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Analyzing effects of strong electron correlation within Kohn-Sham density-functional theory

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A density-functional-theory method for analyzing effects of strong electron correlation is presented, based on a single Kohn-Sham determinant. It yields the population of effectively unpaired (odd) electrons and depicts the strength of nondynamic correlation, both locally and globally. It provides also a quantitative estimate of localized magnetic moments without invoking symmetry-breaking procedures. Preliminary tests on some exemplary systems of strong correlation such as C_2, Cr_2, the NO dimer, and dissociating H_2 and N_2 are discussed in comparison with available post-Hartree-Fock wave-function studies. We show that the bond in C_2 is unlikely to have diradical character in its ground state, but may have it in some excited state. The singlet ground state of the NO dimer, however, does have a diradical character of the bonding. Quite interestingly, the bond in Cr_2 has a quad-radical nature.

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I. INTRODUCTION

Nondynamic (ND) electron correlation, also called static, is conventionally understood as an effect where the single-determinant Hartree-Fock (HF) reference fails to describe it properly and multireference wave functions are generally required [1]. Compounds with polyradical character of bonding are examples of "strongly correlated" chemical systems. Solid-state phenomena such as metal-insulator transitions, various magnetic phenomena, and superconductivity are examples of strongly correlated solid-state systems [2–5]. With density-functional theory (DFT), some of these effects have been analyzed in terms of left-right correlation [1,6], fractional-spin, and fractional-charge analysis [7], and using an alternative reference state [8]. The "simplest" example of left-right correlation is the stretched hydrogen molecule, where the two electrons forming the bond electron pair at equilibrium become only weakly paired and mostly localized each on a separate atom. Molecular magnets and singlet diradicaloids are other examples where such a weak pairing exists even at equilibrium. At the single-determinant self-consistent field (SCF) level, the valence electrons of a singlet system remain perfectly paired. Left-right correlation partly decouples the bond electron pairs, giving rise to a formation of effectively unpaired ("odd") electrons [9–11]. When the left-right correlation is strong, these electrons remain mostly unpaired and localized in the atomic regions of a molecule or solid. The formation of polyradical states is another example of unusually high generation of odd-electron density [11] localized on the atomic centers. In solid-state theory, this phenomenon is known as a narrow-band electron localization [12]. The formation of odd electrons is related to the nonidempotency of the correlated first-order reduced density matrix (RDM-1) evaluated via multideterminant wave functions, which in turn reflects the partial decoupling of the electron bond pairs [9]. At the SCF level [HF or Kohn-Sham (KS)], RDM-1 is idempotent and such effects cannot be described.

In this paper, we establish the concept of effectively unpaired (odd) electrons to describe the effects of ND correlation and measure its strength in the framework of Kohn-Sham (KS) DFT, without using a multideterminant approach. The method also gives a quantitative estimate of localized magnetic moments, which can be used in studies of magnetic materials [4,5].

II. THEORY

The formation of effectively unpaired (odd) electrons has been described so far in the literature only through the use of correlated wave functions. In this paper, we propose a method that formulates and describes this phenomenon based on a single-determinant KS DFT approach. We start from the existing wave-function-based formalism [9,11,13,14] related to properties of the first-order reduced density matrix (RDM-1). At the SCF level, RDM-1 is idempotent for the simple reason that the occupancy of a molecular orbital ($\psi_{i\sigma}^{\mathrm{ks}}$) is either one or zero with a single-determinant trial wave function:

$$\int \gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_2;\mathbf{r}_1)d\mathbf{r}_2 = \rho_\sigma(\mathbf{r}_1),$$
$$\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2) = \sum_i^{\mathrm{occ}} \psi_{i\sigma}^{\mathrm{ks}}(\mathbf{r}_1)\psi_{i\sigma}^{\mathrm{ks}}(\mathbf{r}_2), \tag{1}$$

where $\rho_\sigma(\mathbf{r}_1)$ is the electron density of spin σ at position $\mathbf{r_1}$, $\gamma_\sigma^{\mathrm{scf}}$ is the spin-resolved RDM-1 at the SCF level, and

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$\psi^{\rm ks}_{i\sigma}$ are the canonical Kohn-Sham orbitals. The cross product of nondiagonal elements, $\gamma^{\rm scf}_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma^{\rm scf}_\sigma(\mathbf{r}_2;\mathbf{r}_1)$, reflects a Hartree-Fock-like exchange and can be readily expressed in terms of a special two-electron function, i.e., the HF exchange hole $h_{{\rm X}\sigma\sigma}$:

$$\begin{gathered}\gamma^{\rm scf}_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma^{\rm scf}_\sigma(\mathbf{r}_2;\mathbf{r}_1) = \rho_\sigma(\mathbf{r}_1)h_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2),\\ \int h_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = 1.\end{gathered} \tag{2}$$

The notion of the exchange-correlation hole $h_{\rm XC}$, on the other hand, is related to the quantum-mechanical conditional pair probability $P_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)$ of finding a given electron at position $\mathbf{r}_2$ when another electron is at position $\mathbf{r}_1$ (please note that the functions $h_{{\rm X}\sigma\sigma}$ and $h_{{\rm XC}\sigma\sigma}$ are considered positively defined in this work for convenience, and energy expressions using them must include the required negative sign explicitly):

$$P_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\sigma(\mathbf{r}_2) - h_{{\rm XC}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2). \tag{3}$$

The important properties of these two-electron functions are summarized in the Appendix.

