PHYSICAL REVIEW A **100**, 062507 (2019)

Density- and spin-density-functional theories through spin-free wave functions

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(Received 18 August 2019; published 13 December 2019; corrected 25 June 2020)

It is proven that entirely spin-free wave functions can be utilized in the basic definitions of the universal functionals in density-functional theory and spin-density-functional theory. Then, for the purpose of approximating these functionals, it is shown that the knowledge of certain properties of the functionals, such as those involving the coordinate scaling of just one of the spin densities, is made feasible precisely because the wave functions in the functional definitions are free of explicit spins. Among the examples, a conjectured spin-density scaling relation for the correlation energy is studied.

DOI: 10.1103/PhysRevA.100.062507

I. INTRODUCTION

Although density-functional theory (among the texts, see, for instance [1–3]) simplifies the many-electron problem for computations by replacing complicated wave functions with functionals of the much simpler three-dimensional electron densities and spin-densities, wave functions have clearly played starring roles in establishing the existence of exact energy functionals and for finding ways to approximate them. With this in mind, we shall show that spin-free wave functions may be nicely used for these purposes. In fact, the understanding of how functionals are supposed to behave when individual spin densities change is made much easier through the employment of spin-free wave functions. By “spin-free wave function” we mean $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M; \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$, where the first M coordinates are associated with the up-spin electrons and the last (N-M) coordinates are associated with the down-spin electrons, and where this wave function is antisymmetric in the first M coordinates and is antisymmetric in the last (N-M) coordinates.

In density-functional theory, the ground state energy E_{GS} and corresponding density $\rho_{\mathrm{gs}}(\boldsymbol{r})$, for the attractive potential $v(\boldsymbol{r})$, are given by

$$E_{\mathrm{GS}} = \min_{\rho}\left\{\int v(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + F[\rho]\right\} = \int v(\boldsymbol{r})\rho_{\mathrm{gs}}(\boldsymbol{r})d\boldsymbol{r} + F[\rho_{\mathrm{gs}}], \tag{1}$$

where the universal functional [4] in its generalized constrained-search form [5,6] is

$$F[\rho] = \min_{\Psi\to\rho}\{\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle\}, \tag{2}$$

and where the kinetic part of the Hamiltonian is $\hat{T} = -\frac{1}{2}\sum_{1\leqslant i\leqslant N}\nabla_i^2$ and the electron-electron repulsion part of the Hamiltonian is $\hat{V}_{ee} = \sum_{1\leqslant i<j\leqslant N}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$.

Further, we now observe that

$$F[\rho] = \min_{\rho_\uparrow+\rho_\downarrow=\rho} F[\rho_\uparrow, \rho_\downarrow], \tag{3}$$

where $\rho_\uparrow(\boldsymbol{r})$ and $\rho_\downarrow(\boldsymbol{r})$ are up- and down-spin densities, such that

$$\rho(\boldsymbol{r}) = \rho_\uparrow(\boldsymbol{r}) + \rho_\downarrow(\boldsymbol{r}), \tag{4}$$

and where, of course,

$$F[\rho_\uparrow, \rho_\downarrow] = \min_{\Psi\to(\rho_\uparrow,\rho_\downarrow)}\{\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle\}. \tag{5}$$

[Alternatively, wave functions can be replaced by ensemble density matrices in expressions (2) and (5), where traces would replace expectation values.]

If the external potential contains spin-dependent contributions, such as with magnetism in spin-density functional theory, then [7,8]

$$E_{\mathrm{GS}} = \min_{\rho_\uparrow,\rho_\downarrow}\left\{\int v(\boldsymbol{r})[\rho_\uparrow(\boldsymbol{r}) + \rho_\downarrow(\boldsymbol{r})]d\boldsymbol{r} + \int v_\uparrow(\boldsymbol{r})\rho_\uparrow(\boldsymbol{r})d\boldsymbol{r} + \int v_\downarrow(\boldsymbol{r})\rho_\downarrow(\boldsymbol{r})d\boldsymbol{r} + F[\rho_\uparrow, \rho_\downarrow]\right\}. \tag{6}$$

The $F[\rho]$, in expressions (2) and (3), and the $F[\rho_\uparrow, \rho_\downarrow]$, in expressions (3) and (5), must be approximated for practical electronic structure calculations. For this purpose, exact properties (constraints) of these functionals, such as equalities and inequalities involving coordinate scaling, adiabatic-connection relations, and asymptotic limits have been first derived and then approximations to these functionals have been constructed to satisfy as many of the known properties (constraints) as feasible.

The traditional spin-wave functions in functional definitions (2) and (5), which have been utilized for functional property derivations, have contained spin coordinates as well

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as spatial coordinates. However, for the derivation of certain important properties, such as those involving the coordinate scaling of individual spin-densities in $F[\rho_\uparrow, \rho_\downarrow]$ and $F[\rho]$ and in their components, we have come to the realization that it is *greatly beneficial to employ spin-free wave functions* in the definitions, even when the external potential contains spin-dependent contributions.

