Hamiltonian and the occupation numbers as in Eq. (41) for the canonical ensemble does not exist. Therefore we do not know if every 1RDM with  $0 < n_i < 1$  is a canonical eq-1RDM. Nevertheless, we can reconstruct the KS Hamiltonian by iterative methods [52] once we know that a given 1RDM corresponds to a canonical equilibrium.

Furthermore, the finite-temperature version of Wick's theorem [53] breaks down for canonical ensembles because it relies on the interplay of states of different particle numbers. Hence our perturbative approach for constructing approximations to the correlation functional cannot be applied to the canonical ensemble in general. However, there is a loophole. When we consider the system in the thermodynamic limit, the thermodynamic variables of grand-canonical and canonical ensembles coincide. In this case, we can still use functionals derived by our perturbative methodology in Sec. II E for the grand potential  $\Omega[\gamma]$  and calculate the free energy via

$$\mathcal{F}[\gamma] = \Omega[\gamma] + \mu N[\gamma]. \quad (\text{D6})$$

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