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Two new constraints for the cumulant matrix

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We suggest new strict constraints that the two-particle cumulant matrix should fulfill. The constraints are obtained from the decomposition of $\langle \hat{S}^2 \rangle$, previously developed in our laboratory, and the vanishing number of electrons shared by two non-interacting fragments. The conditions impose stringent constraints into the cumulant structure without any need to perform an orbital optimization procedure thus carrying very small or no computational effort. These constraints are tested on the series of Piris natural orbital functionals (PNOF), which are among the most accurate ones available in the literature. Interestingly, even though all PNOF cumulants ensure correct overall $\langle \hat{S}^2 \rangle$ values, none of them is consistent with the *local* spin structure of systems that dissociate more than one pair of electrons. A careful analysis of the local spin components reveals the most important missing contributions in the cumulant expression thus suggesting a means to improve PNOF5. The constraints provide an inexpensive tool for the construction and testing of cumulant structures that complement previously known conditions such as the N -representability or the square of the total spin angular momentum, $\langle \hat{S}^2 \rangle$. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4903449>]

I. INTRODUCTION

The quest for a means to provide accurate electronic energies and properties of molecular systems at reduced computational cost has brought a plethora of methods. A fully satisfactory approach has not been found yet and ongoing attempts include, among others, developments in density matrix functional theory (DMFT)¹ and cumulant density functional theory (CDFT).² The latter method belongs to the group of approaches that implicitly uses the exact second-order density matrix (2-RDM) and enforces some N -representability conditions, whereas the former uses the first-order reduced density matrix (1-RDM) to approximate the diagonal of the 2-RDM following a bottom-up approach.³

There are many different ways to construct approximate expressions to the 2-RDM in terms of the 1-RDM, the goodness of the approach being assessed by the known (applicable) N -representability conditions⁴ and its ability to reproduce energies of molecular systems. These methods, on one hand, do not guarantee the N -representability of the 2-RDM and, on the other hand, provide approximations that are biased towards the electronic energy and are not necessarily adequate to describe other molecular properties. In this sense, uncovering new physical constraints for the 2-RDM not based on the electronic energy is relevant for the development of new approximate methods.

In this work, we suggest two constraints that the two-particle cumulant matrix (2C) of a molecular system should fulfill. These conditions impose serious restrictions on the 2C expression that complement previously known constraints^{5,6} such as the N -representability or the computation of the square of the total spin of the angular momentum, $\langle \hat{S}^2 \rangle$. The constraints do not require the cumulant obtained after some

orbital optimization procedure, only the general cumulant expression thus providing an inexpensive means to check the 2C (or the 2-RDM) structure. They are obtained from the decomposition of $\langle \hat{S}^2 \rangle$, previously developed in our laboratory,⁷ and imposing a vanishing number of electrons shared between two non-interacting fragments.

These new constraints provide a means to check the local spin structure, which is a more restrictive condition than the fulfillment of the global $\langle \hat{S}^2 \rangle$ itself. The importance of the correct spin structure of the 2-RDM (or the 2C) manifests in different chemical contexts, such as the analysis of spin states in transition metal complexes or nuclear magnetic resonance calculations. This feature, to the best of our knowledge, was not explicitly checked on the 2-RDM by any other conditions reported thus far in the literature.

The constraints are tested on the expressions of Piris natural orbital functionals (PNOF), proving that no PNOF provides a 2C expression that is consistent with the conditions suggested in this work. The PNOF functionals are chosen because they are among the most accurate ones and, unlike most natural orbital functionals available, they ensure correct $\langle \hat{S}^2 \rangle$.⁸

II. THE APPROXIMATE CUMULANTS

The spinless 2C for singlet systems can be written as

$$\Gamma_{ij:kl} = {}^2D_{ij:kl} - D_{ik}D_{jl} + \frac{1}{2}D_{il}D_{jk}, \quad (1)$$

where ${}^2D_{ij:kl}$ is the 2-RDM normalized to $N(N-1)$ and D_{ij} is the 1-RDM normalized to N . The spinless 2C gathers the sum

of the four spin-dependent 2C components

$$\Gamma_{ij;kl} = \Gamma_{ij;kl}^{\alpha\alpha\alpha\alpha} + \Gamma_{ij;kl}^{\alpha\beta\alpha\beta} + \Gamma_{ij;kl}^{\beta\alpha\beta\alpha} + \Gamma_{ij;kl}^{\beta\beta\beta\beta}. \quad (2)$$