However, is the use of spin-free wave functions allowed? As we shall show, the answer is yes. Then we shall illustrate how the use of these spin-free wave functions allows for the derivations of exact properties of $F[\rho_\uparrow, \rho_\downarrow]$ and $F[\rho]$ that would otherwise be difficult to derive because of the indistinguishability of all of the electrons in fully antisymmetric spin-wave functions.

II. EQUIVALENCE OF SPIN-FREE AND CONVENTIONAL DEFINITIONS OF $F[\rho_\uparrow, \rho_\downarrow]$

We present below two constrained-search definitions of the universal functional $F[\rho_\uparrow, \rho_\downarrow]$ and prove their equivalence. The first is the conventional one that is based on the use of spin-wave functions, while the new one is based on the use of purely spatial (spin-free) wave functions.

A. Conventional definition

$$\begin{aligned}F[\rho_\uparrow, \rho_\downarrow] &= \min_{\Psi\to(\rho_\uparrow,\rho_\downarrow)} \langle \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\rangle_x \\ &= \left\langle \Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\middle|\hat{T} + \hat{V}_{ee}\middle|\Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\right\rangle_x, \end{aligned} \tag{7}$$

where each spin-wave function

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N), \quad \boldsymbol{x}_i = (\boldsymbol{r}_i, s_i), \tag{8}$$

depends on both the spatial coordinates $\boldsymbol{r}_i$ and spin variables s_i, and Ψ is a function that is antisymmetric in the interchange of any of the $\boldsymbol{x}$ variables and normalized to unity. The corresponding (kinetic + electron-electron repulsion) energy expectation value for each Ψ in expression (7) is given by

$$\begin{aligned}&\langle \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\rangle_x \\ &= \sum_{s_1,s_2,\ldots,s_N=-\frac{1}{2},\frac{1}{2}} \int \Psi^*(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N)(\hat{T} + \hat{V}_{ee})\Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N,\end{aligned} \tag{9}$$

where $-\frac{1}{2}$ and $\frac{1}{2}$ correspond to “down” and “up” spins, and the spin-wave functions in Eq. (7) yield the same set of up- and down-spin densities, given by

$$\begin{aligned}\rho_\uparrow(\boldsymbol{r}) &= N \sum_{s_2,\ldots,s_N=-\frac{1}{2},\frac{1}{2}} \int \left|\Psi\left(\boldsymbol{r}, \frac{1}{2}, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)\right|^2 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N, \\ \rho_\downarrow(r) &= N \sum_{s_2,\ldots,s_N=-\frac{1}{2},\frac{1}{2}} \int \left|\Psi\left(\boldsymbol{r}, -\frac{1}{2}, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)\right|^2 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N.\end{aligned} \tag{10}$$

B. Spin-free definition

$$\begin{aligned}\tilde{F}[\rho_\uparrow, \rho_\downarrow] &= \min_{\Psi\to(\rho_\uparrow,\rho_\downarrow)} \langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r \\ &= \left\langle \Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\middle|\hat{T} + \hat{V}_{ee}\middle|\Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\right\rangle_r,\end{aligned} \tag{11}$$

where each spatial (spin-free) wave function

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \tag{12}$$

is antisymmetric in the first M coordinates and is antisymmetric in the last (N-M) coordinates, and is normalized to unity.

The corresponding (kinetic + electron-electron repulsion) energy expectation value for each Ψ in expression (11) is given by

$$\begin{aligned}&\langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r \\ &= \int \Psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)(\hat{T} + \hat{V}_{ee})\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \\ &\quad \times d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_M d\boldsymbol{r}_{M+1} d\boldsymbol{r}_{M+2} \cdots d\boldsymbol{r}_N,\end{aligned} \tag{13}$$

where the above Dirac bracket differs from the one in expression (9), and all the spin-free wave functions in Eq. (11) yield the same set of up- and down-spin densities, given by

$$\rho_\uparrow(\boldsymbol{r}) = M\int |\Psi(\boldsymbol{r},\ldots,\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1},\ldots,\boldsymbol{r}_N)|^2 d\boldsymbol{r}_2,\ldots,d\boldsymbol{r}_M d\boldsymbol{r}_{M+1},\ldots,d\boldsymbol{r}_N,$$
$$\rho_\downarrow(\boldsymbol{r}) = (N-M)\int |\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_M;\ \boldsymbol{r},\ldots,\boldsymbol{r}_N)|^2 d\boldsymbol{r}_1,\ldots,d\boldsymbol{r}_M d\boldsymbol{r}_{M+2},\ldots,d\boldsymbol{r}_N. \quad (14)$$

Theorem. The spin-free definition of $\tilde{F}[\rho_\uparrow,\rho_\downarrow]$ equals the conventional definition of $F[\rho_\uparrow,\rho_\downarrow]$, when the spin densities in expression (14) are the same as those in expression (10).

