

## Energy components in spin-density functional theory

Federico Zahariev<sup>1,\*</sup>, Mark S. Gordon,<sup>1,†</sup> and Mel Levy<sup>2,‡</sup>

<sup>1</sup>*Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA*

<sup>2</sup>*Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118, USA*



(Received 16 March 2021; revised 9 July 2021; accepted 9 July 2021; published 16 August 2021)

It has recently been shown how to replace spin-wave functions with purely spatial wave functions in the formulation of spin-density functional theory (SDFT), without any change to the resultant density functional expressions [F. Zahariev and M. Levy, *Phys. Rev. A* **100**, 062507 (2019)]. The purely spatial wave functions that are obtained are much more convenient to use and thus allow for a relatively easy decomposition and manipulation of terms in the constrained-search formulation of SDFT. All the essential ingredients of SDFT, including the kinetic, exchange, and correlation contributions, are explicitly defined in terms of the universal functional expressed in this spin-free manner. Constrained-search derivations of the Oliver-Perdew relations for the kinetic and exchange terms are presented. The up-down spin component of the correlation term is found to contain the up-down spin component of the Hartree term. A spin-dependent generalization of the adiabatic connection is put forth and a connection with spin-dependent coordinate scaling is established for the correlation energy.

DOI: [10.1103/PhysRevA.104.022815](https://doi.org/10.1103/PhysRevA.104.022815)

### I. INTRODUCTION

An effective way of approximating the exchange-correlation density functional [1–7] is to construct an approximate functional that satisfies as many properties of the exact exchange-correlation density functional as possible [8,9]. With this in mind, we further expand on the spin-free approach of Ref. [10].

While the conventional approach to spin-density functional theory (SDFT) uses spin-wave functions [11,12], in Ref. [10] we constructed the SDFT universal functional directly in terms of one of the spatial components of a given spin function and proved the equivalency of the conventional and spin-free constructions. This definition dramatically simplifies the formal construction of the SDFT universal functional and allows for simpler explicit definitions of the subsequent SDFT expressions that unfold from the universal functional.

The explicit definitions of the essential ingredients of SDFT that are presented here in terms of the spin-free SDFT constrained-search approach are generalizations of the respective definitions from the standard spinless DFT.

The kinetic and electron-electron repulsion operators can be naturally split into spin related components. Consequently, the kinetic and electron-electron repulsion terms of the universal functional reflect the respective operator split. As a final result, the exchange consists of up-up and down-down spin components, while the correlation consists of up-up, up-down, and down-down spin components, and we

observe that the up-down correlation component contains the up-down spin component of the Hartree term in its definition. This observation suggests the possibility of redefining the SDFT correlation energy by subtracting the up-down Hartree component from the definition of the correlation energy.

Constrained-search derivations of the Oliver-Perdew relations for the kinetic and exchange terms are presented. Spin-dependent coordinate scaling equalities for the kinetic and exchange terms are found herein on the basis of the Oliver-Perdew relations.

A spin-dependent generalization of the adiabatic connection [13–15], in which there are three different constants in front of the up-up, up-down, and down-down spin components of the electron-electron repulsion term, is also proposed and a connection with spin-dependent coordinate scaling is established.

The presented approach is a convenient foundation for deriving different scaling and adiabatic-connection constraints that are important for functional approximations.

### II. SPIN-FREE IDENTIFICATION OF THE SDFT UNIVERSAL FUNCTIONAL

An  $N$ -electron system will be considered. The Hamiltonian is  $\hat{H} = \hat{T} + \hat{V}$ , where the kinetic part is  $\hat{T} = -\frac{1}{2} \sum_{1 \leq i \leq N} \nabla_i^2$  and the potential part is  $\hat{V} = \hat{V}_{ee} + \sum_{1 \leq i \leq M} v_{\uparrow}(\mathbf{r}_i) + \sum_{M+1 \leq i \leq N} v_{\downarrow}(\mathbf{r}_i)$ . The first term in  $\hat{V}$  is the electron-electron repulsion  $\hat{V}_{ee} = \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ , while  $v_{\uparrow}(\mathbf{r})$  and  $v_{\downarrow}(\mathbf{r})$  are external potentials that are acting on the up-spin and down-spin variables, respectively. In the absence of external fields, the external potentials  $v_{\uparrow}(\mathbf{r})$  and  $v_{\downarrow}(\mathbf{r})$  typically signify the electron-nuclear attraction potential

\*fzahari@iastate.edu

†mark@si.msg.chem.iastate.edu

‡mlevy@tulane.edu

$v_{en}(\mathbf{r})$ , i.e.  $v_{\uparrow}(\mathbf{r}) = v_{\downarrow}(\mathbf{r}) = v_{en}(\mathbf{r})$ . When a homogeneous magnetic field  $\vec{B}$  along the spin direction is present, however,  $v_{\uparrow}(\mathbf{r})$  and  $v_{\downarrow}(\mathbf{r})$  split according to  $v_{\uparrow}(\mathbf{r}) = v_{en}(\mathbf{r}) + \mu_B |\vec{B}|$  and  $v_{\downarrow}(\mathbf{r}) = v_{en}(\mathbf{r}) - \mu_B |\vec{B}|$ , where  $\mu_B$  is the magneton of Bohr.

As done in [16], following [17,18], purely spatial wave functions can be used in the variational principle. That is, the ground-state energy  $E_{GS}$  is

$$E_{GS} = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{1 \leq i \leq M} v_{\uparrow}(\mathbf{r}_i) + \sum_{M+1 \leq i \leq N} v_{\downarrow}(\mathbf{r}_i) | \Psi \rangle, \quad (1)$$

where, in expression (1), the purely spatial normalized wave functions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N) \quad (2)$$

are antisymmetric in the first  $M$  and, separately, in the last  $(N-M)$  variables.

