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REGULAR ARTICLE

A study of the relationships between unpaired electron density, spin-density and cumulant matrices

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Abstract This work describes the derivation of simple relationships between the density matrix of effectively unpaired electrons and the spin-density matrix in N-electron systems. The link between both devices turns out to be the one-electron matrix arising from the diagonal contraction of the cumulant matrix corresponding to the second-order reduced density matrix. We study some features of this contracted matrix, showing its usefulness to describe the electronic correlation. Numerical determinations performed in selected systems with different spin symmetries confirm the theoretical predictions.

Keywords Reduced density matrices · Cumulant matrices · Electron correlation

1 Introduction

The effectively unpaired electron density matrix or density matrix of odd electrons, originally proposed by Takatsuka et al. [1] and Takatsuka and Fueno [2], has proven to be a suitable tool to describe the spatial separation of electrons with opposite spins. The connection of this matrix with the valence and free valence indices [3–7] has promoted the rigorous study of its mathematical properties as well as the implementation of the formulations this matrix acquires when an N-electron system is described by determined wave functions [8]. Another interesting feature of this matrix is its ability to determine the extent of the radical and diradical character in molecules and other species of any spin multiplicity, including singlets [9, 10]. Likewise, the effectively unpaired electron density matrix has been used successfully in studies of population analysis, performed in the Hilbert space and in the three-dimensional physical space, at level of correlated wave functions in systems possessing conventional and three-center bondings [7, 11–13]. Alternative definitions of this device have also been reported along with the corresponding comparisons of their results with those arising from the Takatsuka approach [14–16].

On the other hand, as is well known the numerical determination of any two-electron property of an N-electron system in a determined state requires the knowledge of the second-order reduced density matrix corresponding to the wave function describing the system. One of the most suitable approaches for dealing with this matrix is to express its elements by means of a sum of two terms; one of them is the Grassmann (or wedge) product of the elements of its corresponding first-order reduced density matrix, the other one is defined by the elements of its cumulant matrix or irreducible part of the second-order reduced density matrix [17–19]. The cumulant matrices are extensive quantities, that is, they are additively separable in the case of systems composed of noninteracting subsystems. This useful feature and an appropriate treatment of

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the cumulant matrix elements have enabled one to reconstruct satisfactorily reduced density matrices of second and higher orders [20–25]. The cumulant matrices of the second-order reduced density matrices have also been utilized in the determinations of bond orders [26, 27], in partitionings of the molecular energy [28, 29] as well as in evaluations of local spin [30, 31]; this kind of studies relates the cumulant matrix with the effectively unpaired electron density one [5–10]. Consequently, during the last two decades, the cumulant matrices of the reduced density matrices have received a considerable attention in many-electron theory, although the cumulants were introduced in statistics a very long time ago.

The relationship between the effectively unpaired electron density matrix and the spin-free version of the cumulant matrix [32, 33] was reported in Ref. [5]. In that reference, it was shown that the former matrix is a simple tensorial contraction of the spin-free cumulant matrix multiplied by a normalization factor. However, the treatments involving the cumulant matrix often require the knowledge of its spin components [20] and their sum [27]. Our purpose is to go on studying the properties of these quantum-chemical tools and to extend their application scope. The main aim of this work is to provide a precise relationship between the effectively unpaired electron density matrix and the cumulant matrix of the second-order reduced density matrix which is not limited to the spin-free version of the cumulant matrix. Moreover, in Ref. [8], it was shown that the effectively unpaired electron density matrix coincides with the spin-density matrix when the wave function is a pure Slater determinant. Another purpose of this paper is to provide a general relationship between these two entities which is valid for multideterminantal correlated wave functions, so that the links between the spin-density and the effectively unpaired electron density matrices can be described for any wave function. A preliminary study at the level of traces of these matrices has recently been reported [34]. The obtained relationships clarify the physical meaning of the upper bound of the trace of the effectively unpaired electron density matrix and provide a quantitative information on the correlation in the description of N-electron systems.