Proof. The spin-wave function with $M = N_\uparrow$ (up-spin) and $N - M = N_\downarrow$ (down-spin) electrons ($N = N_\uparrow + N_\downarrow$) can be expanded into a sum of space-spin products as [9,10]

$$\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) = \sum_{i=1}^{K} G_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\zeta_i(s_1,s_2,\ldots,s_N). \quad (15)$$

The spin functions $\zeta_i(s_1,s_2,\ldots,s_N)$ are orthonormal, where the first spin function, which is associated with $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$, is conveniently chosen to be

$$\zeta_1(s_1,s_2,\ldots,s_N) = \alpha(s_1)\cdots\alpha(s_{N_\uparrow})\beta(s_{N_\uparrow+1})\cdots\beta(s_N). \quad (16)$$

The upper limit in the sum of Eq. (15) is $K = \frac{N!}{N_\uparrow! N_\downarrow!}$. [$K = \frac{N!}{N_\uparrow! N_\downarrow!}$ results from the fact that, in general, there are $N!$ possibilities of ordering the N terms on the right-hand side of Eq. (16). But since all the $N_\uparrow!$ possibilities of ordering the $N_\uparrow$ terms of type $\alpha(s_i)$ and all the $N_\downarrow!$ possibilities of ordering the $N_\downarrow$ terms of type $\beta(s_i)$ are equivalent, $N!$ has to be divided by $N_\uparrow!$ times $N_\downarrow!$.]

From the antisymmetry of the spin-wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$, it follows that all the spatial functions $G_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ are equivalent to $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$, after relabeling of indices and a possible change of sign. From the same argument, it also follows that each $G_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is antisymmetric in the interchange of like-spin coordinates.

In the following, we first observe that there is a one-to-one correspondence between the first spatial component $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ and the full spin-wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$. Then we show that the $\hat{T}+\hat{V}_{ee}$ expectation values of the appropriately normalized $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ and $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ equal each other. Further, we shall show that the spin densities of the two wave functions are also equal, according to the given in the formulation of the theorem. Finally, since there is a one-to-one correspondence between the two wave functions yielding the same spin densities as well as the $\hat{T}+\hat{V}_{ee}$ expectation value at every point in the minimization processes, their respective minima are, clearly, also equivalent.

On the one hand, since the spin functions $\{\zeta_i(s_1,s_2,\ldots,s_N)\}$ form an orthonormal set, it follows that $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ can be projected from $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ through

$$\sum_{s_1,s_2,\ldots,s_N} \zeta_1(s_1,s_2,\ldots,s_N)\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) = G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N). \quad (17)$$

The utility of this mapping from $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ to $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ will be evident later for expectation values of operators that are independent of spin.

On the other hand, the spin-wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ on the left-hand side of expression (15) can be obtained by antisymmetrization of any component in the sum on the right-hand side of this expression. In particular, antisymmetrization of the first component gives

$$A\{G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\zeta_1(s_1,s_2,\ldots,s_N)\} = \sum_{i=1}^{K} G_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\zeta_i(s_1,s_2,\ldots,s_N) = \Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N). \quad (18)$$

Expressions (17) and (18) establish a one-to-one correspondence between the spin-wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ and its first spatial component $G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$. That is,

$$\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) \leftrightarrow \sqrt{K}G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N). \quad (19)$$

Thus, the normalized first spatial component $\sqrt{K}G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is equated with the spin-free wave function $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1},\boldsymbol{r}_{M+2},\ldots,\boldsymbol{r}_N)$ in the spin-free definition of $\tilde{F}[\rho_\uparrow,\rho_\downarrow]$,

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1},\boldsymbol{r}_{M+2},\ldots,\boldsymbol{r}_N) = \sqrt{K}G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N). \quad (20)$$

Indeed, $\sqrt{K}G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is a function that is antisymmetric in the first M, or $N_\uparrow$, coordinates and in the last $(N-M)$, or $N_\downarrow$, coordinates. Also, $\sqrt{K}G_1(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is normalized to unity.

We now show that the expectation value of $\hat{T}+\hat{V}_{ee}$ in Eq. (9), with $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ given by Eq. (15), equals the expectation value of $\hat{T}+\hat{V}_{ee}$ in Eq. (13), with $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1},\boldsymbol{r}_{M+2},\ldots,\boldsymbol{r}_N)$ given by Eq. (20). To prove the equality of expectation values, use is made of the fact that the *orthonormality of the spin functions*

$\zeta_i(s_1, s_2, \ldots, s_N)$ causes *the cross terms to vanish,*

$$
\begin{aligned}
&\langle\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\rangle_x \\
&= \sum_{s_1, s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int \Psi^*(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N)(\hat{T} + \hat{V}_{ee})\Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 ... d\boldsymbol{r}_N \\
&= \sum_{s_1, s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \sum_{i,j=1}^{K} \int G_i^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\zeta_i(s_1, s_2, \ldots, s_N)(\hat{T} + \hat{V}_{ee})G_j(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\zeta_j(s_1, s_2, \ldots, s_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= \sum_{i=1}^{K} \int G_i^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)(\hat{T} + \hat{V}_{ee})G_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N, \\
&= K \int G_1^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)(\hat{T} + \hat{V}_{ee})G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= \int [\sqrt{K} G_1^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)](\hat{T} + \hat{V}_{ee})[\sqrt{K} G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)]d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= \langle\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M; \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M; \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r, \qquad (21)
\end{aligned}
$$

where use is also made of the fact that each $G_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ differs from $G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ by an antisymmetric interchange of coordinates corresponding to the like-spin electrons.

