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Fractional spin in reduced density-matrix functional theory

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We study the behavior of different functionals of the one-body reduced density matrix (1RDM) for systems with fractional z -component of the total spin. We define these systems as ensembles of integer spin states. It is shown that, similarly to density functional theory, the error in the dissociation of diatomic molecules is directly related to the deviation from constancy of the atomic total energies as functions of the fractional spin. However, several functionals of the 1RDM show a size inconsistency which leads to additional errors. We also investigate the difference between a direct evaluation of the energy of an ensemble of integer-spin systems and a direct minimization of the energy of a fractional-spin system. © 2011 American Institute of Physics. [doi:10.1063/1.3615955]

I. INTRODUCTION

Density functional theory (DFT) (Refs. 1 and 2) is one of the most commonly used tools in calculating electronic structures. Applications range from atoms and small molecules to clusters and solids. Despite its success in describing a wide variety of systems, there are several problems for which DFT results are not satisfactory. Two such problems are the calculation of the band gaps of solids and the description of the dissociation of molecules. Even hydrogen molecule is not described correctly at the dissociation limit by most functionals.

The first of the aforementioned problems, i.e., the band gap problem, is related to the pathologic behavior of the DFT functionals in the regime of fractional total number of particles.^{3–6} In particular, most functionals fail to produce the derivative discontinuity at integer particle number.^{7,8} The incorrect convex behavior of functionals like LDA was recently attributed to the so-called delocalization error, i.e., the tendency of these functionals to produce a disperse distribution of the extra electron or hole.^{8,9}

The second problem, i.e., the difficulties in describing the dissociation of molecules, is related to the incorrect behavior of functionals in the regime of fractional spin, as demonstrated recently.^{9,10} For a system with g degenerate ground states, the total energy is the same for any ensemble created out of these degenerate states. Within DFT, this implies that the energy functional has to satisfy⁶

$$E \left[\sum_{j=1}^g c_j \rho_j \right] = E[\rho_i], \quad \forall i = 1 \dots g, \quad (1)$$

where ρ_j denotes the density of state j and the coefficients c_j satisfy $0 \leq c_j \leq 1$, $\sum_{j=1}^g |c_j|^2 = 1$. In the special case where the degenerate space is spanned by states with different spin configurations, Eq. (1) was found to be violated by Hartree-Fock (HF) as well as various DFT functionals.^{9,10}

A possible cure for both problems might be offered by reduced density matrix functional theory (RDMFT) which has shown promising results in the calculation of band gaps^{11–13} as well as in the dissociation of molecules.^{14–16} Although the underlying theorem due to Gilbert dates back to 1975,¹⁷ applications to realistic systems only emerged in the last two decades.^{11–16,18–22} As a consequence of Gilbert's theorem, the total energy is expressed as a functional of the one-body reduced density matrix (1RDM), $\gamma(\mathbf{x}, \mathbf{x}')$, which is defined as

$$\gamma(\mathbf{x}, \mathbf{x}') = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}', \mathbf{x}_2 \dots \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_N), \quad (2)$$

where Ψ denotes the N -particle wave function and $\mathbf{x} = (\mathbf{r}, \sigma)$ is a combined space and spin variable with $\sigma = \uparrow, \downarrow$ and $\int d\mathbf{x} = \sum_{\sigma} \int d^3r$.

For systems where the Hamiltonian does not depend on spin, it is reasonable to assume that the 1RDM is diagonal in spin, i.e.,

$$\gamma(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \gamma_{\sigma}(\mathbf{r}, \mathbf{r}') \delta_{\sigma\sigma'}. \quad (3)$$

Thus, using the 1RDM as the kernel of an integral operator, we have two separate eigenvalue equations, one for each spin,

$$\int d^3r' \gamma_{\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{j\sigma}(\mathbf{r}') = n_{j\sigma} \varphi_{j\sigma}(\mathbf{r}) \quad (4)$$

defining the natural orbitals, $\varphi_{j\sigma}$, and the occupation numbers, $n_{j\sigma}$. In order for the 1RDM to be N -representable, i.e., to correspond to a fermionic N -particle system, it is necessary and sufficient to satisfy the following two conditions:²³

$$0 \leq n_{j\sigma} \leq 1, \quad \sum_{j=1}^{\infty} \sum_{\sigma=\uparrow, \downarrow} n_{j\sigma} = N. \quad (5)$$

For closed-shell systems, the two spin directions are identical and we have $\varphi_{j\uparrow} = \varphi_{j\downarrow} = \varphi_j$ and $n_{j\uparrow} = n_{j\downarrow} = n_j$.

A main advantage of RDMFT is that the kinetic energy, $E_{\text{kin}}[\gamma]$, of the system is a simple explicit functional of the

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1RDM of the ground state, as are the external and the Hartree energies, $E_{\text{ext}}[\gamma]$ and $E_{\text{H}}[\gamma]$. The total energy can hence be written as

$$E_{\text{tot}}[\gamma] = E_{\text{kin}}[\gamma] + E_{\text{ext}}[\gamma] + E_{\text{H}}[\gamma] + E_{\text{xc}}[\gamma], \quad (6)$$

where only the exchange-correlation energy $E_{\text{xc}}[\gamma]$ needs to be approximated.

In the present work, we introduce RDMFT for fractional spins and discuss the relation between treating fractional spin and the problems occurring in the dissociation of molecules. By fractional spin we mean, in analogy to DFT, fractional z -component S_z of the total spin, i.e., values between the eigenvalues of S_z . A discussion of the total spin S^2 is beyond the scope of this work as explained briefly in Sec. II, where we review selected approximations for E_{xc} for closed-shell and open-shell systems. Our selection contains functionals with different behavior for systems with fractional spin but is, of course, far from complete. In Sec. III, we discuss the extension of RDMFT to fractional spins. In Sec. IV we present our numerical results on the behavior of some 1RDM functionals in the regime of fractional spin for hydrogen, lithium, and carbon atoms. We also discuss how these calculations are connected to the dissociation of H_2 , Li_2 , and C_2 .

II. RDMFT FUNCTIONALS FOR CLOSED- AND OPEN-SHELL SYSTEMS

Most currently available approximations for E_{xc} are explicit functionals of the natural orbitals, $\varphi_{j\sigma}$, and their corresponding occupation numbers $n_{j\sigma}$, rather than the 1RDM itself. Since most functionals were introduced for closed-shell systems we will drop the spin index for the moment and come back to the treatment of open-shell systems later.