There are a few approximations to the 2-RDM defined in the literature. Among those, we are only interested in the ones that have a non-vanishing 2C and afford correct $\langle \hat{S}^2 \rangle$ values. In the recent years, Piris has defined a general formula for the 2C known as Piris natural orbital functionals,¹ PNOFi ($i = 1, 5$),⁹⁻¹³ that has the following structure:¹⁴

$$\Gamma_{ij;kl}^{\sigma\sigma\sigma\sigma} = -\Delta_{ij}^{\sigma\sigma}(\delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}), \quad (3)$$

$$\Gamma_{ij;kl}^{\sigma\sigma'\sigma\sigma'} = -\Delta_{ij}^{\sigma\sigma'}\delta_{ik}\delta_{jl} + \Pi_{ik}\delta_{ij}\delta_{kl}, \quad (4)$$

where σ and σ' are either α or β , giving the approximate spinless 2C that follows

$$\Gamma_{ij;kl} = -(\Delta_{ij}^{\alpha\alpha} + \Delta_{ij}^{\beta\beta})(\delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}) - (\Delta_{ij}^{\alpha\beta} + \Delta_{ij}^{\beta\alpha})\delta_{ik}\delta_{jl} + 2\Pi_{ik}\delta_{ij}\delta_{kl}, \quad (5)$$

where the diagonal terms of matrices Δ and Π guarantee the conservation of $\langle \hat{S}^2 \rangle$ and,⁸ regardless of PNOF version, read

$$\Delta_{ii} = n_i n_i, \quad (6)$$

$$\Pi_{ii} = n_i, \quad (7)$$

n_i being the occupation of the i^{th} natural orbital and restricted to the range $0 \leq n_i \leq 1$. The PNOFi differ from each other by the form of the off-diagonal elements of matrices Δ and Π . We do not consider here the extended PNOF5¹⁵ because for the present purpose it provides qualitatively similar results to PNOF5.

In this work, we will analyze the structure of several PNOF functionals that provide a complete expression of the 2C, i.e., PNOF2, PNOF4, and PNOF5. In PNOF2 and PNOF4, Δ depends on the type of orbitals involved and thus these cumulant expressions do not lend themselves to an easy analytical manipulation. On the other hand, PNOF5,¹³ the most successful functional of the series, has a very simple structure, thus permitting an exhaustive analysis. PNOF2, PNOF4, and PNOF5 are defined for pure singlet states, $\Delta = \Delta^{\sigma\sigma} = \Delta^{\sigma\sigma'}$. In particular, PNOF5 has the following structure for the off-diagonal terms of Δ and Π matrices:

$$\Delta_{\tilde{i}i} = n_{\tilde{i}} n_i, \quad (8)$$

$$\Pi_{\tilde{i}i} = -\sqrt{n_{\tilde{i}} n_i}. \quad (9)$$

The pairs (\tilde{i}, i) are called coupled natural orbitals and $\tilde{i} = N - i + 1$ where N is the total number of electrons. This pair-coupled arrangement actually grants PNOF5 the structure of an antisymmetrized product of strongly orthogonal geminals (APSG).^{16,17} Therefore, one could anticipate that PNOF5 will not attain one of the constraints suggested in this work because for multiple bond dissociations APSG does not reproduce the proper spin states of the separated products.^{18,19} Such methods do not describe properly multiple bond dissociation, since the separated products are of incorrect spin states. Indeed, the analysis of these new constraints uncovers this

feature and provides a plausible solution to remedy this situation.

III. LOCAL SPIN AND DELOCALIZATION INDEX (DI)

Lately,^{7,20-24} there has been an interest in assigning local spin values by decomposing the expectation value of the total spin angular momentum as

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A, B \neq A} \langle \hat{S}^2 \rangle_{AB}, \quad (10)$$

where A and B are atoms or molecular fragments and $\langle \hat{S}^2 \rangle_A$ is the local spin of fragment A . There are infinitely many ways⁷ to define the terms entering the r.h.s. of the latter expression. In a recent work, some of us have suggested a proper general definition of $\langle \hat{S}^2 \rangle$ that avoids the arbitrariness by imposing a number of physical requirements and for pure singlet states yields^{7,24}

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4}u_A + \Lambda_{AA} + \Lambda'_{AA} \quad (11)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \Lambda_{AB} + \Lambda'_{AB}, \quad (12)$$

where the following compact forms in terms of the matrix representation (in molecular or natural orbitals) of the 1-RDM (\mathbf{D}), the 2C (Γ), and the fragment overlap matrix (\mathbf{S}^A) are used,

$$u_A = 2 \text{Tr}(\mathbf{D}\mathbf{S}^A) - \text{Tr}(\mathbf{D}\mathbf{S}^A\mathbf{D}), \quad (13)$$

$$\Lambda_{AA} = \frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{ki}^A S_{lj}^A \quad \Lambda'_{AA} = -\frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{li}^A S_{kj}^A, \quad (14)$$

$$\Lambda_{AB} = \frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{ki}^A S_{lj}^B \quad \Lambda'_{AB} = -\frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{li}^A S_{kj}^B. \quad (15)$$