For other purposes, instead of $\hat{T} + \hat{V}_{ee}$, *other spin-free operators* could be used in Eq. (21), including just $\hat{T}$, $\hat{V}_{ee}$, or $\hat{I}$. In the latter case the equivalence of normalizations is established.

Next, we prove that $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$, as given by Eq. (15), and the corresponding $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$, as given by Eq. (20), yield the same spin densities, through Eqs. (10) and (14), respectively. We accomplish this by starting with the definition of spin densities in Eq. (10) and transform it in a multistep fashion to the definition of the spin densities in Eq. (14).

First, on the right-hand side of the definition of the up-spin density in Eq. (10), replace $\Psi(\boldsymbol{r}, \frac{1}{2}, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N)$ with the expansion terms of Eq. (15) that all start with $\alpha(s_1)$ in their spin components $\zeta_i(s_1, s_2, \ldots, s_N)$, as the choice of $s_1 = \frac{1}{2}$ requires. Also, use the orthonormality of the spin components $\zeta_i(s_1, s_2, \ldots, s_N)$ as well as the fact that each spatial component $G_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ is equivalent to $G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ up to an antisymmetric interchange of coordinates, to obtain

$$
N \sum_{s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int \left|\Psi\left(\boldsymbol{r}, \frac{1}{2}, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)\right|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N = N\left\{\frac{KM}{N} \int |G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N\right\}. \qquad (22)
$$

Notice that there are $\frac{(N-1)!}{(N_\uparrow - 1)!N_\downarrow!} = \frac{KN_\uparrow}{N} = \frac{KM}{N}$ terms in the above expansion. [The number of terms, where the first spin in each spin component $\zeta_i(s_1, s_2, \ldots, s_N)$ is fixed to spin-up $\alpha(s_1)$, is the same as the number of terms of $(N-1)$ electrons with $(N_\uparrow - 1)$ up- and $N_\downarrow$ down-spin electrons. Note the definition of K below Eq. (16).]

Next, further modify Eq. (22) by using Eq. (20),

$$
KM \int |G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N = M \int |\Psi(r, \ldots, \boldsymbol{r}_M; \boldsymbol{r}_{M+1}, \ldots, \boldsymbol{r}_N)|^2 d\boldsymbol{r}_2, \ldots, d\boldsymbol{r}_M d\boldsymbol{r}_{M+1}, \ldots, d\boldsymbol{r}_N. \qquad (23)
$$

Finally, observe that the right-hand side of Eq. (23) is equivalent to the definition of the up-spin density on the right-hand side of Eq. (14).

The equivalence of the down-spin definitions in Eqs. (10) and (14) proceeds in a similar manner, by first establishing

$$
\begin{aligned}
&N \sum_{s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int \left|\Psi\left(\boldsymbol{r}, -\frac{1}{2}, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)\right|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= N \sum_{s_1, \ldots, s_{N_\uparrow}, s_{N_\downarrow + 1}, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int \left|\Psi\left(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_{N_\uparrow}, s_{N_\uparrow}, \boldsymbol{r}, -\frac{1}{2}, \ldots, \boldsymbol{r}_N, s_N\right)\right|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_{N_\uparrow} d\boldsymbol{r}_{N_\uparrow + 1} d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N. \qquad (24)
\end{aligned}
$$

That is, the coordinate that is not integrated on the right-hand side of the down-spin definition in Eq. (10) is moved from the first position to the position that corresponds to the first down-spin electron in $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$. Further, proceed as in the up-spin density case.

We now proceed right to left in Eq. (21) and apply expression (18). We obtain that for every $\langle\hat{T} + \hat{V}_{ee}\rangle_r$, with a $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$, there is the same $\langle\hat{T} + \hat{V}_{ee}\rangle_x$, with the corresponding $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$.