As in the original constrained-search formulation [3,4], the wave function minimization in Eq. (1),  $\min_{\Psi}$ , can be split into two steps,  $\min_{(\rho_{\uparrow}, \rho_{\downarrow})} \min_{\Psi \rightarrow (\rho_{\uparrow}, \rho_{\downarrow})}$ . That is, the whole space of wave functions is split into classes of wave functions. All the wave functions in a given class yield the same up- and down-spin densities,

$$\begin{aligned} \rho_{\uparrow}(\mathbf{r}) &= M \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2, \dots, d\mathbf{r}_M d\mathbf{r}_{M+1}, \dots, d\mathbf{r}_N, \\ \rho_{\downarrow}(\mathbf{r}) &= (N-M) \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1, \dots, d\mathbf{r}_M d\mathbf{r}_{M+2}, \dots, d\mathbf{r}_N. \end{aligned} \quad (3)$$

The first minimization step aims to find the minima in each wave function class, while the second minimization step compares these local class minima and finds the global minimum among them. Hence,  $\min_{\Psi}$  is indeed equivalent to  $\min_{(\rho_{\uparrow}, \rho_{\downarrow})} \min_{\Psi \rightarrow (\rho_{\uparrow}, \rho_{\downarrow})}$  and Eq. (1) can be expressed as

$$\begin{aligned} E_{GS} &= \min_{(\rho_{\uparrow}, \rho_{\downarrow})} \min_{\Psi \rightarrow (\rho_{\uparrow}, \rho_{\downarrow})} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{1 \leq i \leq M} v_{\uparrow}(\mathbf{r}_i) + \sum_{M+1 \leq i \leq N} v_{\downarrow}(\mathbf{r}_i) + \sum_{1 \leq i \leq N} v(\mathbf{r}_i) | \Psi \rangle \\ &= \min_{(\rho_{\uparrow}, \rho_{\downarrow})} \left\{ \min_{\Psi \rightarrow (\rho_{\uparrow}, \rho_{\downarrow})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int \rho_{\uparrow}(\mathbf{r}) v_{\uparrow}(\mathbf{r}) d\mathbf{r} + \int \rho_{\downarrow}(\mathbf{r}) v_{\downarrow}(\mathbf{r}) d\mathbf{r} \right\} \\ &= \min_{(\rho_{\uparrow}, \rho_{\downarrow})} \left\{ F[\rho_{\uparrow}, \rho_{\downarrow}] + \int \rho_{\uparrow}(\mathbf{r}) v_{\uparrow}(\mathbf{r}) d\mathbf{r} + \int \rho_{\downarrow}(\mathbf{r}) v_{\downarrow}(\mathbf{r}) d\mathbf{r} \right\} \\ &= F[\rho_{gs\uparrow}, \rho_{gs\downarrow}] + \int \rho_{gs\uparrow}(\mathbf{r}) v_{\uparrow}(\mathbf{r}) d\mathbf{r} + \int \rho_{gs\downarrow}(\mathbf{r}) v_{\downarrow}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (4)$$

where the universal functional in minimizing expression (4) is identified as

$$F[\rho_{\uparrow}, \rho_{\downarrow}] = \min_{\Psi \rightarrow (\rho_{\uparrow}, \rho_{\downarrow})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_{(\rho_{\uparrow}, \rho_{\downarrow})}^{\min} | \hat{T} + \hat{V}_{ee} | \Psi_{(\rho_{\uparrow}, \rho_{\downarrow})}^{\min} \rangle, \quad (5)$$

and  $\rho_{gs\uparrow}(\mathbf{r})$  and  $\rho_{gs\downarrow}(\mathbf{r})$  are the ground-state up- and down-spin densities, respectively. The total density is

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}). \quad (6)$$

In the original density-functional theory [1–7], the ground-state energy  $E_{GS}$  and corresponding total density  $\rho_{gs}(\mathbf{r})$ , for the attractive potential  $v(\mathbf{r})$ , are given by

$$\begin{aligned} E_{GS} &= \min_{\rho} \left\{ F[\rho] + \int v_{en}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \\ &= F[\rho_{gs}] + \int v_{en}(\mathbf{r}) \rho_{gs}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (7)$$

where the universal functional in its constrained-search form [3,4] is

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \quad (8)$$

The connection between the universal functionals  $F[\rho]$  and  $F[\rho_{\uparrow}, \rho_{\downarrow}]$  [10] is

$$F[\rho] = \min_{\rho_{\uparrow} + \rho_{\downarrow} = \rho} F[\rho_{\uparrow}, \rho_{\downarrow}]. \quad (9)$$

In the case of an external potential  $v_{en}(\mathbf{r})$  and an electronic open shell, when the number of up and down electrons differ, the up and down densities  $\rho_{\uparrow}(\mathbf{r})$  and  $\rho_{\downarrow}(\mathbf{r})$  differ as well. According to the generalized Hohenberg-Kohn theorem [1,4], all the properties of the electronic systems, including the up- and down-spin ground-state densities  $\rho_{gs\uparrow}(\mathbf{r})$  and  $\rho_{gs\downarrow}(\mathbf{r})$  are determined by the total ground-state density  $\rho_{gs}(\mathbf{r})$ .

If one is given the total ground-state density  $\rho_{gs}(\mathbf{r})$ , which is then inserted as a variable in the universal functional  $F[\rho]$ , the constrained minimization of Eq. (9) finds the pair of up- and down-spin ground-state densities  $\rho_{gs\uparrow}(\mathbf{r})$  and  $\rho_{gs\downarrow}(\mathbf{r})$ ,

$$F[\rho_{gs}] = \min_{\rho_{\uparrow} + \rho_{\downarrow} = \rho_{gs}} F[\rho_{\uparrow}, \rho_{\downarrow}] = F[\rho_{gs\uparrow}, \rho_{gs\downarrow}]. \quad (10)$$

Observe that Eq. (10) constructs, in the above manner, the Hohenberg-Kohn correspondences  $\rho_{\text{gs}}(\mathbf{r}) \rightarrow \rho_{\text{gs}\uparrow}(\mathbf{r})$  and  $\rho_{\text{gs}}(\mathbf{r}) \rightarrow \rho_{\text{gs}\downarrow}(\mathbf{r})$ .

### III. NONINTERACTING LIMIT OF THE SDFT UNIVERSAL FUNCTIONAL

The definition of the universal functional from Eq. (1) can be generalized, by including the adiabatic-connection coupling constant  $\lambda$  in front of the electron-electron repulsion term  $\hat{V}_{ee}$  [13–15], to obtain

$$\begin{aligned} F_\lambda[\rho_\uparrow, \rho_\downarrow] &= \min_{\Psi \rightarrow (\rho_\uparrow, \rho_\downarrow)} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle \\ &= \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda} | \hat{T} + \lambda \hat{V}_{ee} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda} \rangle. \end{aligned} \quad (11)$$

The noninteracting limit of the universal functional (i.e.,  $\lambda = 0$ ) is denoted as

$$T_s[\rho_\uparrow, \rho_\downarrow] = F_{\lambda=0}[\rho_\uparrow, \rho_\downarrow] = \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0} | \hat{T} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0} \rangle. \quad (12)$$

The kinetic energy operator can be split into up- and down-spin components:

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 = \hat{T}_\uparrow + \hat{T}_\downarrow, \quad (13)$$

where

$$\hat{T}_\uparrow = -\frac{1}{2} \sum_{i=1}^M \nabla_{\mathbf{r}_i}^2, \quad \hat{T}_\downarrow = -\frac{1}{2} \sum_{i=M+1}^N \nabla_{\mathbf{r}_i}^2, \quad (14)$$

and, as a result, the minimization in Eq. (12) can be similarly split:

$$\begin{aligned} T_s[\rho_\uparrow, \rho_\downarrow] &= \min_{\Psi \rightarrow (\rho_\uparrow, \rho_\downarrow)} \langle \Psi | \hat{T} | \Psi \rangle = \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0} | \hat{T} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0} \rangle \\ &= \min_{\Psi \rightarrow (\rho_\uparrow, \rho_\downarrow)} \{ \langle \Psi | \hat{T}_\uparrow | \Psi \rangle + \langle \Psi | \hat{T}_\downarrow | \Psi \rangle \}. \end{aligned} \quad (15)$$

After a partial integration on the right-hand side of Eq. (15) of the  $N_\downarrow = (N-M)$  variables in  $\langle \Psi | \hat{T}_\uparrow | \Psi \rangle$ , corresponding to the down-spin electrons, and the  $N_\uparrow = M$  variables in  $\langle \Psi | \hat{T}_\downarrow | \Psi \rangle$ , corresponding to the up-spin electrons, it follows that

$$T_s[\rho_\uparrow, \rho_\downarrow] = T_{s,\uparrow}[\rho_\uparrow] + T_{s,\downarrow}[\rho_\downarrow], \quad (16)$$

where

$$T_{s,\uparrow}[\rho_\uparrow] = \min_{\Psi \rightarrow \rho_\uparrow} \langle \Psi | \hat{T}_\uparrow | \Psi \rangle = \langle \Psi_{\rho_\uparrow}^{\min} | \hat{T}_\uparrow | \Psi_{\rho_\uparrow}^{\min} \rangle, \quad (17a)$$

$$T_{s,\downarrow}[\rho_\downarrow] = \min_{\Psi \rightarrow \rho_\downarrow} \langle \Psi | \hat{T}_\downarrow | \Psi \rangle = \langle \Psi_{\rho_\downarrow}^{\min} | \hat{T}_\downarrow | \Psi_{\rho_\downarrow}^{\min} \rangle. \quad (17b)$$

The wave functions in Eq. (17a) and Eq. (17b) are of the types  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M)$  and  $\Psi(\mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N)$ , respectively.

In the following the shorthand notation  $\Phi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0}$  is used.

If the densities  $\rho_\uparrow(\mathbf{r})$  and  $\rho_\downarrow(\mathbf{r})$  are pure-state noninteracting  $v$ -representable with respect to  $\hat{T}_\uparrow$  and  $\hat{T}_\downarrow$ , respectively,  $\Psi_{\rho_\uparrow}^{\min}$  and  $\Psi_{\rho_\downarrow}^{\min}$  are single determinants (denote them as  $\Phi_{\rho_\uparrow}$

and  $\Phi_{\rho_\downarrow}$ , respectively) and the minimizing noninteracting wave function  $\Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=0}$  is a product of these two determinants,

$$\Phi_{(\rho_\uparrow, \rho_\downarrow)} = \Phi_{\rho_\uparrow} \Phi_{\rho_\downarrow}. \quad (18)$$

A density is termed ‘‘pure-state noninteracting  $v$ -representable,’’ if it arises from a ground eigenstate of the noninteracting electronic Hamiltonian  $\hat{T} + \sum_i v(\mathbf{r}_i)$  with some external potential  $v(\mathbf{r})$  [5].

In the most general case, the pure-state constrained-search definitions in Eqs. (5), (8), (11), (12), (15), and (17) have to be generalized to ensemble constrained-search definitions, where Eq. (18) is replaced by a product of two minimizing single-determinant ensembles [see Eqs. (A13)–(A15) in the Appendix for details].

In a similar vein, the forthcoming derivations for the exchange and correlation energy also use Eq. (18). Nevertheless, the final results are valid in the most general case. The general proofs use the ensemble approach of the Appendix. Equation (18) in all cases is used for simplicity of presentation.

The analog of Eq. (9) for the noninteracting case, on the basis of Eqs. (11), (12), and (16), is

$$T_s[\rho] = \min_{\rho_\uparrow + \rho_\downarrow = \rho} T_s[\rho_\uparrow, \rho_\downarrow] = \min_{\rho_\uparrow + \rho_\downarrow = \rho} \{ T_{s,\uparrow}[\rho_\uparrow] + T_{s,\downarrow}[\rho_\downarrow] \}. \quad (19)$$

### IV. KINETIC AND ELECTRON-ELECTRON REPULSION COMPONENTS IN SDFT

The universal functional can be split into its kinetic and electron-electron repulsion components:

$$F_{\lambda=1}[\rho_\uparrow, \rho_\downarrow] = T[\rho_\uparrow, \rho_\downarrow] + V_{ee}[\rho_\uparrow, \rho_\downarrow], \quad (20)$$

where

$$T[\rho_\uparrow, \rho_\downarrow] = \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} | \hat{T} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} \rangle, \quad (21a)$$

$$V_{ee}[\rho_\uparrow, \rho_\downarrow] = \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} | \hat{V}_{ee} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} \rangle. \quad (21b)$$

Based on the kinetic operator split in expressions (13) and (14), the kinetic part of the universal functional is split into up- and down-spin components:

$$\begin{aligned} T[\rho_\uparrow, \rho_\downarrow] &= \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} | -\frac{1}{2} \sum_{i=1}^M \nabla_{\mathbf{r}_i}^2 | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} \rangle \\ &\quad + \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} | -\frac{1}{2} \sum_{i=M+1}^N \nabla_{\mathbf{r}_i}^2 | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} \rangle \\ &= T_\uparrow[\rho_\uparrow, \rho_\downarrow] + T_\downarrow[\rho_\uparrow, \rho_\downarrow]. \end{aligned} \quad (22)$$

The electron-electron repulsion operator can be respectively split into up-up, up-down, and down-down spin components:

$$\hat{V}_{ee} = \sum_{j>i}^N \sum_{i=1}^{N-1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \hat{V}_{ee,\uparrow\uparrow} + \hat{V}_{ee,\uparrow\downarrow} + \hat{V}_{ee,\downarrow\downarrow}, \quad (23)$$

where

$$\begin{aligned}\hat{V}_{ee,\uparrow\uparrow} &= \sum_{i=1}^{M-1} \sum_{j>i}^M \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, & \hat{V}_{ee,\uparrow\downarrow} &= \sum_{i=1}^M \sum_{j=M+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \\ \hat{V}_{ee,\downarrow\downarrow} &= \sum_{i=M+1}^{N-1} \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.\end{aligned}\quad (24)$$

The electron-electron repulsion part of the universal functional can be correspondingly split into up-up, up-down, and down-down spin components:

$$\begin{aligned}V_{ee}[\rho_\uparrow, \rho_\downarrow] &= \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} | V_{ee,\uparrow\uparrow} + V_{ee,\uparrow\downarrow} + V_{ee,\downarrow\downarrow} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, \lambda=1} \rangle \\ &= V_{ee,\uparrow\uparrow}[\rho_\uparrow, \rho_\downarrow] + V_{ee,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] + V_{ee,\downarrow\downarrow}[\rho_\uparrow, \rho_\downarrow].\end{aligned}\quad (25)$$