When RDM-1 includes electron correlation, it becomes nonidempotent,

$$D_\sigma(\mathbf{r}_1) \equiv \rho_\sigma(\mathbf{r}_1) - \int \gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1)d\mathbf{r}_2 \geqslant 0. \tag{4}$$

The function $D_\sigma(\mathbf{r}_1)$ measures the deviation from idempotency of the correlated RDM-1 and represents the density of odd electrons of spin σ at point $\mathbf{r}_1$ [9,14]. It is positively defined since the orbital occupancies with a correlated wave function are all between 0 and 1. This also shows that electron correlation tends to reduce the value of the RDM-1 cross product globally. From this perspective, the formation of effectively unpaired (odd) electrons in singlet systems is exclusively a correlation-based phenomenon with a subtle quantum origin. Summing $D_\sigma(\mathbf{r}_1)$ over the spin components gives the total density of odd electrons, and integrating the latter over space gives the mean total number of odd electrons $\bar{N}_u$:

$$D_u(\mathbf{r}) = 2\sum_\sigma D_\sigma(\mathbf{r}), \quad \bar{N}_u = \int D_u(\mathbf{r})d\mathbf{r}. \tag{5}$$

The appearance of a factor of 2 in Eq. (5) above is required for reasons discussed in Ref. [14]. We proceed further with the observation that the correlated RDM-1 cross product reflects an effective exchange, also known as cumulant exchange [10]. The KS exact-exchange hole is itself artificially too delocalized. However, the total exchange-correlation interaction in a finite system with strong left-right correlation is normally fairly localized, i.e., largely confined within a region of roughly atomic size [15]. The effective exchange described with the correlated RDM-1 cross product should be fairly localized as well. With this in mind, and following an analogy with the SCF formula given by Eq. (2), we explore the following ansatz for the sake of evaluating the number of odd electrons in closed-shell systems:

$$\begin{gathered}\gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1) \approx \rho_\sigma(\mathbf{r}_1)\bar{h}^{\rm eff}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2),\\ \int \bar{h}^{\rm eff}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 \leqslant 1,\end{gathered} \tag{6}$$

where $\bar{h}^{\rm eff}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)$ is a certain effective exchange hole yet to be determined. Note that in this representation, RDM-1 becomes nonidempotent only if the normalization of the effective hole is less than 1. To find a suitable expression of this form that would lead to accurate estimates of the odd-electron density, we resort to some ideas of Becke's B05 DFT model. This model describes ND left-right correlation effects in terms of certain real-space properties of the exchange-correlation hole [6]. The extra delocalization of the exchange hole alone is compensated in the B05 model by suitable real-space corrections, resulting in the following exchange-correlation ND hole for α spin:

$$\bar{h}_{{\rm XC}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \bar{h}^{\rm aux}_{{\rm X}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + f_{\rm c}(\mathbf{r}_1)\,\bar{h}^{\rm aux}_{{\rm X}\beta\beta}(\mathbf{r}_1,\mathbf{r}_2). \tag{7}$$

Its β counterpart, $\bar{h}_{{\rm XC}\beta\beta}$, can be obtained by simply switching α to β and β to α. We note that the same rule applies to all spin-specific quantities in the rest of this work. The function $\bar{h}^{\rm aux}_{{\rm X}\sigma\sigma}(\mathbf{r}_1;\mathbf{r}_2)$ is a model DFT exchange hole of Becke-Roussel (BR) form [16]. The original BR hole is localized within a region of roughly atomic size and has the same curvature as the exact-exchange hole at the reference point. In the B05 model, this BR hole is used with a relaxed (effective) normalization, such that the potential from the relaxed BR hole equals that of the exact-exchange hole. This results in values of the relaxed normalization less than or equal to 1 [compare with Eq. (6)]:

$$\int \bar{h}^{\rm aux}_{{\rm X}\sigma\sigma}(\mathbf{r}_1;\mathbf{r}_2)d\mathbf{r}_2 = N^{\rm eff}_{X\sigma}(\mathbf{r}_1) \ \leqslant 1. \tag{8}$$

The form of $N^{\rm eff}_{{\rm X}\sigma}(\mathbf{r})$ is quite complicated, but it is possible to represent it in closed analytic form [17,18]. The smaller the relaxed normalization $N^{\rm eff}_{X\alpha}(\mathbf{r})$, the more delocalized the corresponding exact-exchange hole about the reference electron at $\mathbf{r}$ [6]. The α-α exchange hole is further deepened by a fraction of the β-β exchange hole, $f_{\rm c}(\mathbf{r}_1)\,\bar{h}^{\rm aux}_{{\rm X}\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)$, which gives rise to ND correlation. The local correlation factor $f_{\rm c}$ in Eq. (7) governs this deepening and hence the strength of ND correlation at each point, and is given as [6]

$$\begin{aligned} f_{\rm c}(\mathbf{r}) &= \min[f_\alpha(\mathbf{r}), f_\beta(\mathbf{r}), 1],\\ 0 &\leqslant f_{\rm c}(\mathbf{r}) \leqslant 1,\\ f_\alpha(\mathbf{r}) &= \frac{1 - N^{\rm eff}_{{\rm X}\alpha}(\mathbf{r})}{N^{\rm eff}_{{\rm X}\beta}(\mathbf{r})}.\end{aligned} \tag{9}$$

Based on the above analysis, we propose the following formula of the correlated RDM-1 cross product by substituting, in Eq. (6), $\bar{h}^{\rm eff}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)$ with $\bar{h}^{\rm aux}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)$ for the sake of evaluating the odd-electron density in closed-shell systems:

$$\gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\,\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1) = \rho_\sigma(\mathbf{r}_1)\bar{h}^{\rm aux}_{{\rm X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2). \tag{10}$$

Using this expression in Eqs. (4) and (5), the density of odd electrons (5) becomes

$$D_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r})\big[1 - N^{\rm eff}_{X\sigma}(\mathbf{r})\big]. \tag{11}$$

In the Appendix, we present an alternative derivation that has a more general validity than Eq. (10) and can be used in open-shell cases as well.