That is,

$$\begin{aligned}
&\langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r \\
&= \sum_{s_1, s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int \sqrt{K} G_1^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\zeta_1(s_1, s_2, \ldots, s_N)(\hat{T} + \hat{V}_{ee})\sqrt{K} G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\zeta_1(s_1, s_2, \ldots, s_N) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= \sum_{s_1, s_2, \ldots, s_N = -\frac{1}{2}, \frac{1}{2}} \int A\{\sqrt{K} G_1^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\zeta_1(s_1, s_2, \ldots, s_N)\}(\hat{T} + \hat{V}_{ee}) A\{\sqrt{K} G_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \\
&\quad \times \zeta_1(s_1, s_2, \ldots, s_N)\} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \\
&= \langle \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\rangle_x.
\end{aligned} \tag{25}$$

The combination of expressions (21) and (25), and the fact that $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ and $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$ have the same spin densities, proves the desired result, which is of course,

$$\begin{aligned}
&\min_{\Psi \to (\rho_\uparrow, \rho_\downarrow)} \langle \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\rangle_x \\
&\quad = \min_{\Psi \to (\rho_\uparrow, \rho_\downarrow)} \langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r.
\end{aligned} \tag{26}$$

A generalization of the universal functional, where spin-free eignenfunctions of the spin operator $\hat{S}^2$ are used in the constrained search, is given in the Appendix.

The theorem and proof can be further generalized to ensemble density matrices in the constrained searches.

III. SPIN-DEPENDENT COORDINATE SCALING

Our observation that space only (spin-free) wave functions may be used in the constrained search, for the expectation value of $\hat{T} + \hat{V}_{ee}$, enables the derivation of constraints, such as those involved in coordinate scaling, for approximating $F[\rho_\uparrow, \rho_\downarrow]$ and its components in spin-density-functional theory. Along these lines, spin-dependent coordinate scaling for the correlation energy was introduced in Ref. [11], and the use of spin-free wave functions enables further significant progress.

As a fundamental example, we are now able to assert that

$$\begin{aligned}
F[\rho_\uparrow^\lambda, \rho_\downarrow] \leqslant \big\langle \lambda^{\frac{3M}{2}} \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}(\lambda \boldsymbol{r}_1, \lambda \boldsymbol{r}_2, \ldots, \lambda \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\big|\hat{T} \\
+ \hat{V}_{ee}\big|\lambda^{\frac{3M}{2}} \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}(\lambda \boldsymbol{r}_1, \lambda \boldsymbol{r}_2, \ldots, \lambda \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\big\rangle
\end{aligned} \tag{27}$$

follows from the reasoning [12–14] used in the study of the uniform scaling properties of $F[\rho]$. That is, the inequality in Eq. (27) arises from the fact that the scaled wave function on its right-hand side is not equal to $\Psi^{\min}_{(\rho_\uparrow^\lambda, \rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$, where

$$\rho_\uparrow^\lambda(\boldsymbol{r}) = \rho_\uparrow^\lambda(x, y, z) = \lambda^3 \rho_\uparrow(\lambda x, \lambda y, \lambda z). \tag{28}$$

More generally, we have

$$\begin{aligned}
F[\rho_\uparrow^{\lambda_\uparrow}, \rho_\downarrow^{\lambda_\downarrow}] \leqslant \big\langle \lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}} \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}(\lambda_\uparrow \boldsymbol{r}_1, \lambda_\uparrow \boldsymbol{r}_2, \ldots, \lambda_\uparrow \boldsymbol{r}_M;\ \lambda_\downarrow \boldsymbol{r}_{M+1}, \lambda_\downarrow \boldsymbol{r}_{M+2}, \ldots, \lambda_\downarrow \boldsymbol{r}_N)\big|\hat{T} \\
+ \hat{V}_{ee}\big|\lambda_\uparrow^{\frac{3M}{2}} \lambda_\downarrow^{\frac{3(N-M)}{2}} \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}(\lambda_\uparrow \boldsymbol{r}_1, \lambda_\uparrow \boldsymbol{r}_2, \ldots, \lambda_\uparrow \boldsymbol{r}_M;\ \lambda_\downarrow \boldsymbol{r}_{M+1}, \lambda_\downarrow \boldsymbol{r}_{M+2}, \ldots, \lambda_\downarrow \boldsymbol{r}_N)\big\rangle.
\end{aligned} \tag{29}$$

Further generalizations include the use of nonuniform scale factors for the x, y, z components of the up- and down-spin densities. But for the purposes here, inequality (27) should suffice.

Inequality (27) leads to

$$F[\rho_\uparrow^\lambda, \rho_\downarrow] \leqslant \lambda^2 T_\uparrow[\rho_\uparrow, \rho_\downarrow] + T_\downarrow[\rho_\uparrow, \rho_\downarrow] + \lambda V_{ee,\uparrow}[\rho_\uparrow, \rho_\downarrow] + V_{ee,\downarrow}[\rho_\uparrow, \rho_\downarrow] + N_\uparrow N_\downarrow \big\langle \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big|\frac{1}{|\frac{\boldsymbol{r}_1}{\lambda} - \boldsymbol{r}_N|}\big|\Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big\rangle, \tag{30}$$

where

$$T_\uparrow[\rho_\uparrow, \rho_\downarrow] = M\big\langle \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big|\hat{T}_1\big|\Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big\rangle, \tag{31}$$

$$T_\downarrow[\rho_\uparrow, \rho_\downarrow] = (N - M)\big\langle \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big|\hat{T}_N\big|\Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big\rangle, \tag{32}$$

$$V_{ee,\uparrow}[\rho_\uparrow, \rho_\downarrow] = \frac{M(M-1)}{2}\big\langle \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big|\frac{1}{|r_1 - r_2|}\big|\Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big\rangle, \tag{33}$$

$$V_{ee,\downarrow}[\rho_\uparrow, \rho_\downarrow] = \frac{(N-M)(N-M-1)}{2}\big\langle \Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big|\frac{1}{|r_{N-1} - r_N|}\big|\Psi^{\min}_{(\rho_\uparrow, \rho_\downarrow)}\big\rangle. \tag{34}$$