An important class of approximations to E_{xc} , which includes all functionals of interest to this work, can be cast into the form^{13–16, 18, 21, 24–27} (atomic units are used throughout the paper)

$$E_{\text{xc}} = - \sum_{j,k=1}^{\infty} f(n_j, n_k) \iint d^3r d^3r' \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_k^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (7)$$

with the occupation numbers entering through the function $f(n_j, n_k)$ which distinguishes between different functionals. A factor of two is included in Eq. (7) due to spin degeneracy. The simplest such functional is the HF approximation, where $f_{\text{HF}}(n_j, n_k) = n_j n_k$. The first true RDMFT functional was first given by Müller^{14, 24} who used the function $f_{\text{M}}(n_j, n_k) = \sqrt{n_j n_k}$. Applications to various systems have shown that the Müller functional systematically overestimates the correlation energy.^{26, 28–30} Many of the more recent approximations aim at correcting this overcorrelation which lead to the GU,¹⁵ the series of BBC functionals,¹⁶ the AC3 (Ref. 21) functional, and the ML functional.²⁷ Piriš followed a different approach and employed the cumulant expansion to derive a reconstructive approximation of the two-body reduced density matrix resulting in the PNOF functionals.^{18, 25} All the above functionals are mostly used in the calculation of molecular systems but some were also applied to the homogeneous electron

gas (HEG),²⁶ which lead to the BBC++ functional, the only functional in the group which is exact for the HEG.³¹ Applying RDMFT to periodic systems in order to solve the band gap problem, one of the pathologies of most popular density functionals, lead to the development of the power functional by Sharma *et al.*^{13, 22} One important distinction between the functionals is the treatment of the self-interaction terms, i.e., those terms with $j = k$ in Eq. (7). In the GU and PNOF functionals these terms are completely removed while BBC3 only partially removes these terms. Most functionals have been tested in a benchmark test.²⁰

RDMFT functionals of the form (7) were extended to open-shell systems in Ref. 32 assuming that the occupation numbers are spin dependent but the natural orbitals are not. In that way, there are pairs of natural spin-orbitals which are identical in space and correspond to different occupation numbers for the two spins. The xc energy then has the form

$$E_{\text{xc}} = - \frac{1}{2} \sum_{\sigma=\uparrow, \downarrow} \sum_{j,k=1}^{\infty} f(n_{j\sigma}, n_{k\sigma}) \times \iint d^3r d^3r' \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_k^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

i.e., there are no terms coupling the two spins, in analogy to the HF functional. Contrary to HF, where the missing spin coupling is a direct consequence of the Pauli principle, in the case of RDMFT it is an arbitrary assumption although a rather reasonable one. Introducing opposite-spin terms in Eq. (8), while keeping the same form for the function f , would introduce opposite-spin exchange which is a more serious pathology than neglecting opposite-spin correlations. Of course, one can introduce additional opposite-spin correlation terms but this requires at least a different ansatz for the function f and is clearly beyond the purpose of this work.

The expectation value of the z -component of the total spin, $\langle \hat{S}_z \rangle$, is easily expressed in terms of the occupation numbers

$$\langle \hat{S}_z \rangle = \frac{1}{2} \sum_{j=1}^{\infty} (n_{j\uparrow} - n_{j\downarrow}) = \frac{1}{2} (N_{\uparrow} - N_{\downarrow}), \quad (9)$$

where $N_{\uparrow}$ ($N_{\downarrow}$) denote the number of spin-up (spin-down) particles and $N = N_{\uparrow} + N_{\downarrow}$. In Ref. 32 it was demonstrated that the optimal γ , resulting from a minimization of the total energy (6), does not yield the correct expectation value for $\hat{S}_z$ for the approximate functionals. Therefore, it is necessary to implement Eq. (9) as an extra condition in the minimization. Combined with the N -representability conditions (5) we obtain

$$0 \leq n_{j\sigma} \leq 1, \quad \sum_{j=1}^{\infty} n_{j\sigma} = N_{\sigma}, \quad (10)$$

where N_{σ} is the predefined number of electrons of spin σ that is consistent with the expectation value of $\hat{S}_z$. These conditions guarantee that the optimal γ corresponds to an N -particle fermionic state and, in addition, produces the correct expectation value of $\hat{S}_z$.

Some of the functionals introduced above include the division of the natural orbitals into strongly and weakly

occupied orbitals, as well as bonding and anti-bonding. Obviously, for open-shell systems this division is different for the two different spins complicating the application of these functionals. The details of their extension to open-shell systems were discussed in Ref. 32.

A different, very important question is whether one can also restrict the expectation value of $\hat{S}^2$ to one of its eigenvalues using the extension to open-shell systems of Ref. 32. This question cannot be answered easily for a large number of approximations including those considered here. Contrary to S_z , the expectation value of $\hat{S}^2$ requires the knowledge of off-diagonal elements of the two-body reduced density matrix,

$$\begin{aligned} \gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) &= \frac{N(N-1)}{2} \\ &\times \sum_{\sigma_3 \dots \sigma_N} \int d^3r_3 \dots d^3r_N \Psi^*(\mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2, \mathbf{r}_3\sigma_3 \dots \mathbf{r}_N\sigma_N) \\ &\times \Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \mathbf{r}_3\sigma_3 \dots \mathbf{r}_N\sigma_N). \end{aligned} \quad (11)$$

More specifically, for the calculation of $\hat{S}^2$, one needs $\gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_2, \mathbf{r}_2\sigma_1)$,³³ in addition to the two-body density, $\gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)$, which enters the total energy. Thus, since for most functionals only the total energy expressions are available, there is no access to $\gamma_2(\mathbf{r}_1\sigma_2, \mathbf{r}_2\sigma_1; \mathbf{r}_1\sigma_2, \mathbf{r}_2\sigma_1)$. Hence, most approximations leave us a freedom to choose the off-diagonal elements of γ_2 under the obvious condition that we keep the diagonal unchanged. We should mention, however, that there are approximations which are built to reproduce the correct expectation value for $\hat{S}^2$.^{34,35} Although it is interesting to extend the present study to such functionals, in this work, we restrict ourselves to traditional approximations that concern a total energy ansatz only, thus leaving the total spin undetermined.