Equation (11) has a clear physical meaning: the smaller $N^{\rm eff}_{X\sigma}(\mathbf{r})$, the stronger the ND correlation at $\mathbf{r}$, the larger the odd-electron density $D_\sigma(\mathbf{r})$. One should note that the ansatz given by Eq. (10) is not limited to the B05 model specifically, as long as an appropriate alternative form of $\bar{h}^{\text{eff}}_{X\sigma\sigma}$ can be defined. The final formulas for the spin-summed odd-electron density and the total mean number of odd electrons read (see the Appendix)

$$D_u(\mathbf{r}) = 4\, a^{\text{op}}_{\text{nd}} \sum_{\sigma} \rho_\sigma(\mathbf{r})\big[1 - N^{\text{eff}}_{X\sigma}(\mathbf{r})\big],$$
$$\bar{N}_u = \int D_u(\mathbf{r})d\mathbf{r}. \tag{12}$$

Here, $a^{\text{op}}_{\text{nd}} = 0.526$ is the SCF-optimized linear coefficient multiplying the opposite-spin B05 ND energy term [18].

Properties of atoms in molecules are often used in qualitative chemical analysis of reactivity and bonding. It is hence instructive to decompose the total mean number of odd electrons into atomic contributions. By partitioning in real space the mean total number of odd electrons $\bar{N}_u$ as a sum of atomic contributions, we obtain the atomic population of odd electrons $[F_r(A)]$ as

$$F_r(A) = \int_{\Omega_A} D_u(\mathbf{r})d\mathbf{r}, \tag{13}$$

where Ω_A is a subregion assigned to atom A in the system. To define these atomic regions in a simple way, we use the partitioning of the grid space into atomic subgroups within Becke's grid-integration scheme [19]. All calculations are done with a development version of the Q-CHEM program [20], using the G3LARGE basis set [21]. For the quadrature, we used an unpruned grid composed of 192 radial and 434 angular points per atomic region. The exact-exchange energy density required for the evaluation of $N^{\text{eff}}_{X\sigma}$ is calculated with the resolution-of-identity (RI) technique described in Ref. [18]. Since the present method does not require symmetry breaking, singlet states are calculated in a restricted Kohn-Sham (RKS) manner, even at large bond stretches. In this way, we avoid the destructive effects that the spin contamination has on $F_r(A)$.

III. RESULTS AND DISCUSSION

To validate the present method, we first compare the calculated odd-electron atomic population and total mean number of odd electrons $\bar{N}_u$ [Eq. (13)] with literature results, as shown in Table I. The literature results for the odd-electron populations listed in the last column of Table I are from the configuration-interaction singles-and-doubles (CISD) wave-function method with geometries optimized at the CISD/6-31G** level [13]. As explained in the preceding section, our method requires only a single-determinant SCF solution. The calculations were done at two sets of geometries, optimized at the CISD/6-31G** level (Table I, columns 4 and 5) and experimental level (Table I, column 3). At the CISD geometries, we first calculated the odd-electron populations using HF SCF molecular orbitals as an input (Table I, column 4) and then using converged RI-B05 orbitals (Table I, column 5). Converged RI-B05 SCF orbitals were used at the experimental geometries as well (Table I, column 3). Our results are, on average, in qualitative agreement with CISD results, with mean absolute percental deviation (MAPD) between 22.3% (Table I, column 3) and 24.0% (Table I, column 4). Note that the difference in the odd-electron population on the H atoms is, in most cases, somewhat larger and this is the dominant contribution to the MAPD between the two methods. This could, in part, be due to the different way the atomic regions are defined. In Ref. [13], Bader's topological-atom partitioning is used, while we use the partitioning of the grid points into atomic subgroups as mentioned above. It is seen from the data in Table I that changes in input densities and geometries, such as the ones studied here, do not alter the results significantly since the electronic structures are not altered appreciably by those changes. We note that accurate estimates of odd-electron atomic populations are still scarce in the literature. The CISD method does not include most of the ND correlation in strongly correlated systems, for which our method aims. Still, it includes a large portion of the correlation effect for the stable molecules listed in Table I. The comparative analysis indicates that our method yields qualitatively reasonable results for such systems, in spite of the fact that it uses no information from correlated wave functions.

TABLE I. Comparison of calculated population of odd electrons in this work with literature data.

System	Atom	$F_r(A)$[a]	$F_r(A)$[b]	$F_r(A)$[c]	$F_r(A)$[d]
H_2	H	0.049(0.055)	0.049	0.049	0.060
N_2	N	0.414(0.423)	0.406	0.423	0.346
H_2O	O	0.295(0.346)	0.282	0.296	0.325
	H	0.053(0.052)	0.055	0.053	0.033
NH_3	N	0.248(0.282)	0.233	0.249	0.309
	H	0.065(0.066)	0.065	0.065	0.044
CH_4	C	0.182(0.178)	0.176	0.181	0.219
	H	0.063(0.063)	0.063	0.063	0.060
C_2H_4	C	0.244(0.249)	0.237	0.246	0.257
	C	0.244(0.249)	0.237	0.246	0.257
	H	0.076(0.076)	0.075	0.076	0.055
MAPD (%)		22.3%	24.0%	22.4%	

[a] Results of the present model using 6-31G** (6-311+G** bases in parentheses) at experimental geometries with converged RI-B05 RKS calculations.

[b] Results with RI-B05 used in a post-CISD perturbative fashion, using 6-31G** at CISD-optimized geometries.

[c] Results with converged RI-B05 RKS using 6-31G** at CISD-optimized geometries.

[d] CISD/6-31G** results of Ref. [13]. $F_r(A)$ is the atomic population of odd electrons, denoted in Ref. [13] as u_{Ω_A}.

TABLE II. RI-B05/G3LARGE SCF RKS results for the population of odd electrons in H_2 at several R(H-H) distances (Å).