From inequality (30) and the corresponding one for $F[\rho_\uparrow, \rho_\downarrow^\lambda]$, it follows that

$$\lim_{\lambda\to 0} F[\rho_\uparrow^\lambda, \rho_\downarrow] + \lim_{\lambda\to 0} F[\rho_\uparrow, \rho_\downarrow^\lambda] \leqslant F[\rho_\uparrow, \rho_\downarrow] - N_\uparrow N_\downarrow \left\langle \Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)} \right| \frac{1}{|r_1 - r_N|} \left| \Psi^{\min}_{(\rho_\uparrow,\rho_\downarrow)} \right\rangle \leqslant F[\rho_\uparrow, \rho_\downarrow]. \tag{35}$$

Also, inequality (30) and the corresponding one for $F[\rho_\uparrow, \rho_\downarrow^\lambda]$ imply

$$\lim_{\lambda\to\infty} \frac{F[\rho_\uparrow^\lambda, \rho_\downarrow]}{\lambda^2} + \lim_{\lambda\to\infty} \frac{F[\rho_\uparrow, \rho_\downarrow^\lambda]}{\lambda^2} \leqslant T_\uparrow[\rho_\uparrow, \rho_\downarrow] + T_\downarrow[\rho_\uparrow, \rho_\downarrow], \tag{36}$$

which means that

$$0 \leqslant \lim_{\lambda\to\infty} \frac{F[\rho_\uparrow^\lambda, \rho_\downarrow]}{\lambda^2} + \lim_{\lambda\to\infty} \frac{F[\rho_\uparrow, \rho_\downarrow^\lambda]}{\lambda^2} \leqslant \left(\frac{\partial F[\rho_\uparrow^\lambda, \rho_\downarrow]}{\partial\lambda}\right)_{\lambda=1} + \left(\frac{\partial F[\rho_\uparrow, \rho_\downarrow^\lambda]}{\partial\lambda}\right)_{\lambda=1} - F[\rho_\uparrow, \rho_\downarrow], \tag{37}$$

where use has been made of

$$T_\uparrow[\rho_\uparrow, \rho_\downarrow] + T_\downarrow[\rho_\uparrow, \rho_\downarrow] = \left(\frac{\partial F[\rho_\uparrow^\lambda, \rho_\downarrow]}{\partial\lambda}\right)_{\lambda=1} + \left(\frac{\partial F[\rho_\uparrow, \rho_\downarrow^\lambda]}{\partial\lambda}\right)_{\lambda=1} - F[\rho_\uparrow, \rho_\downarrow], \tag{38}$$

which follows from the fact that expression (30) and its counterpart involving $\rho_\downarrow^\lambda$ are equalities at $\lambda = 1$.

From the reasoning in Refs. [12–14], the fundamental equality counterpart to inequality (27) is

$$F[\rho_\uparrow^\lambda, \rho_\downarrow] = \left\langle \Psi^{\min}_{(\rho_\uparrow^\lambda,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right| \hat{T} + \hat{V}_{ee} \left| \Psi^{\min}_{(\rho_\uparrow^\lambda,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right\rangle, \tag{39}$$

or

$$\begin{aligned} F[\rho_\uparrow^\lambda, \rho_\downarrow] = \Big\langle \lambda^{\frac{3M}{2}} \Psi^{\min,\lambda}_{(\rho_\uparrow,\rho_\downarrow)}(\lambda\boldsymbol{r}_1, \lambda\boldsymbol{r}_2, \ldots, \lambda\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \Big| \hat{T} \\ + \hat{V}_{ee} \Big| \lambda^{\frac{3M}{2}} \Psi^{\min,\lambda}_{(\rho_\uparrow,\rho_\downarrow)}(\lambda\boldsymbol{r}_1, \lambda\boldsymbol{r}_2, \ldots, \lambda\boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \Big\rangle, \end{aligned} \tag{40}$$

or

$$F[\rho_\uparrow^\lambda, \rho_\downarrow] = \left\langle \Psi^{\min,\lambda}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right| \hat{B}(\lambda) \left| \Psi^{\min,\lambda}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right\rangle, \tag{41}$$

where $\Psi^{\min,\lambda}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$ is the wave function that yields $\rho_\uparrow$ and $\rho_\downarrow$ and simultaneously minimizes the expectation value of $\hat{B}(\lambda)$, where

$$\hat{B}(\lambda) = -\frac{1}{2}\lambda^2 \sum_{i=1}^{M} \nabla^2_{\vec{r}_i} - \frac{1}{2} \sum_{i=M+1}^{N} \nabla^2_{\vec{r}_i} + \lambda \sum_{j=i+1}^{M} \sum_{i=1}^{M-1} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{j=i+1}^{N} \sum_{i=M+1}^{N-1} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{j=M+1}^{N} \sum_{i=1}^{M} \frac{1}{\left|\frac{\vec{r}_i}{\lambda} - \vec{r}_j\right|}. \tag{42}$$