III. FRACTIONAL SPINS IN RDMFT

We use the term integer spin for the cases that the total number of spin-up and spin-down electrons are both integer. Thus, for odd number of electrons the values of integer spin, or more precisely of integer z -component of the total spin, are $\pm 1/2, \pm 3/2, \dots$. Similarly, for even total number of electrons the values for integer spin are $0, \pm 1, \pm 2, \dots$. We define a state of fractional spin s (corresponding to total number of electrons N) as the ensemble of the closest two integer-spin states, $S_z = s^+, s^-$, i.e., $s = (s^+ + s^-)/2$, and, obviously, $s^+ - s^- = 1$. With this definition the 1RDM of the ensemble state is

$$\gamma^s(\mathbf{r}, \mathbf{r}') = \omega \gamma^{s^+}(\mathbf{r}, \mathbf{r}') + (1 - \omega) \gamma^{s^-}(\mathbf{r}, \mathbf{r}'), \quad (12)$$

where $\omega = s^+ - s = 1 + s^- - s$. The choice to include only the two states with closest integer spins is justified in the Appendix. It is shown there that the domain of γ^s defined in Eq. (12) coincides with the domain of the most general ensembles

$$\gamma^s(\mathbf{r}, \mathbf{r}') = \sum_{\alpha=-|S_z|}^{|S_z|} \omega_\alpha \gamma_\alpha(\mathbf{r}, \mathbf{r}'), \quad (13)$$

where $\pm|S_z|$ are the maximal and minimal spin of the system, and α runs over all possible spin configurations. The coefficients, ω_α , satisfy

$$0 \leq \omega_\alpha \leq 1, \quad \sum_{\alpha=-|S_z|}^{|S_z|} \omega_\alpha = 1 \quad (14)$$

as well as the spin condition

$$\sum_{\alpha=-|S_z|}^{|S_z|} \alpha \omega_\alpha = s. \quad (15)$$

The conditions (14) and (15) do not specify ω_α uniquely. The definition (12), however, provides a unique definition of fractional spin ensembles.

Similarly to the case of fractional particle number, we show in the Appendix that the necessary and sufficient conditions for γ_s to be written according to Eq. (12) are given by

$$0 \leq n_{j\sigma}^s \leq 1, \quad \sum_{j=1}^{\infty} n_{j\sigma}^s = M_\sigma^s, \quad (16)$$

where M_σ^s denotes the number of particles with spin σ in the system and the use of the letter M instead of N emphasizes that this number is actually fractional. We denote the spin s of the system with an additional upper index. Obviously, $s = (M_\uparrow^s - M_\downarrow^s)/2$ and the total number of particles $N = M_\uparrow^s + M_\downarrow^s$ is integer. For example, the Li atom, a doublet of degenerate states with $S_z = \pm 1/2$, has $M_\uparrow^{1/2} = 2$, $M_\downarrow^{1/2} = 1$ and $M_\uparrow^{-1/2} = 1$, $M_\downarrow^{-1/2} = 2$. Out of these we can build any ensemble using $0 \leq \omega \leq 1$, e.g., for $\omega = 1/2$ we obtain $s = 0$ and $M_\uparrow^0 = 3/2$, $M_\downarrow^0 = 3/2$.

Alternatively to using Eq. (12) or (13), one can minimize the total energy enforcing the correct number of particles in each spin channel directly, i.e., use the conditions

$$M_\uparrow^s = \frac{N}{2} + s, \quad M_\downarrow^s = \frac{N}{2} - s. \quad (17)$$

For the Li atom with $s = 0$ mentioned above we minimize the total energy under the conditions $\sum_j^\infty n_{j\uparrow}^0 = 3/2$ and $\sum_j^\infty n_{j\downarrow}^0 = 3/2$. With these conditions the minimization is restricted in the domain of 1RDMs with the correct spin $S_z = s$. This approach is equivalent to the way RDMFT was extended to fractional total number of particles.^{11,12,36} For the exact functional, both approaches, the ensemble and the direct enforcement of the correct particle numbers, lead to the same solution. However, this might not be the case for approximate functionals. Since the second approach involves a minimization of the total energy at each particular spin the resulting energy is expected to be lower, or ideally equal, to the one from the ensemble. Building the ensemble of the closest integer spin states is only possible for doublet states in which case they coincide with the maximum and minimum spin states of the multiplet. The reason is that for a particular multiplicity we have access only to optimal 1RDMs of the highest and lowest S_z . Thus, for a triplet we have no access to the $S_z = 0$ state which is necessary for the ensembles described in Eq. (12). Therefore, we consider ensembles of the two spin states $S_z = \pm 1$ instead. This can be an additional reason for

the difference of the total energies of the ensemble and the minimization enforcing the fractional spin conditions. We discuss results from both the explicit ensemble and the minimization approaches in Sec. IV.

The description of systems with fractional spin is directly related to the dissociation problem. For a diatomic molecule A_2 , where A is an open-shell atom with z -spin component S_z , the energy at infinite separation is given as

$$E_{d=\infty}^{A_2} = 2E_{s=\pm S_z}^A, \quad (18)$$

where $E_{d=\infty}^{A_2}$ is the energy of the diatomic molecule at the dissociation limit and $E_{s=\pm S_z}^A$ is the ground-state energy of the open-shell atom A. Calculating $E_{d=\infty}^{A_2}$ (the calculation is of course performed at large finite d , here we use $d = 10 \text{ \AA}$) one uses that the molecular system is closed-shell. Since the two subsystems do not interact due to the large separation the result corresponds to two closed-shell atoms A, i.e.,

$$E_{d=\infty}^{A_2} = 2E_{s=0}^A, \quad (19)$$

where $E_{s=0}^A$ is the energy of atom A with spin $S_z = 0$. This equation is satisfied for functionals that are size consistent. The question, whether 1RDM functionals are size consistent, i.e., they do not violate Eq. (19) is discussed in detail in Ref. 37. There it is shown that 1RDM energy functionals that are not invariant under a unitary transformation which delocalizes the natural orbitals are size inconsistent if their minimization favors delocalization of the natural orbitals. Thus, a functional reproduces the correct dissociation limit if (i) it does not suffer from the size inconsistency described in Ref. 37 and (ii) it respects spin constancy,^{9,10} which implies that $E_{s=\pm S_z}^A = E_{s=0}^A$. We define the spin-constancy error, Δ_s , as

$$\Delta_s = 2(E_{s=0}^A - E_{s=\pm S_z}^A). \quad (20)$$

For size-consistent functionals it is identical to the dissociation error

$$\Delta_d = E_{d=\infty}^{A_2} - 2E_{s=\pm S_z}^A. \quad (21)$$

The question, whether several approximations in RDMFT respect spin constancy, and its relation to dissociation error in diatomic molecules is the subject of Sec. IV.