## V. HARTREE, EXCHANGE, AND CORRELATION COMPONENTS OF THE UNIVERSAL FUNCTIONAL IN SDFT

The exchange term is defined as

$$\begin{aligned}E_x[\rho_\uparrow, \rho_\downarrow] &= \langle \Phi_{(\rho_\uparrow, \rho_\downarrow)} | \hat{V}_{ee} | \Phi_{(\rho_\uparrow, \rho_\downarrow)} \rangle - J[\rho_\uparrow + \rho_\downarrow] \\ &= (\langle \Phi_{\rho_\uparrow} | \hat{V}_{ee,\uparrow\uparrow} | \Phi_{\rho_\uparrow} \rangle - J[\rho_\uparrow]) + (\langle \Phi_{\rho_\downarrow} | \hat{V}_{ee,\downarrow\downarrow} | \Phi_{\rho_\downarrow} \rangle - J[\rho_\downarrow]) \\ &\quad + \left( \langle \Phi_{\rho_\uparrow} \Phi_{\rho_\downarrow} | \hat{V}_{ee,\uparrow\downarrow} | \Phi_{\rho_\uparrow} \Phi_{\rho_\downarrow} \rangle - \iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \right) \\ &= (\langle \Phi_{\rho_\uparrow} | \hat{V}_{ee,\uparrow\uparrow} | \Phi_{\rho_\uparrow} \rangle - J[\rho_\uparrow]) + (\langle \Phi_{\rho_\downarrow} | \hat{V}_{ee,\downarrow\downarrow} | \Phi_{\rho_\downarrow} \rangle - J[\rho_\downarrow]) \\ &= E_{x,\uparrow\uparrow}[\rho_\uparrow] + E_{x,\downarrow\downarrow}[\rho_\downarrow],\end{aligned}\quad (26)$$

where the third term in the second equality,  $\langle \Phi_{\rho_\uparrow} \Phi_{\rho_\downarrow} | \hat{V}_{ee,\uparrow\downarrow} | \Phi_{\rho_\uparrow} \Phi_{\rho_\downarrow} \rangle - \iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ , vanishes and the definition of the Hartree term

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (27)$$

is used in the third equality.

As a result, the exchange term is split into up-up and down-down spin components on the right-hand side of Eq. (26).

The correlation term is defined as

$$\begin{aligned}E_c[\rho_\uparrow, \rho_\downarrow] &= \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min} | \hat{T} + \hat{V}_{ee} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min} \rangle \\ &\quad - \langle \Phi_{(\rho_\uparrow, \rho_\downarrow)}^{\min} | \hat{T} + \hat{V}_{ee} | \Phi_{(\rho_\uparrow, \rho_\downarrow)}^{\min} \rangle,\end{aligned}\quad (28)$$

or equivalently as

$$E_c[\rho_\uparrow, \rho_\downarrow] = E_{xc}[\rho_\uparrow, \rho_\downarrow] - E_x[\rho_\uparrow, \rho_\downarrow], \quad (29)$$

where the exchange-correlation is defined as

$$\begin{aligned}E_{xc}[\rho_\uparrow, \rho_\downarrow] &= T[\rho_\uparrow, \rho_\downarrow] + V_{ee}[\rho_\uparrow, \rho_\downarrow] - T_s[\rho_\uparrow, \rho_\downarrow] \\ &\quad - J[\rho_\uparrow + \rho_\downarrow] \\ &= T[\rho_\uparrow, \rho_\downarrow] + V_{ee}[\rho_\uparrow, \rho_\downarrow] - T_s[\rho_\uparrow, \rho_\downarrow] - J[\rho_\uparrow] \\ &\quad - J[\rho_\downarrow] - \iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2\end{aligned}\quad (30)$$

Equation (28) can be transformed to

$$\begin{aligned}E_c[\rho_\uparrow, \rho_\downarrow] &= (T_\uparrow[\rho_\uparrow, \rho_\downarrow] - T_{s,\uparrow}[\rho_\uparrow]) \\ &\quad + (T_\downarrow[\rho_\uparrow, \rho_\downarrow] - T_{s,\downarrow}[\rho_\downarrow]) \\ &\quad + (V_{ee,\uparrow\uparrow}[\rho_\uparrow, \rho_\downarrow] - \langle \Phi_{\rho_\uparrow} | \hat{V}_{ee,\uparrow\uparrow} | \Phi_{\rho_\uparrow} \rangle) \\ &\quad + \left( V_{ee,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] - \iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \right) \\ &\quad + (V_{ee,\downarrow\downarrow}[\rho_\uparrow, \rho_\downarrow] - \langle \Phi_{\rho_\downarrow} | \hat{V}_{ee,\downarrow\downarrow} | \Phi_{\rho_\downarrow} \rangle),\end{aligned}\quad (31)$$

with a natural split of the correlation energy into up- and down-spin components for the kinetic part as well as up-up, up-down, and down-down spin components for the repulsion part:

$$\begin{aligned}E_c[\rho_\uparrow, \rho_\downarrow] &= T_{c,\uparrow}[\rho_\uparrow, \rho_\downarrow] + T_{c,\downarrow}[\rho_\uparrow, \rho_\downarrow] + V_{ee,c,\uparrow\uparrow}[\rho_\uparrow, \rho_\downarrow] \\ &\quad + V_{ee,c,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] + V_{ee,c,\downarrow\downarrow}[\rho_\uparrow, \rho_\downarrow],\end{aligned}\quad (32)$$

where

$$\begin{aligned}T_{c,\uparrow}[\rho_\uparrow, \rho_\downarrow] &= T_\uparrow[\rho_\uparrow, \rho_\downarrow] - T_{s,\uparrow}[\rho_\uparrow] \\ T_{c,\downarrow}[\rho_\uparrow, \rho_\downarrow] &= T_\downarrow[\rho_\uparrow, \rho_\downarrow] - T_{s,\downarrow}[\rho_\downarrow] \\ V_{ee,c,\uparrow\uparrow}[\rho_\uparrow, \rho_\downarrow] &= V_{ee,\uparrow\uparrow}[\rho_\uparrow, \rho_\downarrow] - \langle \Phi_{\rho_\uparrow} | \hat{V}_{ee,\uparrow\uparrow} | \Phi_{\rho_\uparrow} \rangle \\ V_{ee,c,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] &= V_{ee,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] - \iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ V_{ee,c,\downarrow\downarrow}[\rho_\uparrow, \rho_\downarrow] &= V_{ee,\downarrow\downarrow}[\rho_\uparrow, \rho_\downarrow] - \langle \Phi_{\rho_\downarrow} | \hat{V}_{ee,\downarrow\downarrow} | \Phi_{\rho_\downarrow} \rangle.\end{aligned}\quad (33)$$