Upon the scaling of $\rho_\uparrow$, F_{KS} is given by

$$F_{\text{KS}}[\rho_\uparrow^\lambda, \rho_\downarrow] = \left\langle \Phi^{\text{KS}}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right| \hat{B}(\lambda) \left| \Phi^{\text{KS}}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \right\rangle, \tag{43}$$

where, consistent with its most common spin-density definition [15], $\Phi^{\text{KS}}_{(\rho_\uparrow,\rho_\downarrow)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) = \Phi^{\text{KS}}_{\rho_\uparrow}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M)\Phi^{\text{KS}}_{\rho_\downarrow}(\boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)$, and where $\Phi^{\text{KS}}_{\rho_\uparrow}$ and $\Phi^{\text{KS}}_{\rho_\downarrow}$ are the antisymmetric Kohn-Sham wave functions for $\rho_\uparrow$ and $\rho_\downarrow$, respectively.

With $F[\rho_\uparrow^\lambda, \rho_\downarrow]$ given by expression (41) and $F_{\text{KS}}[\rho_\uparrow^\lambda, \rho_\downarrow]$ by expression (43), the corresponding correlation energy is

$$E_c[\rho_\uparrow^\lambda, \rho_\downarrow] = F[\rho_\uparrow^\lambda, \rho_\downarrow] - F_{\text{KS}}[\rho_\uparrow^\lambda, \rho_\downarrow]. \tag{44}$$

It can be shown that expressions (41)–(44) lead to

$$\lim_{\lambda\to 0} F[\rho_\uparrow^\lambda, \rho_\downarrow] \leqslant F[0, \rho_\downarrow] \tag{45}$$

and

$$\lim_{\lambda\to 0} F_{\text{KS}}[\rho_\uparrow^\lambda, \rho_\downarrow] = F_{\text{KS}}[0, \rho_\downarrow], \tag{46}$$

because $\hat{B}(\lambda)$ approaches the down-spin Hamiltonian for (N-M) electrons as λ approaches zero. Consequently, we obtain

$$\lim_{\lambda\to 0} E_c[\rho_\uparrow^\lambda, \rho_\downarrow] \leqslant E_c[0, \rho_\downarrow]. \tag{47}$$

However, expressions (45) and (47) are equalities if, and only if, $\rho_\downarrow$ is such that the value of $F[0, \rho_\downarrow]$ cannot be lowered by replacing wave functions with ensembles in its constrained-search definition, as for example, when $\rho_\downarrow$ is pure-state v-representable, for the all down-spin electron case. In an alternative equality case, it can be shown that expressions (45) and (47) are equalities for any $\rho_\downarrow$ when the constrained-search minimizing wave functions are replaced by constrained-search minimizing ensembles in the definitions of $F_{\text{KS}}[\rho_\uparrow^\lambda, \rho_\downarrow]$ and $F[\rho_\uparrow^\lambda, \rho_\downarrow]$. In either equality case,

$$\lim_{\lambda\to 0} E_c[\rho_\uparrow^\lambda, \rho_\downarrow] = E_c[0, \rho_\downarrow], \tag{48}$$

which is what has previously been conjectured [11].

IV. CONCLUDING THOUGHTS

Incidentally, by using the connection of density-functional theory and spin-density-functional theory in Eq. (3), it is interesting to observe that with

$$\rho(\boldsymbol{r}) = \rho_\uparrow(\boldsymbol{r}) + \rho_\downarrow(\boldsymbol{r}), \tag{49}$$

and with the situation where

$$F[\rho] = F[\rho_\uparrow, \rho_\downarrow], \tag{50}$$

the coordinate scaling on both sides of Eq. (50) leads to an inequality rather than an equality,

$$F[\rho^\lambda] \leqslant F[\rho_\uparrow^\lambda, \rho_\downarrow^\lambda]. \tag{51}$$

Through our new expression for $F[\rho_\uparrow, \rho_\downarrow]$ as a constrained search with wave functions (or ensemble density matrices) that are entirely spin free, one is now better able to find exact properties of $F[\rho_\uparrow, \rho_\downarrow]$ and its components, for approximation purposes. As examples, we were able to derive coordinate scaling constraints for $F[\rho_\uparrow, \rho_\downarrow]$ by utilizing the basic inequality in expression (27) and the basic equality in expression (41), which arise from the definition of $F[\rho_\uparrow^\lambda, \rho_\downarrow]$ and by scaling the first M spatial coordinates of the appropriate wave functions. It is significant that the use of spin-free wave functions especially enables the derivation of important exact constraints for approximating the correlation energy functional.