IV. NUMERICAL RESULTS

We compare the spin-constancy errors, Δ_s , and the dissociation error, Δ_d , for the dimers of hydrogen, H_2 , lithium, Li_2 , and carbon, C_2 , for several different functionals of the 1RDM. The calculations were performed using the HIPPO computer code^{38,43} and cc-pVTZ basis sets (excluding f basis functions).

Figure 1 shows the energy in the dissociation of H_2 for several different functionals in the left panels and the corresponding dependence of the total energy on fractional spin on the right. The latter energies have been multiplied by two according to Eqs. (18) and (19). In the dissociation plots we also include results of the multireference single and double configuration interaction (MRDCI) method^{39,40} for comparison. The difference of the total energies from the RDMFT functional and MRDCI calculation at the dissociation limit is

the real dissociation error (within the basis set used), as opposed to Δ_d which is the internal dissociation error of the functional. These two are equal when the atomic RDMFT calculation becomes exact. As we see, for fractional S_z , the total energy obtained by a minimization with the subsidiary conditions, Eq. (17), is equal or lower than the one obtained through the explicit ensemble. For the Müller and power functionals, which are both size consistent, $2E_{S_z=0}^H$ equals the total energy of H_2 in the dissociation limit, $E_{d=\infty}^{H_2}$. Functionals with self-interaction removal, like the GU, suffer from a size inconsistency³⁷ which manifests as an inequality in these energies.

The Müller functional is known to reproduce the correct dissociation for H_2 . As we see in Fig. 1 it also respects the spin constancy. This constancy of the total energy for fractional spin can actually be shown analytically for the Müller functional in the absence of occupation numbers “pinned” at one (border minima). Two electron systems, like H_2 , do not have pinned occupation numbers. As a result, the two ways of extending to fractional spins, i.e., by an explicit ensemble or by modification of the subsidiary conditions, yield the same answer. If we view the dissociation of H_2 with reference to the isolated H atoms calculated with the same functional, then the Müller functional performs optimal: The underestimation of the total energy at the dissociation limit is exactly twice the underestimation of the total energy for the H atom. This is an interesting feature of the Müller functional which unfortunately is not present in later approximations which aimed to correct the overcorrelation of this functional.

The BBC functionals respect the constancy of spin as well. For BBC3, the grouping of the orbitals according to their occupancy is responsible for the slight mismatch between the dissociation and the fractional spin energies shown in Fig. 1. The results for BBCs were obtained by respecting degeneracies in bonding and antibonding orbitals. For example, we assumed two strongly occupied orbitals at the dissociation limit instead of one as implied by the number of electrons. The power functional behaves quite reasonably as well, with only a small variation of the atomic energy with spin. This small spin constancy error matches the dissociation error as seen in Fig. 1. The behavior of AC3 is satisfactory as well with $S_z = 0$ and $\pm 1/2$ giving very close total energies for the H atom. However, the behavior for intermediate spins is not as good as for the Müller, BBCs, and power functionals.

Functionals that do not describe dissociation correctly also fail the constancy test. Such examples are the ML and GU functionals in Fig. 1. Note, however that the ML functional yields $2E_{S_z=0}^H = E_{d=\infty}^{H_2}$, i.e., it is size consistent in this case. As a result, the large dissociation error for ML equals the double of the spin constancy error. For the GU functional the error in the dissociation results from a combination of the spin constancy error and a correction of that error by the delocalization described in Ref. 37. At large separation, one obtains four degenerate natural spin orbitals with each orbital occupied by half an electron. Due to the large separation the system can be treated as two isolated atoms each having fractional spin $S_z = 0$. The first part of the dissociation error results from the fact that this $S_z = 0$ is not degenerate with the

FIG. 1. The dissociation of H_2 using 1RDM functionals (black) and MRDCI (red dotted line) (left panels) compared to the total energy behavior for fractional spin (right panels). In the right panels we include results of both the minimization with the constraint of Eq. (16) (black dashed line) and the ensemble according to Eq. (13) (green line).

$S_z = 1/2$ state, i.e., from a spin constancy error. This error is shown in the right panel of Fig. 1 and one can show that it is equal to $1/2J$, where J is the Coulomb self-interaction energy for the hydrogen $1s$ state. This error is then reduced by the fact that the GU functional is not invariant under unitary transformations of orbitals with degenerate occupation numbers, especially for transformation which delocalize the occupied orbital over both atoms.³⁷ The additional delocalization error lowers the energy which leads to a total error of $1/4J$ which can be seen in the left panel in Fig. 1.

In Table I, we list the total energies in the dissociation limit as well as the total energies of the hydrogen atom for the minimal spin, $S_z = 0$, and the maximal spin, $S_z = 1/2$. The $S_z = 0$ result was obtained from a minimization with the constraint (16), i.e., the result is identical to the midpoint of the red line in the right panels of Fig. 1. We included several more approximations for comparison. Again, functionals with self interaction removal yield an inequality of the values in the first two columns due to size inconsistency.

TABLE I. The total energy of H_2 at the dissociation limit, $E_{d=\infty}^{H_2}$, (calculated with $d = 10$ Å) and twice the total energies of the hydrogen atom for $S_z = 0$, $E_{S_z=0}^H$, and for $S_z = 1/2$, $E_{S_z=1/2}^H$. For $S_z = 0$, we used a minimization with the subsidiary conditions, Eq. (16).