Approximating  $V_{ee,c,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow]$  from Eq. (33) is effectively equivalent to approximating  $\tilde{V}_{ee,c,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow] = V_{ee,\uparrow\downarrow}[\rho_\uparrow, \rho_\downarrow]$ , as the two differ by the explicitly known integral  $\iint \frac{\rho_\uparrow(\mathbf{r}_1)\rho_\downarrow(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ . In the latter choice of approximation, one is using the following form of the exchange-correlation energy,

$$\begin{aligned}\tilde{E}_{xc}[\rho_\uparrow, \rho_\downarrow] &= T[\rho_\uparrow, \rho_\downarrow] + V_{ee}[\rho_\uparrow, \rho_\downarrow] - T_s[\rho_\uparrow, \rho_\downarrow] \\ &\quad - J[\rho_\uparrow] - J[\rho_\downarrow],\end{aligned}\quad (34)$$

instead of the form given by Eq. (30).

## VI. COORDINATE SCALING OF THE WAVE FUNCTION, DENSITIES, AND OPERATORS

In Ref. [10], we introduced the spin-dependent coordinate scaling of the wave function and densities, and a basic inequality was presented,

$$\begin{aligned}F[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow^{\lambda_\downarrow}] &\leq \langle \lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}} \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\lambda_\uparrow \mathbf{r}_1, \lambda_\uparrow \mathbf{r}_2, \dots, \lambda_\uparrow \mathbf{r}_M; \lambda_\downarrow \mathbf{r}_{M+1}, \lambda_\downarrow \mathbf{r}_{M+2}, \dots, \lambda_\downarrow \mathbf{r}_N) | \hat{T} \\ &\quad + \hat{V}_{ee} | \lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}} \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\lambda_\uparrow \mathbf{r}_1, \lambda_\uparrow \mathbf{r}_2, \dots, \lambda_\uparrow \mathbf{r}_M; \lambda_\downarrow \mathbf{r}_{M+1}, \lambda_\downarrow \mathbf{r}_{M+2}, \dots, \lambda_\downarrow \mathbf{r}_N) \rangle,\end{aligned}\quad (35)$$

where the up- and down-spin variables in the wave function  $\Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\lambda_\uparrow \mathbf{r}_1, \lambda_\uparrow \mathbf{r}_2, \dots, \lambda_\uparrow \mathbf{r}_M; \lambda_\downarrow \mathbf{r}_{M+1}, \lambda_\downarrow \mathbf{r}_{M+2}, \dots, \lambda_\downarrow \mathbf{r}_N)$  were scaled by  $\lambda_\uparrow$  and  $\lambda_\downarrow$ , respectively. The prefactor  $\lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}}$  is to keep the normalization of the coordinate-scaled wave function fixed. The coordinate-scaled densities in Eq. (35) are

$$\begin{aligned}\rho_\uparrow^{\lambda_\uparrow}(\mathbf{r}) &= \rho_\uparrow^{\lambda_\uparrow}(x, y, z) = \lambda_\uparrow^3 \rho_\uparrow(\lambda_\uparrow x, \lambda_\uparrow y, \lambda_\uparrow z), \\ \rho_\downarrow^{\lambda_\downarrow}(\mathbf{r}) &= \rho_\downarrow^{\lambda_\downarrow}(x, y, z) = \lambda_\downarrow^3 \rho_\downarrow(\lambda_\downarrow x, \lambda_\downarrow y, \lambda_\downarrow z).\end{aligned}\quad (36)$$

At  $\lambda_\uparrow = \lambda_\downarrow = 1$ , the inequality in Eq. (35) becomes the equality in Eq. (5).

The Oliver-Perdew relations of the kinetic and exchange parts [19] follow from Eqs. (16)–(18), and Eqs. (26) and (27),

$$\begin{aligned}T_s[\rho_\uparrow, \rho_\downarrow] &= \frac{1}{2}\{T_s[\rho_\uparrow, \rho_\uparrow] + T_s[\rho_\downarrow, \rho_\downarrow]\} \\ &= \frac{1}{2}\{T_{s,\uparrow}[2\rho_\uparrow] + T_{s,\downarrow}[2\rho_\downarrow]\},\end{aligned}\quad (37)$$

and

$$\begin{aligned}E_x[\rho_\uparrow, \rho_\downarrow] &= \frac{1}{2}\{E_x[\rho_\uparrow, \rho_\uparrow] + E_x[\rho_\downarrow, \rho_\downarrow]\} \\ &= \frac{1}{2}\{E_{x,\uparrow}[2\rho_\uparrow] + E_{x,\downarrow}[2\rho_\downarrow]\}.\end{aligned}\quad (38)$$

Magyar *et al.* [20] used the Oliver-Perdew relation for the exchange in Eq. (38) to obtain the following spin-dependent coordinate scaling equation:

$$E_x[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow] = \frac{1}{2}\{\lambda_\uparrow E_x[\rho_\uparrow, \rho_\uparrow] + E_x[\rho_\downarrow, \rho_\downarrow]\}.\quad (39)$$

Simple spin-dependent coordinate scaling generalizations of Eq. (39) based on the Oliver-Perdew relations in Eqs. (37) and (38) are

$$T_s[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow^{\lambda_\downarrow}] = \lambda_\uparrow^2 T_{s,\uparrow}[\rho_\uparrow^{\lambda_\uparrow}] + \lambda_\downarrow^2 T_{s,\downarrow}[\rho_\downarrow^{\lambda_\downarrow}],\quad (40)$$

and

$$E_x[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow^{\lambda_\downarrow}] = \lambda_\uparrow E_{x,\uparrow}[\rho_\uparrow^{\lambda_\uparrow}] + \lambda_\downarrow E_{x,\downarrow}[\rho_\downarrow^{\lambda_\downarrow}].\quad (41)$$

Additionally, one can modify the basic operators of the Hamiltonian by spin-dependent coordinate scaling.