R(H-H)	0.741	1.5	2.5	3.5	4.5	6.0	10.0
F_r(H)-pert[a]	0.050	0.140	0.356	0.538	0.658	0.766	0.882
F_r(H)[b]	0.056	0.171	0.417	0.592	0.705	0.803	0.902
$\bar{N}_u$[b]	0.112	0.242	0.834	1.184	1.410	1.606	1.804

[a] Post-HF perturbative result with RI-B05.

[b] Converged RKS RI-B05 results using a preceding HF solution as initial guess.

Next we consider the trend of $F_r(A)$ and $\bar{N}_u$ upon bond stretching. H_2 is the "simplest" example of a single covalent

TABLE III. RI-B05/G3LARGE SCF RKS results for the odd-electron atomic population in N_2 at different R(N-N) distances (Å).

R(N-N)	1.098	1.80	2.5	3.0	5.0	7.0	8.0
F_r(N)-pert	0.355	1.044	1.559	1.792	2.239	2.417	2.471
F_r(N)	0.411	1.027	1.544	1.779	2.236	2.418	2.469
$\bar{N}_u$	0.822	2.054	3.088	3.558	4.472	4.836	4.938
%TAE$[T_4+T_5]$[a]	0.51						

[a] From Ref. [22].

bond, where $\bar{N}_u$ should be near zero at equilibrium and increase to about 2 at the dissociation limit since F_r(H) attains 1 in that limit. The results in Table II largely reflect this trend. Note that we have calculated $F_r(A)$ and $\bar{N}_u$ using two different SCF KS solutions. The first row of Table II shows results with RI-B05 obtained in a post-SCF manner [F_r(H)-pert] starting from a converged HF solution, similar to the way the results in column 4 of Table I were obtained. The second row contains the converged RI-B05 DFT results for F_r(H) using the HF solution as an initial guess. Both sets of values show a similar trend.

Table III lists the RI-B05/G3LARGE results for the dissociation of the N_2 molecule. F_r(N) increases reasonably upon bond stretching. At equilibrium [R(N-N) = 1.098 Å], N_2 displays a certain degree of strong ND correlation with $\bar{N}_u \approx 0.82$. This value is not far from the multireference configuration interaction (MRCI) estimate of Staroverov and Davidson of about 0.7 [11]. Martin's %TAE$[T_4+T_5]$ index of estimating the strength of the ND correlation from another many-electron perspective [22] is about 0.51. Our method somewhat underestimates F_r(N) in the dissociation limit. This could be due to the way the atomic regions are defined here and/or the use of the B05 fitting parameters that were optimized previously just on thermochemistry data [18]. This problem will be investigated in a follow-up study.

Systems with strong nondynamic correlation are of special interest for the present model. One notoriously difficult such system is Cr_2, which has a highly multiconfigurational singlet ground state [23–25]. To describe the antiferromagneticlike character of Cr_2 with DFT, Ruiz-Díaz *et al.* [24] applied the popular broken-symmetry DFT approach in which localization of nonzero spin density is enforced into the atomic regions by breaking the spin symmetry. They have estimated that the effective magnetic moment on each Cr atom is between $\pm1.0\ \mu_B$ and $\pm2.0\ \mu_B$, depending on the functional used [24]. We calculated F_r(Cr) with our method using the SCF solutions of various functionals and obtained it between 1.94 (B3LYP-B05) and 1.82 (SCF RI-B05) without using a symmetry-breaking procedure (Table IV). These comparisons indicate that the present method may be useful in DFT studies of this type.

TABLE V. RI-B05/G3LARGE RKS results for the ground state and two singlet excited states of C_2. (RI-B05 RKS calculations using converged Hartree-Fock solutions as initial guess. The SCF solutions are obtained in combination with the MOM method [33].)

State	ΔE (eV)	R_e(C-C) (Å)	F_r(C)	$\bar{N}_u$	%TAE(T_4+T_5)[a]
$X\,^1\Sigma_g^+$	0.00	1.25	0.678	1.356	1.83
$B\,^1\Delta_g$	0.78	1.39	0.323	0.646	
$^{1'}\Sigma_g$	5.04	1.16	0.811	1.622	

[a] From Ref. [22].

Another interesting aspect of Cr_2 is its multiple bond nature. A Cr atom has six valence electrons and Cr_2 should form formally a hextuple bond. The bond order reported by Brynda *et al.* [26] and calculated with a single-determinant DFT is indeed about six. They also calculated the effective bond order using symmetry-broken DFT and multireference wavefunction methods and obtained lower multiplicity of about 3.46 and 4.51, respectively, with the former estimate being perhaps less reliable due to the spin contamination. Our estimates of the odd-electron atomic population F_r(Cr) of slightly less than 2 (Table IV) correspond to an effective correlated bond order that is slightly larger than 4, i.e., about two electron pairs out of six are not contributing to the bond multiplicity.

We note that the present method needs only SCF molecular orbitals as an input and thus can be applied with any functional in a post-SCF fashion, as shown by the results in Table IV discussed above. It can also be applied to excited states as long as the weight of the dominant configuration is sufficiently large. To illustrate this point, we have analyzed a few electronic states of the C_2 molecule. It is another difficult case for single-reference methods that has been studied extensively at various levels including full CI (FCI) [27,28] and DFT methods [29]. Our results for F_r(C) and $\bar{N}_u$ in the singlet ground state $X\,^1\Sigma_g^+$ of C_2 are $F_r(C) = 0.68$ and $\bar{N}_u = 1.36$ (Table V). These values indicate a certain degree of strong ND correlation. However, the equilibrium $\bar{N}_u$ value is closer to 1 rather than 2, indicating that the ground state might not be of the diradical type, which is in agreement with the conclusions of Sherrill *et al.* based on FCI analysis [30]. This observation is also in line with the conclusion of Shaik *et al.* [31] based on valence-bond theory that C_2 has an "almost-quadruple" bond multiplicity.