Functional	$E_{d=\infty}^{H_2}$ (Ha)	$2E_{S_z=0}^H$ (Ha)	$2E_{S_z=1/2}^H$ (Ha)
Müller	-1.0473	-1.0473	-1.0473
GU	-0.8743	-0.7450	-1.0281
BBC1/2	-1.0370	-1.0370	-1.0370
BBC3	-1.0302	-1.0316	-1.0316
PNOF	-0.8451	-0.7379	-1.0235
BBC++	-1.0213	-1.0146	-1.0417
AC3	-1.0010	-1.0024	-1.0266
Power	-0.9459	-0.9459	-1.0113
ML	-0.8043	-0.7969	-1.0327

The case of Li_2 is interesting, since it dissociates into doublet Li atoms for which most functionals produce a pinned state. In this case, the analytic proof for the Müller functional that the total energy does not depend on spin does not hold anymore. As we see in the upper left panel of Fig. 2, the consequence of having a pinned state is dramatic and spin constancy is violated with the energy difference between different spin values being larger than the dissociation energy of Li_2 . This failure, however, should not be overrated since it is partly a result of the binding energy of Li_2 being very small, i.e., the minimum is very shallow. For size consistent functionals, we again find $2E_{S_z=0}^{Li} = E_{d=\infty}^{Li_2}$. A small deviation from equality, like for the ML functional, is mainly a result of the calculation being performed at a finite distance of $d = 10$ Å. The best behavior for Li_2 is obtained with the power functional. The size inconsistency of the BBC3 functional is again a consequence of the orbital grouping. In Table II, the total energy at the dissociation limit, $E_{d=\infty}^{Li_2}$, and the atomic energies for spin $S_z = 0$ and $S_z = 1/2$, $E_{S_z=0}^{Li}$ and $E_{S_z=1/2}^{Li}$, are given for different functionals.

TABLE II. Same as Table I but for Li_2 . For the calculation of $E_{d=\infty}^{Li_2}$ we used $d = 10$ Å.

Functional	$E_{d=\infty}^{Li_2}$ (Ha)	$2E_{S_z=0}^{Li}$ (Ha)	$2E_{S_z=1/2}^{Li}$ (Ha)
Müller	-15.0646	-15.0645	-15.0191
GU	-14.9356	-14.8743	-14.9290
BBC1	-14.9537	-14.9886	-14.9548
BBC2	-14.9438	-14.9675	-14.9519
BBC3	-14.9170	-14.9409	-14.9286
PNOF	-14.8677	-14.8003	-14.9149
BBC++	-14.9486	-14.9793	-14.9452
AC3	-14.9087	-14.9136	-14.9211
Power	-14.8978	-14.8977	-14.9054
ML	-14.9252	-14.9244	-14.9310

FIG. 2. Same as in Fig. 1 but for Li_2 . Note that the results for the Müller functional deviate significantly from the MRDCI results which are not included in the corresponding plot.

Finally, we studied the dissociation of C_2 , see Fig. 3 and Table III, into atomic C which is a triplet state. For this system, the ensemble of Eq. (12) cannot be constructed since we only have access to the 1RDMs of the $S_z = \pm 1$ states and not the triplet with $S_z = 0$. Still, an ensemble of these two states yields a 1RDM which satisfies Eq. (16) and it has to satisfy the constancy of spin. However, we were not able to prove that any 1RDM which satisfies Eq. (16) can be written as an ensemble of the maximal and minimal S_z states. This can lead to an enlarged energy difference between the ensemble and minimization calculations of the energy for fractional spin. Generally, the spin constancy errors, as seen in Fig. 3, are again fairly large compared to the dissociation energy itself. As in the case of Li, the power functional seems to produce an acceptable behavior. ML, GU, and power functionals give accurate results for the C atom triplet as it is shown in Fig. 3 by the agreement between $2E_{S_z=\pm 1}^{\text{C}}$ and the dissociation energy of MRDCI. The error in the dissociation energy for the power functional is exactly equal to the spin constancy error. For the ML functional a size inconsistency appears in C_2 manifested by the difference of $E_{d=\infty}^{\text{C}_2}$ and $2E_{S_z=0}^{\text{C}}$.

The C case is complicated by the degeneracy of the atomic p states. The Müller and power functionals yield equal occupation for all three natural orbitals associated to the p

states of a given spin direction for the optimal 1RDM. For $S_z = \pm 1$ one obtains occupations close to $2/3$ for one spin direction and close to zero for the other while for $S_z = 0$ these occupations are close to $1/3$ for both spins. Additionally, the 1RDM of dissociated C_2 contains 6 occupation numbers close to $1/3$, i.e., the solution for dissociated C_2 is consistent with the atomic $S_z = 0$ ensemble. However, the energy changes with fractional spin. The situation is different for the BBC and AC3 functionals which yield either two large degenerate occupation numbers and a smaller one (BBC1,2) or three different occupations (BBC3, AC3). The optimal 1RDM for $S_z = 0$ is not an ensemble of the $S_z = \pm 1$ states, however, it is consistent with the solution for dissociated C_2 , i.e., C_2 yields the same occupation numbers but each values appears twice as often as for the atom. Finally, for functionals such as GU and ML, neither is the $S_z = 0$ state consistent with the C_2 dissociation limit, nor is the optimal $S_z = 0$ an ensemble of the optimal $S_z = \pm 1$ density matrices.

In almost all cases studied here, extending to fractional spins by using the constraint of Eq. (16) leads to a lower energy than using the explicit ensemble. Exceptions are the functionals that respect spin constancy, like the Müller functional for H_2 , in which case the results of these two procedures coincide. This behavior is due to the minimization of the energy in the former procedure while in the latter one uses the density matrices of the endpoints and evaluates the energy functional with the total density matrix, Eq. (13). The energy $2E_{S_z=0}$ obtained with the former procedure is the one that coincides with the dissociation energy of the dimer for size consistent functionals as can be seen in Figs. 1 and 2, and 3.

We should mention that both the dissociations of Li_2 and C_2 are difficult cases for different reasons. The Li dimer has a very shallow minimum while C_2 contains multiple carbon bonds. Thus, the failure of RDMFT functionals in the dissociation of these systems should not lead to negative conclusions about RDMFT. The purpose of the present work is to relate the error at the dissociation limit to the systems of fragments in the regime of fractional spin, not the description of the energy curves in RDMFT. For the later, there exist dedicated applications of the theory with promising results.^{41,42}

TABLE III. Same as Table I but for C_2 . In the last column, though, the total energies, $2E_{S_z=\pm 1}^{\text{C}}$ are included. Again $d = 10 \text{ Å}$ is used for the calculation of $E_{d=\infty}^{\text{C}_2}$.

Functional	$E_{d=\infty}^{\text{C}_2}$ (Ha)	$2E_{S_z=0}^{\text{C}}$ (Ha)	$2E_{S_z=\pm 1}^{\text{C}}$ (Ha)
Müller	-76.2362	-76.2362	-76.0359
GU	-75.7675	-75.6248	-75.6516
BBC1	-75.9028	-75.9028	-75.8208
BBC2	-75.7885	-75.7885	-75.7504
BBC3	-75.5250	-75.5250	-75.6335
PNOF	-76.0691	-75.5437	-75.5914
BBC++	-75.8553	-75.8366	-75.7793
AC3	-75.5376	-75.5376	-75.6033
Power	-75.6941	-75.6941	-75.6218
ML	-75.4925	-75.5821	-75.6238

FIG. 3. Same as in Fig. 1 but for C_2 . Note the rather large differences in the total energies obtained from different functionals.