The most general coordinate scaling of the kinetic operator (together with a new scaling notation) is

$$\hat{T}^{(\lambda_\uparrow, \lambda_\downarrow)} = \hat{T}_\uparrow^{\lambda_\uparrow} + \hat{T}_\downarrow^{\lambda_\downarrow},\quad (42)$$

where

$$\hat{T}_\uparrow^{\lambda_\uparrow} = -\frac{1}{2} \sum_{i=1}^M \nabla_{\lambda_\uparrow \mathbf{r}_i}^2, \quad \hat{T}_\downarrow^{\lambda_\downarrow} = -\frac{1}{2} \sum_{i=M+1}^N \nabla_{\lambda_\downarrow \mathbf{r}_i}^2.\quad (43)$$

The most general coordinate scaling of the three spin components of the electron-electron repulsion operator (together with a new scaling notation) is

$$\hat{V}_{ee}^{(\lambda_\uparrow, \lambda_\downarrow)} = \hat{V}_{ee,\uparrow\uparrow}^{(\lambda_\uparrow, \lambda_\uparrow)} + \hat{V}_{ee,\uparrow\downarrow}^{(\lambda_\uparrow, \lambda_\downarrow)} + \hat{V}_{ee,\downarrow\downarrow}^{(\lambda_\downarrow, \lambda_\downarrow)},\quad (44)$$

where

$$\begin{aligned}\hat{V}_{ee,\uparrow\uparrow}^{(\lambda_\uparrow, \lambda_\uparrow)} &= \sum_{j>i}^M \sum_{i=1}^{M-1} \frac{1}{|\lambda_\uparrow \mathbf{r}_i - \lambda_\uparrow \mathbf{r}_j|}, \\ \hat{V}_{ee,\uparrow\downarrow}^{(\lambda_\uparrow, \lambda_\downarrow)} &= \sum_{j>i}^M \sum_{i=1}^{M-1} \frac{1}{|\lambda_\uparrow \mathbf{r}_i - \lambda_\downarrow \mathbf{r}_j|}, \\ \hat{V}_{ee,\downarrow\downarrow}^{(\lambda_\downarrow, \lambda_\downarrow)} &= \sum_{j>i}^M \sum_{i=1}^{M-1} \frac{1}{|\lambda_\downarrow \mathbf{r}_i - \lambda_\downarrow \mathbf{r}_j|},\end{aligned}\quad (45)$$

for nonzero values of  $\lambda_\uparrow$  and  $\lambda_\downarrow$ .

Define  $\Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, (\lambda_\uparrow, \lambda_\downarrow)}$  as the wave function, which yields  $(\rho_\uparrow, \rho_\downarrow)$  and minimizes  $\langle \hat{T}^{(\lambda_\uparrow, \lambda_\downarrow)} + \hat{V}_{ee}^{(\lambda_\uparrow, \lambda_\downarrow)} \rangle$ , while  $\lambda_\uparrow$  and  $\lambda_\downarrow$  are held fixed. With the above convenient notation, one can derive a generalization of the basic coordinate-scaling equality from Ref. [10],

$$F[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow^{\lambda_\downarrow}] = \langle \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, (\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} | \hat{T}^{(\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} + \hat{V}_{ee}^{(\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} | \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, (\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} \rangle,\quad (46)$$

where  $\Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min, (\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})}$  is the wave function, which yields  $(\rho_\uparrow, \rho_\downarrow)$  and minimizes  $\langle \hat{T}^{(\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} + \hat{V}_{ee}^{(\frac{1}{\lambda_\uparrow}, \frac{1}{\lambda_\downarrow})} \rangle$ , while  $\lambda_\uparrow$  and  $\lambda_\downarrow$  are held fixed.

## VII. GENERALIZED ADIABATIC CONNECTION

The universal functional can also be generalized to

$$\begin{aligned}F_{(\gamma_1, \gamma_2, \gamma_3)}[\rho_\uparrow, \rho_\downarrow] &= \min_{\Psi \rightarrow (\rho_\uparrow, \rho_\downarrow)} \langle \Psi | \hat{T} + \gamma_1 \hat{V}_{ee,\uparrow\uparrow} + \gamma_2 \hat{V}_{ee,\uparrow\downarrow} + \gamma_3 \hat{V}_{ee,\downarrow\downarrow} | \Psi \rangle \\ &= \langle \Psi_{(\gamma_1, \gamma_2, \gamma_3), (\rho_\uparrow, \rho_\downarrow)}^{\min} | \hat{T} + \gamma_1 \hat{V}_{ee,\uparrow\uparrow} + \gamma_2 \hat{V}_{ee,\uparrow\downarrow} + \gamma_3 \hat{V}_{ee,\downarrow\downarrow} | \Psi_{(\gamma_1, \gamma_2, \gamma_3), (\rho_\uparrow, \rho_\downarrow)}^{\min} \rangle,\end{aligned}\quad (47)$$

where  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  are three adiabatic-connection parameters, instead of just one as in Eq. (11).

The following equality establishes a link between the spin-dependent coordinate scaling and the generalized adiabatic connection:

$$\langle \lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}} \Psi(\lambda_\uparrow \mathbf{r}_1, \lambda_\uparrow \mathbf{r}_2, \dots, \lambda_\uparrow \mathbf{r}_M; \lambda_\downarrow \mathbf{r}_{M+1}, \lambda_\downarrow \mathbf{r}_{M+2}, \dots, \lambda_\downarrow \mathbf{r}_N) | \hat{V}_{ee,\uparrow\uparrow} + \hat{V}_{ee,\uparrow\downarrow} + \hat{V}_{ee,\downarrow\downarrow}$$

$$\begin{aligned}
& \times \left| \lambda_{\uparrow}^{\frac{3M}{2}} \lambda_{\downarrow}^{\frac{3(N-M)}{2}} \Psi(\lambda_{\uparrow} \mathbf{r}_1, \lambda_{\uparrow} \mathbf{r}_2, \dots, \lambda_{\uparrow} \mathbf{r}_M; \lambda_{\downarrow} \mathbf{r}_{M+1}, \lambda_{\downarrow} \mathbf{r}_{M+2}, \dots, \lambda_{\downarrow} \mathbf{r}_N) \right\rangle \\
& = \langle \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N) | \lambda_{\uparrow} \hat{V}_{ee, \uparrow\uparrow} + \hat{V}_{ee, \uparrow\downarrow}^{\left(\frac{1}{\lambda_{\uparrow}}, \frac{1}{\lambda_{\downarrow}}\right)} + \lambda_{\downarrow} \hat{V}_{ee, \downarrow\downarrow} | \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N) \rangle. \quad (48)
\end{aligned}$$

The scaling parameters  $\lambda_{\uparrow}$  and  $\lambda_{\downarrow}$  from the left-hand side of Eq. (48) effectively become the adiabatic-connection parameters  $\gamma_1$  and  $\gamma_3$  on the right-hand side of Eq. (48).