It is interesting to see how F_r(C) changes upon dissociation not only in the ground state, but also in excited states. Figure 1(a) contains the dissociation energy curves of the $X\,^1\Sigma_g^+$ ground state and the excited singlet state $B\,^1\Delta_g$ calculated in this work. Both states have been well studied in the literature [27,28,32]; both dissociate to two triplet C atoms. The ground- and excited-state energy curves of C_2 are calculated here using the RI-B05 functional [18] combined

TABLE IV. Population of odd electrons in Cr_2 at its experimental bond length, R(Cr-Cr) = 1.679 Å, calculated with RI-B05/G3LARGE SCF and with RI-B05/G3LARGE post-SCF using SCF solutions from other functionals.

Method	B3LYP-B05	M06HF-B05	M062X-B05	MCY2-B05	RI-B05
F_r(Cr)	1.94	1.80	1.89	1.92	1.82
$\bar{N}_u$	3.88	3.60	3.78	3.84	3.64

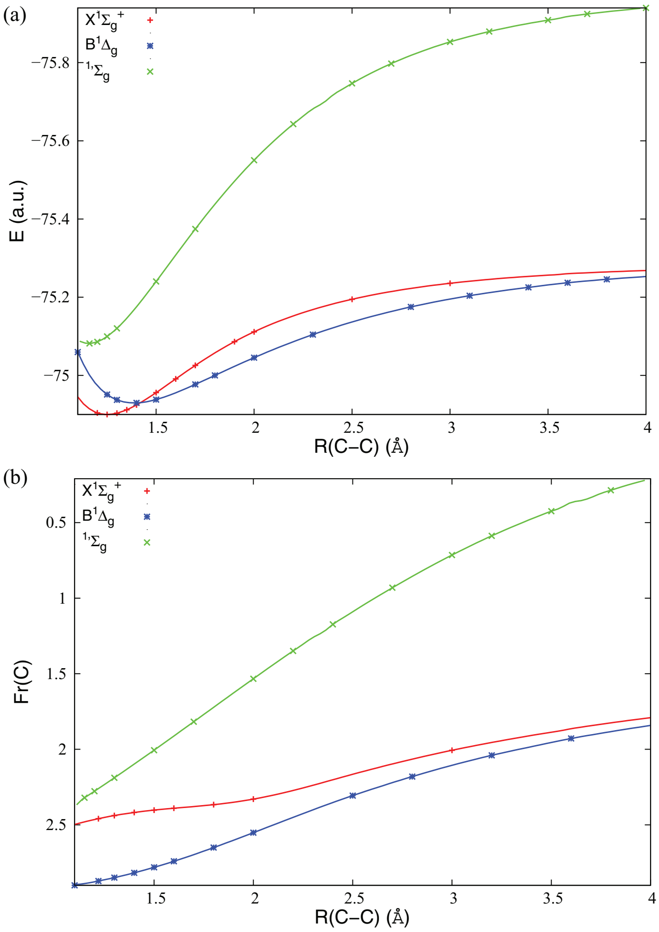

FIG. 1. (Color online) (a) RKS dissociation energy curves of three singlet states of C_2 calculated with RI-B05/G3LARGE using the MOM method. (b) Odd-electron atomic population vs the C-C distance for three singlet states of C_2 calculated with RI-B05/G3LARGE RKS using the MOM method.

with the maximum overlap method (MOM) of converging SCF equations to solutions that approximate certain excited states [33]. As shown in Fig. 1(b), the calculated $F_r(\mathrm{C})$ values show the correct trend upon dissociation for both states. The $B\,^1\Delta_g$ excited state originates from electronic configuration $\{(\mathrm{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2\}$ [27], which differs from the ground-state configuration $\{(\mathrm{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^4\}$ by having the former lowest unoccupied molecular orbital (LUMO) $3\sigma_g$ filled by half emptying the doubly degenerate highest occupied molecular orbital (HOMO) $1\pi_u$. This is accompanied by a decrease of $F_r(\mathrm{C})$ and $\bar{N}_u$ in this excited state by about a factor of two (Table V), possibly because the two electrons migrating from $1\pi_u$ to $3\sigma_g$ decrease the degree of *sp* hybridization and thus increase the degree of self-pairing of the two (2*s*) electrons on each C atom. The two energy curves cross at certain stretched C-C distance [Fig. 1(a)], which is a known feature of the $B\,^1\Delta_g$ state [27]. Note that in spite of the energy crossing, the $F_r(\mathrm{C})$ values that remain there are largely different in each state [Fig. 1(b)]. We have also obtained a solution that simulates one high-energy singlet excitation of C_2, denoted here as $^{1'}\Sigma_g$; see Table V and Fig. 1(a). This state has quite a large total number of odd electrons, $\bar{N}_u = 1.6$, suggesting that the (virtual) bonding in this excited state may have a diradical character. This is probably because the former ground-state HOMO remains now completely filled, while emptying the inner orbital $2\sigma_u$ decreases the screening of the $1\pi_u$ valence electrons from the nuclei. This high excited state dissociates toward two quintuplet C atoms, as is seen from Figs. 1(a) and 1(b). We note in passing that the RI-B05 method combined with the MOM technique yields a qualitatively more adequate asymptote of the C_2 energy curves compared to the second-order Møller-Plesset (MP2) and coupled cluster with single, double, and partially triple excitations [CCSD(T)] curves reported in the literature [27,28].

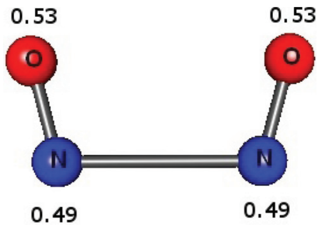

FIG. 2. (Color online) Population of odd electrons in NO dimer calculated with RI-B05/G3LARGE RKS method.