V. CONCLUSION

We considered the extension of functionals of the 1-RDM to the regime of fractional spins through ensembles. Like in DFT, the description of the dissociation of dimers into open-shell fragments is, apart from the size-consistency problem discussed in Ref. 37, equivalent to the constancy of the total energy as a function of the fractional spin. We showed that for H_2 the Müller functional reproduces the spin constancy property of the total energy. Indeed, this functional overcorrelates H_2 at the dissociation limit by an amount that is twice the overcorrelation of the H atom. The spin constancy of the Müller functional can be proven analytically for systems without pinned states (border minima), i.e., when all occupation numbers are fractional. This is the case for two-electron systems. For systems with pinned states, however, which is the typical case for systems with more than two electrons, the spin constancy of the Müller functional is destroyed. For the Li and C atoms, none of the functionals considered here respects the spin constancy. The power functional seems to behave better than the rest yielding the smallest difference between different spin states. The BBC functionals also respect spin constancy for the H atom but not for Li and C. Functionals that suffer from a size-consistency problem fail at the dissociation limit and, in addition, the spin constancy error differs substantially from the dissociation error.

Like in DFT,^{9,10} we believe that the present work opens a new dimension in functional development within RDMFT by showing the advantages and weaknesses of present day approximations in the regime of fractional spins.

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APPENDIX: N-REPRESENTABILITY

We say a 1RDM for fractional spin s is ensemble N -representable if it can be written as an ensemble of the form Eq. (12), i.e.,

$$\gamma^s(\mathbf{r}, \mathbf{r}') = \omega \gamma^{s^+}(\mathbf{r}, \mathbf{r}') + (1 - \omega) \gamma^{s^-}(\mathbf{r}, \mathbf{r}'), \quad (A1)$$

where γ^{s^+} and γ^{s^-} are the 1RDM of ensembles with N particles and integer spin. Here, s^+ and s^- are the two integer spin values closest to the fractional s , and $\omega = s^+ - s^-$.

We prove that the necessary and sufficient conditions for a density matrix γ_s to be written in this way are given by (see also Eq. (16))

$$0 \leq n_{j\sigma}^s \leq 1, \quad \sum_{j=1}^{\infty} n_{j\sigma}^s = N_{\sigma}^s. \quad (A2)$$

In other words, we have to prove that the two sets of density matrices satisfying Eqs. (A1) and (A2) are identical. The proof follows the same arguments as the proof for fractional particle number.³⁶

First, we show that Eq. (A2) is a necessary condition for γ^s to belong to the set of ensembles defined by Eq. (13) which contains the ensembles (12). The triangular inequality for positive definite operators states that the largest and smallest eigenvalues, $n_{j\sigma}^{s,\max}$ and $n_{j\sigma}^{s,\min}$, for the ensemble matrix satisfy

$$n_{j\sigma}^{s,\max} \leq \sum_{\alpha=-|S_z|}^{|S_z|} \omega_{\alpha} n_{j\sigma}^{\alpha,\max} \leq \sum_{\alpha=-|S_z|}^{|S_z|} \omega_{\alpha} = 1, \quad (A3)$$

$$n_{j\sigma}^{s,\min} \geq \sum_{\alpha=-|S_z|}^{|S_z|} \omega_{\alpha} n_{j\sigma}^{\alpha,\min} \geq 0. \quad (A4)$$

Therefore, since the eigenvalues $n_{j\sigma}$ for non-fractional spin are between zero and one, any 1RDM that satisfies Eq. (A1) has eigenvalues between zero and one. Due to the conditions on the coefficients, Eqs. (14) and (15), the occupation numbers of γ^s also sum to $N_{\uparrow}^s$ and $N_{\downarrow}^s$. Hence, we have shown that all 1RDM that satisfy Eq. (13) also satisfy Eq. (A2), i.e., the conditions (A2) are necessary.

In the second part of the proof we show that the conditions Eq. (A2) are also sufficient, but only for the ensembles satisfying Eq. (A1). To this end we define the set G of all vectors $\mathbf{n} = (n_{1\uparrow}^s, n_{2\uparrow}^s, \dots, n_{1\downarrow}^s, n_{2\downarrow}^s, \dots)$ with

$$0 \leq n_{j\sigma}^s \leq 1, \quad \sum_{j=1}^{\infty} n_{j\sigma}^s = M_{\sigma}^s, \quad (A5)$$

$$M_{\uparrow}^s + M_{\downarrow}^s = N, \quad \frac{M_{\uparrow}^s - M_{\downarrow}^s}{2} = s, \quad (A6)$$

for a given particle number N and given spin s . We then prove that this set (i) is convex; (ii) its extreme elements have, for each spin channel, N_σ components equal to 1 and one occupation number equals to η_σ , with $M_\sigma = N_\sigma + \eta_\sigma$ and $0 \leq \eta_\sigma \leq 1$, and all other occupation numbers equal to 0. We call the set of extreme elements G_e . In order for Eq. (A6) to hold true the fractional occupation numbers have to satisfy $\eta_\uparrow = 1 - \eta_\downarrow = \eta$.

For convexity we need to show that: if $\mathbf{n}, \mathbf{m} \in G$ then $\mathbf{k} = \alpha \mathbf{n} + (1 - \alpha) \mathbf{m} \in G$, $\forall 0 \leq \alpha \leq 1$, which is obviously satisfied for the set G . An element $\mathbf{k}$ is an extreme element if one can show that it cannot be written as a weighted sum of any other two elements of the set. We consider an extreme element $\mathbf{k}$ and assume $\mathbf{k} = \alpha \mathbf{n} + (1 - \alpha) \mathbf{m}$. Arranging the entries of $\mathbf{k}$ in descending order we obtain the following relations:

$$\alpha n_{j\sigma} + (1 - \alpha) m_{j\sigma} = \begin{cases} 1, & 1 \leq j \leq N_\sigma \\ \eta_\sigma, & j = N_\sigma + 1 \\ 0, & j > N_\sigma + 1 \end{cases} \quad (\text{A7})$$

from which it is immediately clear that $n_{j\sigma} = m_{j\sigma} = 1$ for $1 \leq j \leq N_\sigma$ and $n_{j\sigma} = m_{j\sigma} = 0$ for $j > N_\sigma + 1$. Since both the entries of $\mathbf{n}$ and $\mathbf{m}$ have to sum to the correct number of particles in each spin channel the remaining entry has to satisfy $n_{N_\sigma+1} = m_{N_\sigma+1} = \eta_\sigma$. In other words, both $\mathbf{n}$ and $\mathbf{m}$ are identical to $\mathbf{k}$ which proves that $\mathbf{k}$ is indeed an extreme element.