The organization of this paper is as follows. Section 2 summarizes the theoretical concepts and the notation used in this work. In Sect. 3, we report the derivation of a simple relation between the effectively unpaired electron density matrix and the spin-density matrix and a contracted cumulant matrix corresponding to the substate $S_z = S$ of the multiplet defined by a spin S. The discussion on this relation, supported by some numerical results, is reported in Sect. 4. Finally, we have dedicated the last section to point out the concluding remarks and perspectives of this work.

2 Notation and background

We will refer to an N-electron system described by a determined wave function, $\Psi(S, S_z)$, where S and S_z stand for the usual spin quantum numbers. The elements of the first- and second-order reduced density matrices corresponding to that state will be denoted by ${}^1D^{i^\sigma}_{j^\sigma}$ and ${}^2D^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}}$, respectively, in which $i, j, k, l, \ldots$ are orbitals of an orthogonal basis set and σ and σ' are the spin coordinates (σ, $\sigma' = \alpha$, β). We will use these reduced matrices normalized by the trace values $\mathrm{tr}({}^1D) = N$ and $\mathrm{tr}({}^2D) = \binom{N}{2}$, respectively.

The elements ${}^2D^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}}$ have been formulated as [19]

$$ {}^2D^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}} = \frac{1}{2}\,{}^1D^{i^\sigma}_{j^\sigma}\,{}^1D^{k^{\sigma'}}_{l^{\sigma'}} - \frac{1}{2}\,{}^1D^{i^\sigma}_{l^{\sigma'}}\,{}^1D^{k^{\sigma'}}_{j^\sigma} + \frac{1}{2}\Gamma^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}} \tag{1} $$

where $[\frac{1}{2}\,{}^1D^{i^\sigma}_{j^\sigma}\,{}^1D^{k^{\sigma'}}_{l^{\sigma'}} - \frac{1}{2}\,{}^1D^{i^\sigma}_{l^{\sigma'}}\,{}^1D^{k^{\sigma'}}_{j^\sigma}]$ is the Grassmann product $({}^1D^{i^\sigma}_{j^\sigma} \wedge {}^1D^{k^{\sigma'}}_{l^{\sigma'}})$ and $\Gamma^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}}$ are the elements of the cumulant matrix of the second-order reduced density matrix (its irreducible part).

A spin-free version of the elements of the second-order reduced density matrix, ${}^2D^{ik}_{jl} = \sum_{\sigma,\sigma'} {}^2D^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}}$, can be obtained substituting in Eq. 1 ${}^1D^{i^\alpha}_{j^\alpha} = \frac{1}{2}[{}^1D^i_j + (P^s)^i_j]$ and ${}^1D^{i^\beta}_{j^\beta} = \frac{1}{2}[{}^1D^i_j - (P^s)^i_j]$ resulting [27]

$$ {}^2D^{ik}_{jl} = \frac{1}{2}\,{}^1D^i_j\,{}^1D^k_l - \frac{1}{4}\,{}^1D^i_l\,{}^1D^k_j - \frac{1}{4}(P^s)^i_l\,(P^s)^k_j + \frac{1}{2}\Gamma^{ik}_{jl} \tag{2} $$

in which ${}^1D^i_j = \sum_\sigma {}^1D^{i^\sigma}_{j^\sigma}$ are the elements of the spin-free first-order reduced density matrix; $(P^s)^i_j = {}^1D^{i^\alpha}_{j^\alpha} - {}^1D^{i^\beta}_{j^\beta}$ are the elements of the spin-density matrix and $\Gamma^{ik}_{jl} = \sum_{\sigma,\sigma'} \Gamma^{i^\sigma k^{\sigma'}}_{j^\sigma l^{\sigma'}}$. The elements ${}^2D^{ik}_{jl}$ and ${}^1D^i_j$ as well as those of the sum $[-\frac{1}{4}(P^s)^i_l\,(P^s)^k_j + \frac{1}{2}\Gamma^{ik}_{jl}]$ in Eq. 2 are independent of the spin substate of quantum number S_z corresponding to the state $\Psi(S)$. In fact, the sum $[-\frac{1}{4}(P^s)^i_l\,(P^s)^k_j + \frac{1}{2}\Gamma^{ik}_{jl}]$ is the spin-free version of the cumulant of the second-order reduced density matrix [27, 32, 33]. However, the terms $(P^s)^i_l\,(P^s)^k_j$ and Γ^{ik}_{jl} separately are S_z-dependent.