Going beyond diatomic molecules, strong ND correlation is the major factor governing the properties of the NO dimer (cis-ONNO) in its singlet ground state [17,34,35]. The usual picture of each monomer sharing a single electron to form a covalent N-N bond pair ia not adequate for this system. Hartree-Fock predicts an unbound dimer with an energy of 50 kcal/mol above the monomers, whereas in reality the dimer is bound by about 3.2 kcal/mol. We have shown previously that the RI-B05 model is able to predict the ground-state energy of cis-ONNO correctly [17,36,37]. Our estimate of the odd-electron atomic population here is depicted in Fig. 2. The total number of odd electrons is $\bar{N}_u = 2.04$, with each monomer having 1.02 radical electrons shared between the oxygen $[F_r(\mathrm{O}) = 0.53]$ and the nitrogen $[F_r(\mathrm{N}) = 0.49]$. This picture supports a diradical type of bonding between the two NO monomers.

IV. CONCLUSIONS

In this work, we propose a method that captures the effects of strong ND correlation with a single-determinant treatment. It yields the population of odd electrons within the standard Kohn-Sham DFT framework, which can be used as a DFT-based descriptor of chemical bonding, especially regarding strongly correlated systems. It also gives a quantitative estimate of localized magnetic moments, which can be used in studies of magnetic materials. The method does not require any symmetry-breaking procedure in order to generate the localized magnetic moments in singlet systems. Our exemplary analysis of some well-known difficult cases shows that the proposed method offers a similar quality of description as the multiconfiguration wave-function methods and helps to elucidate the unusual bonding phenomenon of systems such as Cr_2 and NO dimer. Calculations on the C_2 molecule show that the method is capable of distinguishing bonding patterns of different electronic states. It has the distinct advantage that it can be applied to much larger systems than presently allowed by the conventional multireference methods.

This approach can be further improved in line with the B13 model of Becke [38] that extends the applicability of the B05 method to describe better strong electron correlation.

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APPENDIX

The notion of effectively unpaired (odd) electrons discussed in this paper is related to the nonidempotency of the correlated first-order reduced density matrix (RDM-1). This property stems from certain exact features of the second-order reduced density matrix (RDM-2) $\tilde{\mathbf{\Gamma}}$ with its diagonal elements defined as (in normalization of McWeeny [39])

$$\tilde{\Gamma}(x_1,x_2) = N(N-1)\int \ldots \int \Psi(x_1,x_2,x_3,\ldots,x_N) \\ \times \Psi^*(x_1,x_2,x_3,\ldots,x_N)dx_3dx_4,\ldots,dx_n, \tag{A1}$$

where $x_i \equiv (\mathbf{r}_i\, s_i)$ denotes the space and spin coordinates of an electron, and $N = N_\alpha + N_\beta$ is the total number of electrons. After integrating over the spin coordinates in Eq. (A1), one obtains the spin-traced RDM-2 as a sum of three independent spin-spin components [40],

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2) = \Gamma_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \Gamma_{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2) + 2\Gamma_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2). \tag{A2}$$

We will need here only the parallel-spin diagonal elements of RDM-2. These components obey the following exact normalization and reduction relations [40]:

$$\iint \Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = N_\sigma(N_\sigma - 1), \tag{A3}$$

$$\int \Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = (N_\sigma - 1)\,\rho_\sigma(\mathbf{r}_1), \tag{A4}$$

where $\rho_\sigma(\mathbf{r}_1)$ is the electron density of spin σ at position $\mathbf{r_1}$. The $\mathbf{\Gamma}_{\sigma\sigma}$ components can be cast in different forms. The one we start with is in terms of the exchange-correlation hole h_{XC}, a two-electron function commonly used in DFT studies (h_{XC} is considered positively defined here, which is more convenient for the derivations in this work):

$$\Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\sigma(\mathbf{r}_1)\,\rho_\sigma(\mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)h_{\mathrm{XC}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2). \tag{A5}$$

The reduction relation, given by Eq. (A4), leads to the following sum rule for an isolated system:

$$\int h_{\mathrm{XC}\sigma\sigma}(\mathbf{r}_{\mathbf{r}_1},\mathbf{r}_{\mathbf{r}_2})d\mathbf{r}_2 = 1. \tag{A6}$$

The exchange-correlation hole itself is further partitioned into an exchange hole and a correlation remainder,

$$h_{\mathrm{XC}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = h_{\mathrm{X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) + h_{\mathrm{C}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2). \tag{A7}$$

This leads to the following decomposition of the sum rule given by (A6):

$$\int h_{\mathrm{X}\sigma\sigma}(\mathbf{r}_{\mathbf{r}_1},\mathbf{r}_{\mathbf{r}_2})d\mathbf{r}_2 = 1, \tag{A8}$$

$$\int h_{\mathrm{C}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = 0. \tag{A9}$$

The exchange hole alone can be readily obtained from the occupied Kohn-Sham orbitals and the Kohn-Sham SCF electron density,

$$h_{\mathrm{X}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\rho_\sigma}\sum_{i,j}^{\mathrm{occ}} \psi_{i\sigma}^{\mathrm{ks}}(\mathbf{r}_1)\psi_{i\sigma}^{\mathrm{ks}}(\mathbf{r}_2)\psi_{j\sigma}^{\mathrm{ks}}(\mathbf{r}_2)\psi_{j\sigma}^{\mathrm{ks}}(\mathbf{r}_1) \\ \equiv \frac{1}{\rho_\sigma}\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2)\,\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_2;\mathbf{r}_1), \tag{A10}$$

where $\gamma_\sigma^{\mathrm{scf}}$ is the first-order reduced density matrix (RDM-1) at the Kohn-Sham SCF level. The diagonal elements of RDM-2 in this Kohn-Sham based representation read

$$\Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\sigma(\mathbf{r}_1)\,\rho_\sigma(\mathbf{r}_2) - \gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2)\,\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_2;\mathbf{r}_1) \\ - \rho_\sigma(\mathbf{r}_1)h_{\mathrm{C}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2). \tag{A11}$$