It remains to be shown that there are no extreme elements with a form different than the one stated above. Any element $\mathbf{n}$ which is not extreme can be written as a weighted sum of two other elements of the set, i.e., $\mathbf{n} = \alpha \mathbf{m} + (1 - \alpha) \mathbf{l}$. Assume $\mathbf{n}$ has M_σ nonzero entries and, since $\mathbf{n} \notin G_e$, we know that $M_\sigma \geq N_\sigma + 1$ for at least one spin channel. (If $M_\sigma > N_\sigma + 1$ for both spin channels one can apply the following manipulations to either one or both channels. For notational simplicity we will only discuss one spin channel.) We arrange the nonzero entries of $\mathbf{n}$ in descending order, separately for each spin channel, i.e., $n_1 \geq n_2 \geq n_3 \geq \dots \geq n_{M_\sigma}$ which ensures that $0 < n_{M_\sigma} \leq n_{M_\sigma-1} < 1$ for at least one spin channel. We define an $\epsilon_\sigma > 0$ as $\epsilon = \min(n_{M_\sigma}, n_{M_\sigma-1}, 1 - n_{M_\sigma}, 1 - n_{M_\sigma-1})$ which allows us to define two vectors $\mathbf{m}$ and $\mathbf{l}$, with $\mathbf{m} \neq \mathbf{l}$, as

$$\mathbf{m} = (n_1, n_2, \dots, n_{M_\sigma-1} + \epsilon_\sigma, n_{M_\sigma} - \epsilon_\sigma, \dots), \quad (\text{A8})$$

$$\mathbf{l} = (n_1, n_2, \dots, n_{M_\sigma-1} - \epsilon_\sigma, n_{M_\sigma} + \epsilon_\sigma, \dots). \quad (\text{A9})$$

As one can see, $\mathbf{n} = 1/2(\mathbf{m} + \mathbf{l})$ while both $\mathbf{m}$ and $\mathbf{l}$ are different from $\mathbf{n}$. Hence, $\mathbf{n}$ is not an extreme element of G . Therefore, we have shown that the set G is convex and the only extreme elements have the properties described under (ii) above. The extreme elements, therefore, completely determine the whole set G .

Any density matrix satisfying Eq. (A2) can be written as

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{\infty} \{\mathbf{n}\}_{j\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \\ &= \sum_{l=1}^{\infty} \alpha_l \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{\infty} \{\mathbf{k}^l\}_{j\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}), \end{aligned} \quad (\text{A10})$$

where $\mathbf{n} \in G$ and $\mathbf{k} \in G_e$. The upper index on the vector $\mathbf{k}$ labels the extreme elements while the lower index refers to the vector entry. We can rewrite this equation as

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \alpha_1 \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{\infty} \{\mathbf{k}^1\}_{j\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \\ &\quad + \alpha_2 \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{\infty} \{\mathbf{k}^2\}_{j\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) + \dots \\ &= \alpha_1 \sum_{\sigma=\uparrow,\downarrow} \left[\sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) + \eta_\sigma \varphi_{N_\sigma+1}^*(\mathbf{r}') \varphi_{N_\sigma+1}(\mathbf{r}) \right] + \dots \\ &= \alpha_1 \sum_{\sigma=\uparrow,\downarrow} \left[(1 - \eta_\sigma) \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \right. \\ &\quad \left. + \eta_\sigma \sum_{j=1}^{N_\sigma+1} \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) + \dots \right]. \end{aligned} \quad (\text{A11})$$

Due to the specific relation between $\eta_\uparrow$ and $\eta_\downarrow$ we obtain

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \alpha_1 \left\{ (1 - \eta) \left[\sum_{j=1}^{N_\uparrow} \varphi_{j\uparrow}^*(\mathbf{r}') \varphi_{j\uparrow}(\mathbf{r}) + \sum_{j=1}^{N_\downarrow+1} \varphi_{j\downarrow}^*(\mathbf{r}') \varphi_{j\downarrow}(\mathbf{r}) \right] \right. \\ &\quad \left. + \eta \left[\sum_{j=1}^{N_\uparrow+1} \varphi_{j\uparrow}^*(\mathbf{r}') \varphi_{j\uparrow}(\mathbf{r}) + \sum_{j=1}^{N_\downarrow} \varphi_{j\downarrow}^*(\mathbf{r}') \varphi_{j\downarrow}(\mathbf{r}) \right] \right\} \\ &\quad + \alpha_2 \dots \end{aligned} \quad (\text{A12})$$

The terms multiplying each α_j differ in the orbitals which contribute to the sums in the square brackets. Equation (A12) can be simplified as

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \alpha_1 \left\{ (1 - \eta) \gamma_1^{N_\uparrow, N_\downarrow+1}(\mathbf{r}, \mathbf{r}') + \eta \gamma_1^{N_\uparrow+1, N_\downarrow}(\mathbf{r}, \mathbf{r}') \right\} \\ &\quad + \alpha_2 \left\{ (1 - \eta) \gamma_2^{N_\uparrow, N_\downarrow+1}(\mathbf{r}, \mathbf{r}') + \eta \gamma_2^{N_\uparrow+1, N_\downarrow}(\mathbf{r}, \mathbf{r}') \right\} \\ &\quad + \dots \\ &= (1 - \eta) \sum_j \alpha_j \gamma_j^{N_\uparrow, N_\downarrow+1}(\mathbf{r}, \mathbf{r}') \\ &\quad + \eta \sum_j \alpha_j \gamma_j^{N_\uparrow+1, N_\downarrow}(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (\text{A13})$$

The sums in Eq. (A13) represent N -representable density matrices with $N_\uparrow, N_\downarrow + 1$ and $N_\uparrow + 1, N_\downarrow$ particles in the two spin channels, respectively. Since $N_\uparrow, N_\downarrow$ are the integer parts of $M_\uparrow, M_\downarrow$ these density matrices correspond to states with spin s^- and s^+ . Therefore, the left-hand-side of Eq. (A13) is N -representable according to the conditions (A1).