The Delocalization Index (DI) or electron sharing index will also be used to set up stringent conditions over the 2-RDM.²⁵⁻²⁸ The expression of the DI between two molecular fragments A and B in terms of the 2C reads

$$\delta(A, B) = \text{Tr}(\mathbf{D}\mathbf{S}^A\mathbf{D}\mathbf{S}^B) - 4\Lambda_{AB}. \quad (16)$$

IV. THE NEW CONDITIONS IMPOSED ON THE CUMULANT

Let us consider a system dissociating into two fragments for which we compute: (i) the DI between fragments and (ii) the local spin of each fragment, using the approximate 2C whose expression we want to analyze.

The first condition imposes that the DI between two non-interacting fragments calculated using a given 2C approximation, X , should vanish in the dissociation limit, i.e.,

$$\lim_{|R_{AB}| \rightarrow \infty} \delta^X(A, B) = 0. \quad (17)$$

This condition might seem not too restrictive but, as we shall see, it is not fulfilled by all the 2C approximations studied in this paper. We note in passing the recent work of García-Revilla *et al.*²⁹ where values of the DI upon dissociation of diatomic molecules were analyzed using several approximate natural orbital functionals.

The second constraint requires that the local spin of each fragment at the dissociation limit coincides with the corresponding $\langle \hat{S}^2 \rangle$ value of the isolated fragment *A*. The latter requirement imposes a serious restriction on the structure of the 2C that is actually not attained by any of the functionals tested in this work. The condition is valid for any physical system dissociating into two fragments, *A* and *B*, and for an approximate 2C, *X*, reads

$$\lim_{|R_{AB}| \rightarrow \infty} \langle \hat{S}^2 \rangle_A^X = \langle \hat{S}^2 \rangle_{\text{freeA}}. \quad (18)$$

The last condition is a particularly interesting condition involving off-diagonal terms of the cumulant matrix (Eq. (14), right) that do not enter the energy expression. This condition goes thus beyond the typical constraints and tests that are usually performed in cumulant matrices. These constraints can be easily checked into any 2C structure, and since the $\langle \hat{S}^2 \rangle$ of the free fragment can be anticipated the test does not require expensive benchmark calculations. Therefore, they can be applied to any approximate 2C. DI and $\langle \hat{S}^2 \rangle$ can be manipulated algebraically (see, e.g., Eqs. (21) and (22)) to obtain partial contributions and further analyze the failure of some approximate 2C. Since the calculation of an *exact* 2C is out of reach for most systems, one can use a wavefunction method to obtain a reference 2C, as well as the natural orbitals and their occupancies. Many 2C approximate expressions are given in terms of natural orbitals and their occupancies because they can be readily obtained from the 1-RDM and constitute a complete one-particle basis in terms of which to expand the 2C. One can thus try to reproduce the reference 2C from natural orbitals and its occupancies using the approximate cumulant expression. By doing so, we are testing the ability of the cumulant expression to reproduce the 2C structure from natural orbitals. This procedure does not permit to capture the performance of the approximate 2C to reproduce accurate energies. However, it affords an inexpensive means to analyze the *cumulant structure* similar to other requirements such as the antisymmetry or the sum rule.

V. CONSTRAINTS TESTED ON PNOF CUMULANTS

In order to obtain partial contributions, we will use a complete active space self-consistent field (CASSCF) wavefunction, which provides a qualitatively correct description of fragment dissociations and its wavefunction conforms with correct 2C structure to reproduce the local spin.^{21,22} The use of more accurate wavefunctions would complicate the forthcoming analysis unnecessarily, whereas CASSCF already captures the essence of the local spin upon dissociation. Furthermore, the CASSCF closely resembles PNOF5 but, unlike PNOF5, it reproduces the correct spin structure upon dissociation. For the sake of simplicity, we only include in the active space the orbitals that contain the *n* electron pairs that