### VIII. POSSIBLE EXTENSIONS

In the framework of the current density functional theory (CDFT) [21], where the universal functional is  $F[\rho, \vec{j}]$ , with  $\rho(\mathbf{r})$  and  $\vec{j}(\mathbf{r})$  being the total density and current density, the traditional non-spin-dependent coordinate scaling has already been applied [22]. The spin-dependent coordinate scaling approach presented in this article can be similarly extended and used in the framework of the spin-dependent current density functional theory (SCDFT) [23,24], in which the universal functional  $F[\rho_{\uparrow}, \vec{j}_{\uparrow}, \rho_{\downarrow}, \vec{j}_{\downarrow}]$  depends on the up- and down-spin pairs of densities  $\rho_{\uparrow}(\mathbf{r})$ ,  $\rho_{\downarrow}(\mathbf{r})$  and current densities  $\vec{j}_{\uparrow}(\mathbf{r})$ ,  $\vec{j}_{\downarrow}(\mathbf{r})$ , respectively.

The traditional coordinate scaling has already been applied to both the time-dependent density functional theory (TDDFT) [25] and time-dependent current density functional theory (TDCDFT) [26]. The spin-dependent coordinate scaling can also be extended to the spin-dependent versions of TDDFT and TDCDFT.

The application of the spin-dependent coordinate scaling to the spin-dependent version of Mermin's thermal DFT and its generalizations [27] is another possible extension.

### IX. CONCLUSIONS

We have partitioned the universal spin-density functional into its spin-dependent components, accordingly generalized the adiabatic connection, and related the generalized adiabatic connection to spin-dependent coordinate scaling.

The kinetic and electron-electron repulsion terms of the universal functional, and as a result the exchange and correlation terms, are naturally split into spin components. Explicit

forms of the spin-dependent components of the correlation energy are presented. Constrained-search derivations of the Oliver-Perdew relations for the kinetic and exchange terms are presented. The up-down spin component of the correlation term is found to contain the up-down spin component of the Hartree term. The part of the correlation term that excludes the up-down component of the Hartree term is proposed as the main target of approximations. It is assumed that the explicit partitioning of the correlation term into spin-dependent components and the possibility of omitting the explicit up-down Hartree component will shed a light on the approximation process. A spin-dependent generalization of the adiabatic connection is put forth and a link with spin-dependent coordinate scaling is established for the correlation energy.

The main advantage of the spin-free approach to SDFT is the ease of conceiving and proving new relations. Although all the derivation presented in the article could have been established and proven within the conventional approach, some of the explicit expressions presented in the article, regardless of their simplicity, are nevertheless useful but would have been difficult to guess or derive without the spin-free approach.

The approach described in this work provides a convenient foundation for deriving further scaling and adiabatic-connection constraints that are important for density-functional approximations.

### ACKNOWLEDGMENTS

M.L. thanks the Julian Schwinger Foundation for support. M.S.G. and F.Z. acknowledge support from the Ames Laboratory Chemical Physics program, US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. The authors thank Kieron Burke and Berthold-George Englert for very helpful comments.

### APPENDIX

The ensemble density matrix  $\hat{D}$  is

$$\hat{D}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N) = \sum_{i=1}^{\infty} p_i \Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N) \Psi_i^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N), \quad (A1)$$

where all the wave functions  $\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \mathbf{r}_{M+2}, \dots, \mathbf{r}_N)$  are normalized and, although some of the coefficients  $p_i \geq 0$  may be zero, it is assumed that

$$\sum_{i=1}^{\infty} p_i = 1 \quad (A2)$$



for total normalization purposes, where the normalization is

$$\text{Tr}[\hat{D}] = \sum_{i=1}^{\infty} p_i \int \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_M d\mathbf{r}_{M+1} \cdots d\mathbf{r}_N = 1. \quad (\text{A3})$$

The universal spin-density functional by the ensemble constrained search is

$$F_\lambda[\rho_\uparrow, \rho_\downarrow] = \min_{\hat{D} \rightarrow (\rho_\uparrow, \rho_\downarrow)} \text{Tr}[(\hat{T} + \lambda \hat{V}_{ee}) \hat{D}], \quad (\text{A4})$$

where

$$\text{Tr}[(\hat{T} + \lambda \hat{V}_{ee}) \hat{D}] = \sum_{i=1}^{\infty} p_i \int \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) (\hat{T} + \lambda \hat{V}_{ee}) \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_M d\mathbf{r}_{M+1} \cdots d\mathbf{r}_N, \quad (\text{A5})$$

and  $\hat{D} \rightarrow (\rho_\uparrow, \rho_\downarrow)$  means that

$$\begin{aligned} \rho_\uparrow(\mathbf{r}) &= \sum_{i=1}^{\infty} p_i \int \Psi_i^*(\mathbf{r}, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_i(\mathbf{r}, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_M d\mathbf{r}_{M+1} \cdots d\mathbf{r}_N, \\ \rho_\downarrow(\mathbf{r}) &= \sum_{i=1}^{\infty} p_i \int \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}, \dots, \mathbf{r}_N) \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}, \dots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_M d\mathbf{r}_{M+2} \cdots d\mathbf{r}_N. \end{aligned} \quad (\text{A6})$$

In the noninteracting case  $\lambda = 0$ , due to the split of the kinetic operator in Eq. (13), Eq. (A4) can be simplified as

$$\begin{aligned} T[\rho_\uparrow, \rho_\downarrow] &= \min_{\hat{D} \rightarrow (\rho_\uparrow, \rho_\downarrow)} \text{Tr}[\hat{T} \hat{D}] = \min_{\hat{D} \rightarrow (\rho_\uparrow, \rho_\downarrow)} \{\text{Tr}[\hat{T}_\uparrow \hat{D}_\uparrow] + \text{Tr}[\hat{T}_\downarrow \hat{D}_\downarrow]\} \\ &= \min_{\hat{D}_\uparrow \rightarrow \rho_\uparrow} \text{Tr}[\hat{T}_\uparrow \hat{D}_\uparrow] + \min_{\hat{D}_\downarrow \rightarrow \rho_\downarrow} \text{Tr}[\hat{T}_\downarrow \hat{D}_\downarrow] = T_\uparrow[\rho_\uparrow] + T_\downarrow[\rho_\downarrow], \end{aligned} \quad (\text{A7})$$

where the normalized up- and down-spin ensemble density matrices are

$$\begin{aligned} \hat{D}_\uparrow(\mathbf{r}_1, \dots, \mathbf{r}_M) &= \sum_{i=1}^{\infty} p_i \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_M) \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_M), \\ \hat{D}_\downarrow(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) &= \sum_{i=1}^{\infty} p_i \Psi_i^*(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_i(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N), \end{aligned} \quad (\text{A8})$$

and

$$\begin{aligned} \text{Tr}[\hat{T}_\uparrow \hat{D}_\uparrow] &= \sum_{i=1}^{\infty} p_i \int \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_M) \hat{T}_\uparrow \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_M) d\mathbf{r}_1 \cdots d\mathbf{r}_M, \\ \text{Tr}[\hat{T}_\downarrow \hat{D}_\downarrow] &= \sum_{i=1}^{\infty} p_i \int \Psi_i^*(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \hat{T}_\downarrow \Psi_i(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_{M+1} \cdots d\mathbf{r}_N, \end{aligned} \quad (\text{A9})$$