Hence, we have shown that the domain of density matrices which take the form of Eq. (A1) coincides with the domain of those that satisfy the conditions (A2). On the other hand, Eq. (A2) is a necessary condition for a γ^s to describe a general ensemble defined in Eq. (13). Thus, condition (A2) is

necessary and sufficient for γ^s to belong to the set of general ensembles, Eq. (13), as well. This more general ensemble, however, does not allow for a unique definition of fractional spin ensembles since there are several choices of coefficients ω_α for each s . The coefficients in Eq. (A2), on the other hand, are uniquely defined.

- ¹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ²W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ³J. P. Perdew, R. G. Parr, M. Levy, and J. J. L. Balduz, *Phys. Rev. Lett.* **49**, 1691 (1982).
- ⁴R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
- ⁵R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ⁶W. Yang, Y. Zhang, and P. W. Ayers, *Phys. Rev. Lett.* **84**, 5172 (2000).
- ⁷A. J. Cohen, P. Mori-Sánchez, and W. Yang, *Phys. Rev. B* **77**, 115123 (2008).
- ⁸P. Mori-Sánchez, A. J. Cohen, and W. Yang, *Phys. Rev. Lett.* **100**, 146401 (2008).
- ⁹P. Mori-Sánchez, A. J. Cohen, and W. Yang, *Science* **321**, 792 (2008).
- ¹⁰A. J. Cohen, P. Mori-Sánchez, and W. Yang, *J. Chem. Phys.* **129**, 121104 (2008).
- ¹¹N. Helbig, N. N. Lathiotakis, M. Albrecht, and E. K. U. Gross, *Europhys. Lett.* **77**, 67003 (2007).
- ¹²N. Helbig, N. N. Lathiotakis, and E. K. U. Gross, *Phys. Rev. A* **79**, 022504 (2009).
- ¹³S. Sharma, J. K. Dewhurst, N. N. Lathiotakis, and E. Gross, *Phys. Rev. B* **78**, 201103(R) (2008).
- ¹⁴M. A. Buijse and E. J. Baerends, *Mol. Phys.* **100**, 401 (2002).
- ¹⁵S. Goedecker and C. J. Umrigar, *Phys. Rev. Lett.* **81**, 866 (1998).
- ¹⁶O. Gritsenko, K. Pernal, and E. J. Baerends, *J. Chem. Phys.* **122**, 204102 (2005).
- ¹⁷T. L. Gilbert, *Phys. Rev. B* **12**, 2111 (1975).
- ¹⁸P. Leiva and M. Piris, *J. Chem. Phys.* **123**, 214102 (2005).
- ¹⁹P. Leiva and M. Piris, *J. Mol. Struct.: THEOCHEM* **770**, 45 (2006).
- ²⁰N. N. Lathiotakis and M. A. L. Marques, *J. Chem. Phys.* **128**, 184103 (2008).
- ²¹D. R. Rohr, K. Pernal, O. V. Gritsenko, and E. J. Baerends, *J. Chem. Phys.* **129**, 164105 (2008).
- ²²N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. Eich, M. A. L. Marques, and E. K. U. Gross, *Phys. Rev. A* **79**, 040501(R) (2009).
- ²³A. J. Coleman, *Rev. Mod. Phys.* **35**, 668 (1963).
- ²⁴A. M. K. Müller, *Phys. Lett.* **105A**, 446 (1984).
- ²⁵M. Piris, *Int. J. Quantum Chem.* **106**, 1093 (2006).
- ²⁶N. N. Lathiotakis, N. Helbig, and E. K. U. Gross, *Phys. Rev. B* **75**, 195120 (2007).
- ²⁷M. A. L. Marques and N. N. Lathiotakis, *Phys. Rev. A* **77**, 032509 (2008).
- ²⁸V. N. Staroverov and G. E. Scuseria, *J. Chem. Phys.* **117**, 2489 (2002).
- ²⁹J. M. Herbert and J. E. Harriman, *Chem. Phys. Lett.* **382**, 142 (2003).
- ³⁰R. L. Frank, E. H. Lieb, R. Seiringer, and H. Siedentop, *Phys. Rev. A* **76**, 052517 (2007).
- ³¹N. N. Lathiotakis, N. Helbig, A. Zacarias, and E. K. U. Gross, *J. Chem. Phys.* **130**, 064109 (2009).
- ³²N. N. Lathiotakis, N. Helbig, and E. K. U. Gross, *Phys. Rev. A* **72**, 030501 (2005).
- ³³P. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- ³⁴M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, *J. Chem. Phys.* **131**, 021102 (2009).
- ³⁵M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, *J. Chem. Phys.* **132**, 031103 (2010).
- ³⁶N. N. Lathiotakis, S. Sharma, N. Helbig, J. K. Dewhurst, M. A. L. Marques, F. Eich, T. Baldseifen, A. Zacarias, and E. K. U. Gross, *Z. Phys. Chem.* **224**, 467 (2010).
- ³⁷N. N. Lathiotakis, N. I. Gidopoulos, and N. Helbig, *J. Chem. Phys.* **132**, 084105 (2010).
- ³⁸Numerical results obtained with hippo computer program (info: lathiot@eie.gr), which performs minimization of RDMFT functionals using Gaussian basis set expansion of the natural orbitals. One- and two-electron integrals for the Cartesian Gaussian basis elements were calculated by gamess computer program (Ref. 43).
- ³⁹R. J. Buenker, *Studies in Physical and Theoretical Chemistry*, Current Aspects of Quantum Chemistry, Vol. 2, edited by R. Carbo (Elsevier, Amsterdam, 1981), p. 17.
- ⁴⁰R. J. Buenker and R. A. Phillips, *Journal of Molecular Structure (Theochem)* **123**, 291 (1985).
- ⁴¹D. R. Rohr, J. Toulouse, and K. Pernal, *Phys. Rev. A* **82**, 052502 (2010).
- ⁴²M. Piris, X. Lopez, F. Ruiperez, J. M. Matxain, and J. M. Ugalde, *J. Chem. Phys.* **134**, 164102 (2011).
- ⁴³M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, M. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).