On the other hand, the elements of the effectively unpaired electron density matrix, u^i_j, are defined as [1, 5]

$$ u^i_j = 2\,{}^1D^i_j - \sum_k {}^1D^i_k\,{}^1D^k_j \tag{3} $$

which are spin-free quantities, that is, independent of the quantum number S_z.

The substitution of the r.h.s. of Eq. 3 according to the result arising from the ordinary tensorial contraction of the ${}^2D^{ik}_{jl}$ quantity in Eq. 2 provides to express the elements u^i_j as

$$u_j^i = \sum_k (P^s)_k^i (P^s)_j^k - 2\sum_k \Gamma_{jk}^{ik} \tag{4}$$

Formula (4) relates the effectively unpaired electron density matrix with the spin-density one and with the one-electron matrix arising from the contraction of the cumulant matrix Γ. The two S_z-dependent terms of the r.h.s. of that equation can be evaluated for any S_z substate corresponding to the S quantum number value of the system, because their sum is S_z-independent as mentioned above. In the next Section, we carry out the derivation of a simpler relation, which avoids the squared terms in the spin density, as well as its most suitable expression corresponding to the $S_z = S$ substate of that multiplet.

3 A simpler general relationship between the matrices u, P^s and Γ

We will regard the matrix elements $\sum_k {}^2D_{kj}^{ik}$, which arise from the diagonal contraction of the spin-free second-order reduced density matrix. According to Eq. 2, these elements can be expressed as

$$\sum_k {}^2D_{kj}^{ik} = \frac{1}{2}\sum_k {}^1D_k^i\,{}^1D_j^k - \frac{N}{4}\,{}^1D_j^i - \frac{S_z}{2}(P^s)_j^i + \frac{1}{2}\sum_k \Gamma_{kj}^{ik} \tag{5}$$

in whose derivation, the values of the matrix traces $\sum_k {}^1D_k^k = N$ and $\sum_k (P^s)_k^k = 2S_z$ have been taken into account.

The elements $\sum_k {}^2D_{kj}^{ik}$ have also be calculated in Ref. [31] by means of the sum of the spin components of the second-order reduced density matrix ($\sum_k {}^2D_{kj}^{ik} = \sum_k [{}^2D_{k^\alpha j^\alpha}^{i^\alpha k^\alpha} + {}^2D_{k^\beta j^\beta}^{i^\beta k^\beta} + {}^2D_{k^\alpha j^\beta}^{i^\alpha k^\beta} + {}^2D_{k^\beta j^\alpha}^{i^\beta k^\alpha}]$), resulting

$$\sum_k {}^2D_{kj}^{ik} = \frac{4-N}{4}\,{}^1D_j^i - \frac{S+1}{2}[(P^s)_j^i]_{S_z=S} \tag{6}$$

in which $[(P^s)_j^i]_{S_z=S}$ means that the elements of the spin-density matrix must be calculated for the substate $S_z = S$. The counterpart expression for other substates $S_z \neq S$ requires a different formulation of the r.h.s. of Eq. 6 [31]. However, it is possible to remove that S_z dependence in Eq. 6 taking into account that the matrix elements ρ_j^i defined as

$$\rho_j^i = \frac{(P^s)_j^i}{N_\alpha - N_\beta} \tag{7}$$

are identical for any substate S_z [35]. In that definition, $(P^s)_j^i$, N_α and N_β are the spin-density matrix elements and the number of electrons α and β, respectively, for any selected substate S_z. The substitution of the term $[(P^s)_j^i]_{S_z=S}$ in Eq. 6, according to Eq. 7, taking into account that for the substate $S_z = S, N_\alpha = \frac{N}{2} + S$ and $N_\beta = \frac{N}{2} - S$ [36], leads to

$$\sum_k {}^2D_{kj}^{ik} = \frac{4-N}{4}\,{}^1D_j^i - S(S+1)\,\rho_j^i \tag{8}$$

which is fulfilled for any S_z substate of the S multiplet.