If the correlation term is omitted, the diagonal elements of RDM-2 at the KS SCF level become

$$\Gamma_{\sigma\sigma}^{\mathrm{scf}}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2) - \gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_2;\mathbf{r}_1). \tag{A12}$$

The idempotency relation of RDM-1, discussed in the paper, holds true only at the SCF level: integrating Eq. (A12) over one of the electron coordinates and taking into account the reduction relation (A4) gives

$$\int \Gamma_{\sigma\sigma}^{\mathrm{scf}}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 \\ \equiv (N_\sigma - 1)\rho_\sigma(\mathbf{r}_1) \\ = N_\sigma\rho_\sigma(\mathbf{r}_1) - \int \gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma^{\mathrm{scf}}(\mathbf{r}_2;\mathbf{r}_1)d\mathbf{r}_2, \tag{A13}$$

which leads to Eq. (1).

An alternative representation of the correlated RDM-2 is given by the so-called cumulant expansion [10,41],

$$\Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2) - \gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1) \\ - \Lambda_{\sigma\sigma}^{\mathrm{c}}(\mathbf{r}_1,\mathbf{r}_2), \tag{A14}$$

where $\gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)$ are now elements of the correlated RDM-1. In analogy with the exchange only case, given by Eq. (A10), the correlated RDM-1 cross product $\gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\,\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1)$ can be viewed as representing a "cumulant exchange." It does not obey the idempotency relation any longer. Instead, the following cumulant sum rule stems from the reduction formula, given by Eq. (A4) [10]:

$$\int \Lambda_{\sigma\sigma}^{\mathrm{c}}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = \rho_\sigma(\mathbf{r}_1) - \int \gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1)d\mathbf{r}_2. \tag{A15}$$

In this representation, the cumulant correlation term Λ^{c} is a generator of odd-electron density [10,41].

To use the cumulant expansion for evaluating the density of odd electrons, we need some approximate form of Λ^{c}. The formation of odd electrons is mainly due to the left-right correlation, so we need an approximation for Λ^{c} that would take into account such effects. In multicenter systems with strong nondynamic correlation, the exact-exchange hole alone is artificially too delocalized. In Becke's B05 method

[6], this extra delocalization is compensated for by using a special real-space model of the exchange-correlation (XC) hole $\bar{h}_{\mathrm{XC}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)$,

$$\bar{h}_{\mathrm{XC}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = h^{\mathrm{eff}}_{\mathrm{nd}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) + \bar{h}^{\mathrm{dyn}}_{\mathrm{C}\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2), \quad \text{(A16)}$$

$$h^{\mathrm{eff}}_{\mathrm{nd}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \bar{h}^{\mathrm{aux}}_{\mathrm{X}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \Delta^{\mathrm{nd}}_{\beta\beta\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2), \quad \text{(A17)}$$

$$\Delta^{\mathrm{nd}}_{\beta\beta\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) \equiv f_{\mathrm{c}}(\mathbf{r}_1)\,\bar{h}^{\mathrm{aux}}_{\mathrm{X}\beta\beta}(\mathbf{r}_1,\mathbf{r}_2) + \bar{h}^{\mathrm{nd}}_{\mathrm{C}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2), \quad \text{(A18)}$$

where $f_{\mathrm{c}}(\mathbf{r}_1)$ is the opposite-spin correlation factor given by Eq. (9), $\bar{h}^{\mathrm{nd}}_{\mathrm{C}\alpha\alpha}$ is the second-order parallel-spin ND correction to the XC hole that appears only in the open-shell case [6], and $h^{\mathrm{eff}}_{\mathrm{nd}\alpha\alpha}$ is modified by the ND correlation effective ("screened") exchange hole that now obeys the sum rule (A8), in place of the original exact-exchange hole:

$$\int h^{\mathrm{eff}}_{\mathrm{nd}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = 1. \quad \text{(A19)}$$

In the above expressions, $\bar{h}^{\mathrm{aux}}_{\mathrm{X}\alpha\alpha}(\mathbf{r}_1;\mathbf{r}_2)$ is the auxiliary model exchange hole function of the B05 model described by Eqs. (7) and (8). The last term on the right-hand side (rhs) of Eq. (A16) is the dynamic-correlation hole for electrons with parallel spins, which obeys the sum rule given by Eq. (A9). The B05 real-space model of left-right correlation gives us an idea of how we can find a suitable approximation of the cumulant correlation term. We start with the formally exact expression of RDM-2, given by Eq. (A11), and we modify it in the manner of the method of successive approximations [42]: we first add and subtract one and the same (positively defined) term that reflects the strength of ND correlation in Eq. (A17),

$$\begin{aligned}\Gamma_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = {}& \rho_\alpha(\mathbf{r}_1)\rho_\alpha(\mathbf{r}_2) - \big[\gamma^{\mathrm{scf}}_\alpha(\mathbf{r}_1;\mathbf{r}_2)\,\gamma^{\mathrm{scf}}_\alpha(\mathbf{r}_2;\mathbf{r}_1)\\ &- \rho_\alpha(\mathbf{r}_1)\Delta^{\mathrm{nd}}_{\beta\beta\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\big] - \rho_\alpha(\mathbf{r}_1)\,\Delta^{\mathrm{nd}}_{\beta\beta\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\\ &- \rho_\alpha(\mathbf{r}_1)h_{\mathrm{C}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2). \end{aligned} \quad \text{(A20)}$$