and  $\hat{D}_\uparrow \rightarrow \rho_\uparrow$  and  $\hat{D}_\downarrow \rightarrow \rho_\downarrow$  mean, respectively,

$$\begin{aligned} \rho_\uparrow(\mathbf{r}) &= \sum_{i=1}^{\infty} p_i \int \Psi_i(\mathbf{r}, \dots, \mathbf{r}_M) \Psi_i^*(\mathbf{r}, \dots, \mathbf{r}_M) d\mathbf{r}_2 \cdots d\mathbf{r}_M, \\ \rho_\downarrow(\mathbf{r}) &= \sum_{i=1}^{\infty} p_i \int \Psi_i(\mathbf{r}, \dots, \mathbf{r}_N) \Psi_i^*(\mathbf{r}, \dots, \mathbf{r}_N) d\mathbf{r}_{M+2} \cdots d\mathbf{r}_N, \end{aligned} \quad (\text{A10})$$

From the above, it follows that the minimizing ensemble of  $T[\rho_\uparrow, \rho_\downarrow]$  and the minimizing ensembles of  $T_\uparrow[\rho_\uparrow]$  and  $T_\downarrow[\rho_\downarrow]$  are related in the following ways.

Denote

$$\begin{aligned}\hat{D}_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) &= \sum_{i=1}^{\infty} p_i \Psi_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_{(\rho_\uparrow, \rho_\downarrow), i}^{\min*}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N), \\ \hat{D}_{\rho_\uparrow}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M) &= \sum_{i=1}^{\infty} p_i \Psi_{\rho_\uparrow, i}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M) \Psi_{\rho_\uparrow, i}^{\min*}(\mathbf{r}_1, \dots, \mathbf{r}_M), \\ \hat{D}_{\rho_\downarrow}^{\min}(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) &= \sum_{i=1}^{\infty} p_i \Psi_{\rho_\downarrow, i}^{\min}(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_{\rho_\downarrow, i}^{\min*}(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N),\end{aligned}\tag{A11}$$

such that

$$T[\rho_\uparrow, \rho_\downarrow] = \min_{\hat{D} \rightarrow (\rho_\uparrow, \rho_\downarrow)} \text{Tr}[\hat{T} \hat{D}] = \text{Tr}[\hat{T} \hat{D}_{(\rho_\uparrow, \rho_\downarrow)}^{\min}],\tag{A12}$$

and

$$\begin{aligned}T_\uparrow[\rho_\uparrow] &= \min_{\hat{D}_\uparrow \rightarrow \rho_\uparrow} \text{Tr}[\hat{T}_\uparrow \hat{D}_\uparrow] = \text{Tr}[\hat{T}_\uparrow \hat{D}_{\rho_\uparrow}^{\min}], \\ T_\downarrow[\rho_\downarrow] &= \min_{\hat{D}_\downarrow \rightarrow \rho_\downarrow} \text{Tr}[\hat{T}_\downarrow \hat{D}_\downarrow] = \text{Tr}[\hat{T}_\downarrow \hat{D}_{\rho_\downarrow}^{\min}].\end{aligned}\tag{A13}$$

It can be inferred from Eq. (A7) that

$$\begin{aligned}\hat{D}_{\rho_\uparrow}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M) &= \int \hat{D}_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_{M+1}, \dots, d\mathbf{r}_N, \\ \hat{D}_{\rho_\downarrow}^{\min}(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) &= \int \hat{D}_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) d\mathbf{r}_1, \dots, d\mathbf{r}_M.\end{aligned}\tag{A14}$$

It further follows that

$$\hat{D}_{(\rho_\uparrow, \rho_\downarrow)}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M; \mathbf{r}_{M+1}, \dots, \mathbf{r}_N) = \hat{D}_{\rho_\uparrow}^{\min}(\mathbf{r}_1, \dots, \mathbf{r}_M) \hat{D}_{\rho_\downarrow}^{\min}(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N).\tag{A15}$$

The validity of Eq. (A15) can be double checked by a direct substitution in Eq. (A7).

- 
- [1] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).  
[2] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).  
[3] J. K. Percus, *Int. J. Quantum Chem.* **13**, 89 (1978).  
[4] M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979).  
[5] M. Levy, *Phys. Rev. A* **26**, 1200 (1982).  
[6] E. H. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).  
[7] M. Levy and J. P. Perdew, *Phys. Rev. A* **32**, 2010 (1985).  
[8] J. P. Perdew, A. Ruzsinszky, and J. Tao, *J. Chem. Phys.* **123**, 062201 (2005).  
[9] J. P. Perdew, A. Ruzsinszky, J. Sun, and K. Burke, *J. Chem. Phys.* **140**, 18A533 (2014).  
[10] F. Zahariev and M. Levy, *Phys. Rev. A* **100**, 062507 (2019).  
[11] U. von Barth, L. Hedin, *J. Phys. C* **4** 1629 (1972).  
[12] C. R. Jacob, M. Reiher, *Int. J. Quantum Chem.* **112**, 3661 (2012).  
[13] D. C. Langreth and J. P. Perdew, *Solid. State Commun.* **17**, 1425 (1975).  
[14] O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).  
[15] J. Harris, *Phys. Rev. A* **29**, 1648 (1984).  
[16] F. Zahariev, M. S. Gordon, and M. Levy, *Phys. Rev. A* **98**, 012144 (2018).  
[17] R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic Press, New York, 1989).  
[18] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, *Phys. Rev. Lett.* **60**, 1719 (1988).  
[19] G. L. Oliver and J. P. Perdew, *Phys. Rev. A* **20**, 397 (1979).  
[20] R. J. Magyar, T. K. Whittingham, and K. Burke, *Phys. Rev. A* **66**, 022105 (2002).  
[21] G. Vignale and M. Rasolt, *Phys. Rev. Lett.* **59**, 2360 (1987).  
[22] S. Erhard and E. K. U. Gross, *Phys. Rev. A* **53**, R5 (1996).  
[23] G. Vignale and M. Rasolt, *Phys. Rev. B* **37**, 10685 (1988); Erratum: **39**, 5475 (1989).  
[24] E. Trushin and A. Gorling, *Phys. Rev. B* **98**, 205137 (2018).  
[25] P. Hessler, J. Park, and K. Burke, *Phys. Rev. Lett.* **82**, 378 (1999).  
[26] M. Dion and K. Burke, *Phys. Rev. A* **72**, 020502(R) (2005).  
[27] S. Pittalis, C. R. Proetto, A. Floris, A. Sanna, C. Bersier, K. Burke, and E. K. U. Gross, *Phys. Rev. Lett.* **107**, 163001 (2011).