The removal of the terms $\sum_k {}^2D_{kj}^{ik}$ between Eqs. 5 and 8 allows one to express

$$2\,{}^1D_j^i - \sum_k {}^1D_k^i\,{}^1D_j^k = 2S(S+1)\,\rho_j^i - S_z(P^s)_j^i + \sum_k \Gamma_{kj}^{ik}(S_z) \tag{9}$$

in which we have explicitly pointed out the above-mentioned S_z dependence of the matrix elements $\Gamma_{kj}^{ik}(S_z)$. Regarding Eq. 3 and expressing $\rho_j^i = \frac{(P^s)_j^i}{2S_z}$ [35], one finally finds

$$u_j^i = \frac{S(S+1) - S_z^2}{S_z}(P^s)_j^i + \sum_k \Gamma_{kj}^{ik}(S_z) \tag{10}$$

Equation 10 is simpler than its counterpart Eq. 4 since the u matrix is expressed by a simple sum of two one-electron matrices, being independent of squared matrix terms. This relation generalizes to matrix elements (or electronic densities), the result obtained for traces (or number of electrons) reported in Ref. [34]

$$N_u = 2S + 2S^2 - 2S_z^2 + \sum_{i,k} \Gamma_{ki}^{ik}(S_z) \tag{11}$$

where N_u is the trace of the u matrix.

Although Eqs. 10 and 11 have a general character and can be applied to any S_z substate, their more useful utilizations refer to the highest substate $S_z = S$. In fact, for that substate, Eq. 10 is transformed into

$$u_j^i = \left[(P^s)_j^i\right]_{S_z=S} + \gamma_j^i \tag{12}$$

in which we have introduced the matrix elements $\gamma_j^i = \sum_k [\Gamma_{kj}^{ik}]_{S_z=S}$ to highlight the one-electron character of the matrix $\sum_k [\Gamma_{kj}^{ik}]_{S_z=S}$. Equation 12 enables us to express the u matrix, which is a spin-free quantity, by means of two terms which must be calculated separately for the $S_z = S$ substate. Furthermore, in Ref. [8], it was described that the matrix u coincides with the spin-density matrix in the case of a Slater determinant wave function; Eq. 12 constitutes a general relationship between both matrices, which is valid for any single determinant or multideterminantal wave function. Obviously, in the case of a single Slater determinant wave function, all the matrix elements $\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$ and hence Γ_{jl}^{ik} are zero and both u and P^s matrices are identical. Equation 12 can also be regarded as a decomposition of the odd electron density into two components, the spin-density plus a density related with the correlation of the N-electron system. The result obtained for traces in Ref. [34]

$$N_u = 2S + \sum_i \gamma_i^i \tag{13}$$

can consistently be reproduced by contraction of the three matrices involved in Eq. 12, now derived for matrix elements. The determination of the values of the number of unpaired electrons, $N_u = \sum_i u_i^i$, has been used as a procedure to measure quantitatively the partial split of electron pairs when the N-electron system is described by a multideterminantal correlated wave function [1, 8], which is an electronic correlation effect. According to Eq. 13, the total number of effectively unpaired electrons N_u can be decomposed into two components; the number of net spin unpaired electrons $2S$ and the value $\mathrm{tr}(\gamma) = \sum_{i,k} \left[\Gamma_{ki}^{ik}\right]_{S_z=S}$, which can be interpreted as a consequence of the electronic correlation degree contained in the N-electron wave function; neither N_u nor $\sum_i \gamma_i^i$ are observable quantities in quantum-mechanical sense. In the next section, we report numerical determinations which allow us to evaluate and to discuss these quantities.