Our spin-free constrained-search approach presented in this paper can be further generalized to universal density-matrix functional theories. It would also be interesting to see if this approach could be generalized to the two- and four-component relativistic versions of DFT, so that, for instance, cases involving noncollinear magnetism and spin-orbit coupling could be covered [16].

In closing, we observe that the spin-free constrained search in the universal functional in expression (11) should be useful for the explicit wave-function constructions of it [17–20] and of its functional derivatives [20].

ACKNOWLEDGMENTS

The authors thank Mark S. Gordon for useful suggestions on the manuscript. M.L. thanks the Julian Schwinger Foundation for support. F.Z. acknowledges support from the U.S. 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 U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

APPENDIX

Universal functionals that are defined by constrained search can be symmetry adapted [21]. In particular, they can be restricted to the eigenstates of the spin operator $\hat{S}^2$ [1,2,16]. Since these universal functionals impose additional constraints, they give higher energies compared to the conventional universal functional but can be useful in a variety of contexts, for example, in calculating excited states that are also triplet ground states.

In the spin-explicit approach, a projection operator may be used in the constrained search to restrict the wave functions to the eigenfunctions $\Psi_S(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ of $\hat{S}^2$ with eigenvalue $S(S+1)$.

In the spin-free approach, the equivalent effect is achieved by the following analog of the expansion in Eq. (15),

$$\Psi_S(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \sum_{i=1}^{K} \tilde{G}_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\tilde{\zeta}_i(s_1, s_2, \ldots, s_N), \tag{A1}$$

where

$$\tilde{G}_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \sum_{j=1}^{N_S} T_{ij} G_j(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N),$$

$$\tilde{\zeta}_i(s_1, s_2, \ldots, s_N) = \sum_{j=1}^{N_S} T_{ij}\zeta_j(s_1, s_2, \ldots, s_N). \tag{A2}$$

$\tilde{\zeta}_i(s_1, s_2, \ldots, s_N)$ are the N_S spin eigenstates of $\hat{S}^2$ with the eigenvalue of $S(S+1)$ and T_{ij} is an orthonormal matrix [9,10].

The expectation value of $\Psi_S(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ is computed by an analog of Eq. (21),

$$\begin{aligned}\langle \Psi_S(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)|\hat{T} + \hat{V}_{ee}|\Psi_S(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N)\rangle_r \\ = \sum_{i=1}^{K}\sum_{j=1}^{N_S}\sum_{k=1}^{N_S} T_{ij}T_{ik} \int G_j^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)(\hat{T} + \hat{V}_{ee})G_k(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N.\end{aligned} \tag{A3}$$

As in the case of Eq. (21), instead of $\hat{T} + \hat{V}_{ee}$, *any other spin-free operator* could be used in Eq. (A3), including just $\hat{T}$, $\hat{V}_{ee}$, or $\hat{I}$.

The densities of $\Psi_S(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ are computed in analogy to Eq. (22–24),

$$\begin{aligned}\rho_\uparrow(r) &= M\sum_{i=1}^{K}\sum_{j=1}^{N_S}\sum_{k=1}^{N_S} T_{ij}T_{ik} \int G_j^*(r, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \ldots, \boldsymbol{r}_N)G_k(r, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \ldots, \boldsymbol{r}_N)d\boldsymbol{r}_2, \ldots, d\boldsymbol{r}_M d\boldsymbol{r}_{M+1}, \ldots, d\boldsymbol{r}_N \\ \rho_\downarrow(r) &= (N-M)\sum_{i=1}^{K}\sum_{j=1}^{N_S}\sum_{k=1}^{N_S} T_{ij}T_{ik} \int G_j^*(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M;\ r, \ldots, \boldsymbol{r}_N)G_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M;\ r, \ldots, \boldsymbol{r}_N)d\boldsymbol{r}_1, \ldots, d\boldsymbol{r}_M dr, \ldots, d\boldsymbol{r}_N.\end{aligned} \tag{A4}$$

With all of the above in place, the following is the spin-free version of the universal functional with the $S(S+1)$ eigenfunctions $\Psi_S(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ of $\hat{S}^2$ in the constrained search,

$$F_S[\rho_\uparrow, \rho_\downarrow] = \min_{\Psi_S \to (\rho_\uparrow, \rho_\downarrow)} \langle \Psi_S(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) | \hat{T} + \hat{V}_{ee} | \Psi_S(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M;\ \boldsymbol{r}_{M+1}, \boldsymbol{r}_{M+2}, \ldots, \boldsymbol{r}_N) \rangle_{\boldsymbol{r}}. \quad \text{(A5)}$$

It can be shown that the spin-explicit and spin-free definitions are equivalent in this case as well.

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Correction: Missing support information in the Acknowledgments has been inserted.