break upon dissociation, i.e., we perform CASSCF(2*n*, 2*n*) calculations. Each dissociating fragment has a well-defined spin state, $\langle \hat{S}^2 \rangle_A = \frac{n}{2}(\frac{n}{2} + 1)$. The inner *N* − 2*N* orbitals will not be correlated by either method. These orbitals entering the active space are thus orthogonal (also orthogonal within each fragment, i.e., $S_{ij}(A)=0$ for $j \neq \tilde{i}$) and delocalized over the whole system. These assumptions are genuinely fulfilled by the CASSCF natural orbitals and do not lead to lack of generalization because we are testing the cumulant expression in terms of an *arbitrary* natural orbital set. The pairs of orbitals that share one electron will be labeled *i* and \tilde{i} , so that $n_i + n_{\tilde{i}} = 1$. Notice that we do not need any computational calculation to assess orbital occupancies at the dissociation limit, where there are *n* pairs of spinorbitals with occupation 1/2 (the pairs broken upon dissociation) and other electron pairs sit on orbitals with occupation equal one.

Since we are testing PNOF5, which is defined for singlet states, we will restrict the analysis to singlet systems that dissociate into fragments with different spin states. After algebraic manipulation one obtains the following formulae for PNOF:

$$\langle \hat{S}^2 \rangle_A = 3 \left[\sum_i (n_i - n_{\tilde{i}}^2) S_{ii}^A + \sum_{ij} \Delta_{ij} (S_{ji}^A S_{ij}^A - S_{ii}^A S_{jj}^A) \right], \quad (19)$$

$$\delta(A, B) = 4 \sum_{ij} [(n_i n_j - \Delta_{ij} - \Pi_{ij}) S_{ji}^A S_{ij}^B + 2 S_{ii}^A S_{jj}^B]. \quad (20)$$

Notice that the formula for the local spin, Eq. (19), does not depend on the structure of Π , and thus this part of the PNOF*i* 2C is never tested by the analysis of the local spin.

Under these conditions, in the dissociation limit

$$\lim_{|R_{AB}| \rightarrow \infty} S_{ii}^A S_{\tilde{i}\tilde{i}}^A = \frac{1}{4} = \lim_{|R_{AB}| \rightarrow \infty} S_{ii}^A S_{\tilde{i}\tilde{i}}^A = \frac{1}{4}, \quad (21)$$

consequently, the PNOF5 expression brings

$$\lim_{|R_{AB}| \rightarrow \infty} \langle \hat{S}^2 \rangle_A^{\text{PNOF5}} = \frac{3}{2} \sum_i n_i (1 - n_i) = \frac{3}{4} n. \quad (22)$$

Analogously, by straightforward algebra we can write the local spin, the compacted forms, and the DI as a function of the number of broken electron pairs for the other PNOF expressions (see Table I). All PNOFs provide the wrong local spin

TABLE I. Asymptotic values of the $\langle \hat{S}^2 \rangle_A$, compacted forms, and the DI as a function of the number of broken pairs (*n*) upon dissociation.

	u_A	Λ_{AA}	Λ'_{AA}	Λ_{AB}	$\langle \hat{S}^2 \rangle_A$	DI
CASSCF	<i>n</i>	$-\frac{n}{4}$	$\frac{n^2}{4}$	0	$\frac{n}{2}(\frac{n}{2} + 1)$	0
PNOF2	<i>n</i>	0	$\frac{3}{4}(1 - n)$	$-\frac{n}{4}$	$\frac{3}{4}$	<i>n</i>
PNOF4	<i>n</i>	$-\frac{n}{4}$	$(\frac{3}{4} - \frac{n}{2})$	0	$\frac{3}{4}$	0
PNOF5	<i>n</i>	$-\frac{n}{4}$	$\frac{n}{4}$	0	$\frac{3}{4}n$	0

TABLE II. Nonzero cumulant contributions to Λ_{AA} included in PNOF5 expression at the dissociation limit. The table collects the partial value of each term (multiplied by the corresponding overlaps) as a function of the number of broken pairs, n . There are $2n$ terms for each kind listed on this table.

Kind of term	Contributions to Λ_{AA}	
	CASSCF	PNOF5
$\Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}, \Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}$	$\frac{1}{16n}$	$\frac{1}{16}$
$\Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}, \Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}$	$-\frac{n+1}{16n}$	$-\frac{1}{8}$

upon dissociation except for systems where a single electron pair is broken ($n = 1$), i.e., the dissociation of a singlet system into two doublet fragments. Furthermore, PNOF2 also presents wrong DI between the dissociating fragments. Interestingly, both PNOF4 and PNOF5 provide the correct value for Λ_{AA} but they fail to reproduce the quadratic dependence of Λ'_{AA} on the number of broken pairs.