4 Numerical determinations and applications

We have implemented calculations of configuration interaction (CI) type in singlet, doublet, triplet and quartet systems, in order to compare the values $\sum_i \gamma_i^i$ arising from different correlated wave functions. According to Eqs. 3 and 13, these numerical determinations only require the knowledge of the corresponding spin-free first-order reduced density matrix, which can be drawn from most of the standard codes. We have chosen simple systems, which allow us to use even full configuration interaction (FCI) wave functions with an affordable computational cost. The results reported in Table 1 refer to the ground state of the second row atoms and they have been obtained using the 6-31G basis sets in all cases. We report in that Table energy values arising from CI calculations with single and double excitations (CISD), single, double and triple excitations (CISDT), single, double, triple and quadruple excitations (CISDTC) and so forth. The energies and the spin-free first-order reduced density matrices for these systems have been obtained with a modified GAMESS package [37]. The $\sum_i \gamma_i^i$ values have subsequently been calculated using our own codes. Although we have performed numerical determinations with all the possible excitations for each atom up to the Nth excitation (the FCI level), in Table 1, we have omitted the results arising from the excitations whose $\sum_i \gamma_i^i$ values differ $<10^{-4}$ from the corresponding FCI value. We have also included in that Table the values of the $\sum_i \gamma_\mathrm{i}^\mathrm{i}$ quantity at restricted Hartree-Fock (RHF) and restricted open-shell Hartree-Fock (ROHF) levels as reference values; obviously, all these values are zero since all γ_j^i matrix elements vanish in these cases. As can be seen, the values obtained for $\sum_i \gamma_i^i$ quantity increase from zero (HF values, absence of correlation) to the FCI values (the highest correlation). These increasing values are in perfect agreement with the degree of multiconfigurational character of the used wave function, constituting a quantitative index of its correlation degree. The sequence of the energies obtained for these different levels of approximation highlights this feature.

Table 2 gathers the results of the values of the $\sum_i \gamma_i^i$ quantity and the energies corresponding to the ground states of the molecules N_2, NO and O_2 as prototype of singlet, double and triplet molecules, respectively. These results have been obtained with the experimental geometries, at the level of CISD and CISDT approximations using several standard basis sets. Energies and spin-free first-order reduced density matrices for these systems have also been drawn from the GAMESS code [37]. As can be seen, the values of the trace $\sum_i \gamma_i^i$ depend on the extent of the basis set used; the highest values correspond to the more extended basis sets. This behavior shows a quantitative measure of the quality of the used basis set to introduce the electronic correlation in the description of an N-electron system within a determined approximation level of the wave function. This feature is also confirmed by the energy values included in the Table. The comparison of the results obtained for these three molecules at the two mentioned CI levels shows higher values in the case of the CISDT approximation than in the CISD one, confirming the results reported in Table 1 for atomic systems. For the O_2 molecule, the CISD and CISDT results coincide in the STO basis set, which is due to no contribution of triple excitations in that case.

The determination of values of the $\sum_i \gamma_i^i$ quantity also allows one to shed light on studies of the situations (or states) in which $N_u > N$, that is, when the number of effectively unpaired electrons N_u becomes greater than the number N of electrons of the system itself. In fact, in Ref. [8], it has been reported that the value of N_u lies in the interval $0 \leq N_u \leq 2N$. The possibility of existence of these situations, apparently without physical nature, has been pointed out as a drawback of Takatsuka et al. definition of the density matrix of odd electrons given by Eq. 3, although this is not a serious problem in practice [10]. This drawback has induced some authors to propose alternative definitions of such density matrix [14–16] which avoid the possibility of $N_\mathrm{u} > N$. On the other hand, in Ref. [38], it has been mentioned, in an empirical way, that quantities of type $N_\mathrm{eff}-2S$, where N_eff represents several types of “shell

Table 1 Table1 Calculated values of the $\sum_i \gamma_i^i$ quantity and Energies (in a.u.) for the second row atoms in the ground state at several levels of electronic correlation using the 6-31G basis sets