The expression in brackets in the above equation has the meaning of a RDM-1 cross product that is modified by the ND correlation. This is still just a formal rearrangement and manipulation of the exact expression of $\Gamma_{\sigma\sigma}$. It gives, however, an idea of how to find a suitable successive approximation for the cumulant correlation term. If we consider formally the terms in brackets in Eq. (A20) as a low-order approximation to the correlated RDM-1 cross product, then the last two terms of this equation can be considered as an approximate form of the cumulant correlation term Λ^{c} in the cumulant expansion (A14):

$$\begin{aligned}\Gamma_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) \approx {}& \rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2) - \gamma_\sigma(\mathbf{r}_1;\mathbf{r}_2)\gamma_\sigma(\mathbf{r}_2;\mathbf{r}_1)\\ &- \tilde{\Lambda}^{\mathrm{c}}_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2),\end{aligned} \quad \text{(A21)}$$

$$\tilde{\Lambda}^{\mathrm{c}}_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \rho_\alpha(\mathbf{r}_1)\Delta^{\mathrm{nd}}_{\beta\beta\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \rho_\alpha(\mathbf{r}_1)h_{\mathrm{C}\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2). \quad \text{(A22)}$$

Integrating both sides of Eq. (A21) over $\mathbf{r}_2$ and using Eqs. (A4) and (A9) leads to

$$\begin{aligned}&\int \gamma_\alpha(\mathbf{r}_1;\mathbf{r}_2)\gamma_\alpha(\mathbf{r}_2;\mathbf{r}_1)d\mathbf{r}_2\\ &\quad = \rho_\alpha(\mathbf{r}_1)\left[1 - f_{\mathrm{c}}(\mathbf{r}_1)N^{\mathrm{eff}}_{X\beta}(\mathbf{r}_1) - \frac{1}{2}A_{\alpha\alpha}(\mathbf{r}_1)M^{(2)}_\alpha(\mathbf{r}_1)\right],\end{aligned} \quad \text{(A23)}$$

where the last of the terms in brackets on the rhs of the above equation is the second-order parallel-spin ND contribution, $A_{\alpha\alpha}$ is the corresponding parallel-spin correlation factor, and $M^{(2)}_\alpha$ is the integrated second moment of the auxiliary B05 exchange hole $\bar{h}^{\mathrm{aux}}_{\mathrm{X}\alpha\alpha}$ [6]. Equation (A23) leads directly to the following general expression of the odd-electron density per spin direction:

$$\begin{aligned}D_\alpha(\mathbf{r}_1) &= \int \tilde{\Lambda}^{\mathrm{c}}_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2\\ &= \rho_\alpha(\mathbf{r}_1)f_{\mathrm{c}}(\mathbf{r}_1)N^{\mathrm{eff}}_{X\beta}(\mathbf{r}_1) + \frac{1}{2}\rho_\alpha(\mathbf{r}_1)A_{\alpha\alpha}(\mathbf{r}_1)M^{(2)}_\alpha(\mathbf{r}_1).\end{aligned} \quad \text{(A24)}$$

The main expression of odd-electron density per spin direction for closed-shell systems used in the paper, given by Eq. (11), can now be contemplated from this more general perspective. In the closed-shell case, Eq. (A24) reduces to

$$D_\alpha(\mathbf{r}_1) = \rho_\alpha(\mathbf{r}_1)f_{\mathrm{c}}(\mathbf{r}_1)N^{\mathrm{eff}}_{X\beta}(\mathbf{r}_1). \quad \text{(A25)}$$

Using the formula for the opposite-spin correlation factor f_c, given by Eq. (9), and the fact that in the closed-shell case $f_\alpha = f_\beta$, leads to Eq. (11), provided that f_σ is set to not exceed 1 from the outset. The technique of imposing such an upper bound is described in Refs. [17,18]. Therefore, the ansatz given by Eqs. (10) and (11) is consistent with and is supported by the present, more general analysis.

Since in this work we use mostly the RI-B05 functional to obtain the Kohn-Sham SCF solutions, we have modified slightly Eq. (A25) to be consistent with the corresponding non-dynamic correlation energy expression of the B05 model [6]:

$$\begin{aligned}E^{\mathrm{opp}}_{\mathrm{nd}} = {}& \frac{1}{2}\,a^{\mathrm{nd-opp}}_{\mathrm{c}}\int f_c(\mathbf{r}_1)\big[\rho_\alpha(\mathbf{r}_1)U^{\mathrm{HF}}_\beta(\mathbf{r}_1)\\ &+ \rho_\beta(\mathbf{r}_1)U^{\mathrm{HF}}_\alpha(\mathbf{r}_1)\big]d\mathbf{r}_1,\end{aligned} \quad \text{(A26)}$$

where U^{HF}_α is the Slater HF exchange potential. The value of the RI-B05 opposite-spin linear coefficient is $a^{\mathrm{nd-opp}}_{\mathrm{c}} = 0.526$ from Ref. [18]. The ideal theoretical value of this coefficient is 1/2, which corresponds to a "coefficient" of 1.0 on the rhs of Eq. (A25). Rescaling it from 1/2 to $a^{\mathrm{nd-opp}}_{\mathrm{c}}$ requires a factor of 2 $a^{\mathrm{nd-opp}}_{\mathrm{c}}$ multiplying the rhs of Eq. (A25):

$$D_\alpha(\mathbf{r}_1) = 2a^{\mathrm{nd-opp}}_{\mathrm{c}}\rho_\alpha(\mathbf{r}_1)f_{\mathrm{c}}(\mathbf{r}_1)N^{\mathrm{eff}}_{X\beta}(\mathbf{r}_1). \quad \text{(A27)}$$

This expression lead to Eq. (12) after some algebra using Eq. (9) and following the same considerations as for Eq. (A25) above.

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