In the following, we will focus on PNOF5 cumulant structure and its ability to reproduce CASSCF 2C from its natural orbitals. Tables II and III collect the contributions of different kinds of cumulant components upon dissociation contained and not contained in PNOF5, respectively. Careful examination of the cumulant contributions (see Table II) shows that the values obtained from PNOF5 cumulant expression and the CASSCF ones do not coincide (except for $n = 1$) but, nonetheless, the overall value of Λ_{AA} matches. Essentially, the contributions from PNOF5 expression are independent of the number of pairs, but the number of individual contributions for each cumulant kind ($2n$) does depend on the number of pairs and therefore there is a final dependency on n (see Table II).

One should bear in mind that PNOF5 has a pretty simple cumulant structure that assumes, among other things, vanishing off-diagonal terms. The off-diagonal terms do not enter the expression of Λ_{AA} whereas Λ'_{AA} does have contributions from the off-diagonal terms. On the other hand, the structure of PNOF5 involves only the coupling between pairs of orbitals, one below the Fermi level with one above it. Other couplings are not considered. In Table III, we gather the nonzero cumulant contributions to Λ'_{AA} that are not included in PNOF5 expression, i.e., $\Gamma_{ij;ji}$, $\Gamma_{ij;\tilde{j}\tilde{i}}$, and $\Gamma_{i\tilde{j};\tilde{j}\tilde{i}}$. The first kind involves the coupling of the orbitals below the Fermi level and they contribute to Λ'_{AA} with a term linear on n . These contributions are not contained in PNOF5 but they exist in other PNOFs. Interestingly, $\Gamma_{ij;ji}$ contributes to the local spin

TABLE III. Contributions of the cumulant matrix to Λ'_{AA} at the dissociation limit not included in PNOF5. The table gathers the number of terms, the partial value of each term (multiplied by the corresponding overlaps), and the total contribution as a function of the number of broken pairs, n .

Kind of term	Number of terms	Partial	Total
$\Gamma_{ij;ji}$	$4n(n-1)$	$-\frac{1}{16n}$	$-\frac{n-1}{4}$
$\Gamma_{i\tilde{j};\tilde{j}\tilde{i}}, \Gamma_{i\tilde{j};\tilde{j}\tilde{i}}$	$4n(n-1)/2$	$-\frac{n+1}{16n}$	$\frac{n^2-1}{4}$

as much as $\Gamma_{\tilde{i}\tilde{j};\tilde{i}\tilde{j}}$, which is included in PNOF5. This fact suggests that $\Gamma_{ij;ji}$ could be included in the PNOF5 using an expression analogous to $\Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}$, for instance, by assuming $\Delta_{ij} = n_i n_j$.³⁰ This formulation would give the right asymptotic value of this 2C contribution to the local spin.

The second and the third terms involve the coupling between two pairs of orbitals (i, \tilde{i}) and (j, \tilde{j}) and thus, they are necessarily off-diagonal terms which are not included in PNOF5. These terms are responsible for the n^2 final dependency of the local spin that is missing in PNOF5. Notice that the quadratic dependency comes from the total number of terms included, rather than from the individual cumulant components. Furthermore, these terms have the same value than $\Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}$ and $\Gamma_{\tilde{i}\tilde{i};\tilde{i}\tilde{i}}$, which are included in PNOF5 expression. However, the inclusion of these terms might not be straightforward, as it involves the coupling between two orbital pairs.

Each individual cumulant value of the CASSCF wavefunction that contributes to the local spin depends on n , the number of broken pairs. It is thus advisable to construct approximate cumulant matrices that show this n -dependency at the dissociation limit. Obviously, a natural way to improve the PNOFs is to add off-diagonal terms of the cumulant expression; this could restore the correct n^2 dependency without affecting the trace of the 2C. Finally, for the full correct description of the $\langle \hat{S}^2 \rangle_A$ with PNOF5, one should also consider the coupling between the orbitals below the Fermi level. However, one should conduct these changes in PNOF5 making sure that the performance of PNOF5 is not affected in both energy calculations and ground-state local spin values of molecular systems.

To summarize, Eqs. (17) and (18) are two new stringent conditions to test approximate cumulants at very small computational cost. The fact that very accurate functionals such as PNOF5 do not attain these conditions puts forward the relevance and constraining character of these requirements. Most importantly, we have identified the cumulant contributions to the local spin that are not included in PNOF5 and should be the focus of future improvements.

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- ³⁰The inclusion of these terms is not as straightforward as it might seem because one should impose simultaneously additional cumulant constraints such as the antisymmetry. For instance, in the case of $\Gamma_{i\tilde{j};j\tilde{i}}$, the same formulation does not automatically attain the antisymmetry condition.