System	Correlated level	$\sum_i \gamma_i^i$	Energy	System	Correlated level	$\sum_i \gamma_i^i$	Energy
Li(^{2}S)	ROHF	0.0000	−7.4312	O(^{3}P)	ROHF	0.0000	−74.7782
	CISD	0.0007	−7.4316		CISD	0.1219	−74.8382
	FCI	0.0007	−7.4316		CISDT	0.1244	−74.8386
Be(^{1}S)	RHF	0.0000	−14.5668		CISDTC	0.1290	−74.8394
	CISD	0.7426	−14.6135		CISDTCQ	0.1291	−74.8394
	CISDT	0.7433	−14.6135		FCI	0.1291	−74.8394
	FCI	0.7441	−14.6135	F(^{2}P)	ROHF	0.0000	−99.3602
B(^{2}P)	ROHF	0.0000	−24.5193		CISD	0.1411	−99.4452
	CISD	0.4305	−24.5623		CISDT	0.1432	−99.4457
	CISDT	0.4426	−24.5629		CISDTC	0.1516	−99.4474
	CISDTC	0.4431	−24.5629		CISDTCQ	0.1518	−99.4474
	FCI	0.4431	−24.5629		CISDTCQS	0.1519	−99.4474
C(^{3}P)	ROHF	0.0000	−37.6769		FCI	0.1519	−99.4474
	CISD	0.2179	−37.7156	Ne(^{1}S)	RHF	0.0000	−128.4739
	CISDT	0.2263	−37.7161		CISD	0.1563	−128.5863
	CISDTC	0.2284	−37.7163		CISDT	0.1586	−128.5868
	FCI	0.2284	−37.7163		CISDTC	0.1706	−128.5897
N(^{4}S)	ROHF	0.0000	−54.3821		CISDTCQ	0.1711	−128.5898
	CISD	0.0807	−54.4195		CISDTCQS	0.1712	−128.5898
	CISDT	0.0821	−54.4197		FCI	0.1712	−128.5898
	CISDTC	0.0835	−54.4199				
	FCI	0.0835	−54.4199				

Table 2 Calculated values of the $\sum_i \gamma_i^i$ quantity and Energies (in a.u.) for several molecules in Singlet, Doublet and Triplet spin symmetries at several levels of electronic correlation, using different basis sets

System	Correlation level	STO		6-31G		6-31G(d,p)	
		$\sum_i \gamma_i^i$	Energy	$\sum_i \gamma_i^i$	Energy	$\sum_i \gamma_i^i$	Energy
$N_2(^1\Sigma_g^+)$	RHF	0.0000	−107.4959	0.0000	−108.8678	0.0000	−108.9427
	CISD	0.5266	−107.6405	0.5998	−109.0799	0.6831	−109.2393
	CISDT	0.5461	−107.6423	0.6602	−109.0864	0.7644	−109.2495
NO($^2\Pi$)	ROHF	0.0000	−127.5261	0.0000	−129.1686	0.0000	−129.2397
	CISD	0.4805	−127.6530	0.5480	−129.3872	0.6251	−129.5532
	CISDT	0.5265	−127.6580	0.6436	−129.3994	0.7422	−129.5699
$O_2(^3\Sigma_g^-)$	ROHF	0.0000	−147.6322	0.0000	−149.5280	0.0000	−149.5943
	CISD	0.3460	−147.7440	0.5032	−149.7742	0.5889	−149.9426
	CISDT	0.3460	−147.7440	0.5488	−149.7835	0.6572	−149.9579

openness index", should be regarded as *effective number of correlated electrons, rather than unpaired ones*. Once the quantity $N_u - 2S$ has been formulated precisely, in the previous section, by means of the cumulant matrix elements of the second-order reduced density matrix, leading to the quantity $\sum_i \gamma_i^i$, we can interpret that the value of this trace is the number of effectively correlated electrons, which is in agreement with the above mentioned degree of correlation. The situations in which $N_u > N$ (limited to the $2N$ value) are a consequence of the sum of the number of spin unpaired electrons $2S$ and the number of correlated electrons or degree of correlation $\sum_i \gamma_i^i$, and they do not constitute unphysical states.

5 Concluding remarks and perspectives

In this work, we have reported the derivation of a simple relationship (Eq. 12) which links the density matrix of odd electrons, the spin-density matrix and the one-electron matrix arising from the diagonal contraction of the cumulant matrix of the second-order reduced density matrix. This relationship is expressed in terms of first-order matrices and although the last two matrices refer to the highest substate $S_z = S$ of a multiplet, it produces a spin-free quantity. The traces of these three matrices allow one to decompose the number of effectively unpaired electrons into the sum of net spin unpaired electrons and correlated electrons in the system, providing a quantitative index of the correlation contained in a determined wave function. Moreover, our device $\sum_i \gamma_i^i$ lets an appropriate physical explanation of the states in which the number of effectively unpaired electrons is greater than the number of electrons. We are currently working in our laboratories on the description of the spin entanglement by means of our framework and the results will be reported elsewhere [39].

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