



## A decomposition of the number of effectively unpaired electrons and its physical meaning

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### ABSTRACT

We report a procedure which allows one to decompose the number of effectively unpaired electrons corresponding to an  $N$ -electron system into two components with well-defined physical meaning. One of these terms represents the number of net unpaired electrons arising from the spin. The second one accounts for the partial split of electron pairs that appears when multideterminantal correlated wave functions are used.

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### 1. Introduction

The density matrix of odd electrons was introduced a long time ago by Takatsuka et al. [1,2] as an appropriate tool to characterize the occupancy of different portions of space by spin-up and spin-down electrons. In the past decade and in the present one there has been a growing theoretical interest in studying the features, approaches and constraints of this device [3–9] which has also been termed as *density matrix of effectively unpaired electrons* [4]. In practice, this matrix has been employed extensively in studies of electronic population analyses as in the Hilbert space defined by atomic orbitals as in the ordinary physical space [1,10–12] in order to determine valences and free-valences of the atoms within a molecular system. Another interest of the density matrix of effectively unpaired electrons arises from its ability to describe spatial distributions of odd electrons in open and closed shell systems, what constitutes a method for determining the extent of the radical character in molecules and similar species of any spin multiplicity [13].

The main purpose of this report is to decompose the number of effectively unpaired electrons (the value of the trace of the density matrix of effectively unpaired electrons) into two components. One of them is the number of net spin unpaired electrons; in fact this density matrix coincides with the spin density one when the wave function of the  $N$ -electron system is a single Slater determinant [5]. The other term accounts for the number of unpaired electrons arising from the partial split of electron pairs that appear, even in closed shell systems, when the electronic correlation is taken into account through multideterminantal wave functions [1]. Using suitable tools, such as the cumulant matrix of the second-order reduced density matrix, a meaningful partitioning of the number of

effectively unpaired electrons is achieved, what allows one to describe and to quantify separately both effects.

We have organized this Letter as follows: in the second section we summarize the definitions of the main tools used in this work, the density matrix of effectively unpaired electrons, the reduced density matrices and the cumulant matrices as well as the relationships between them. The third section describes the partitioning of the number of effectively unpaired electrons into two components; this section also describes a discussion of our results supported on numerical determinations which prove the correctness of our proposals. Finally, the last section reports the conclusions of this work.

### 2. Mathematical framework

According to the authors in Ref. [1], the elements of the density matrix of effectively unpaired electrons,  $u_j^i$ , are

$$u_j^i = 2^1 D_j^i - \sum_k {}^1 D_k^i {}^1 D_j^k \quad (1)$$

in which  $i, j, k, \dots$  are orbitals of an orthogonal basis set and  ${}^1 D_j^i$  are the elements of the spin-free first-order reduced density matrix corresponding to a determined  $N$ -electron state  $\Psi$ . As is well-known  ${}^1 D_j^i = \sum_{\sigma} {}^1 D_{j\sigma}^i$  where  $\sigma = \alpha, \beta$  are the spin coordinates and  ${}^1 D_{j\sigma}^i$  are the elements of the first-order reduced density matrix in the basis of the spin-orbitals  $i^\sigma, j^\sigma, \dots$ . The number of effectively unpaired electrons,  $N_u$ , is the trace of the  $u$  matrix

$$N_u = \sum_i u_i^i = 2N - \sum_{i,k} {}^1 D_k^i {}^1 D_i^k, \quad (2)$$

where the trace of the matrix  ${}^1 D$ ,  $\sum_i {}^1 D_i^i = N$ , has been taken into account. Other definitions of the number of effectively unpaired electrons have been reported [7,9]; in this Letter we will refer to the definition given by Eq. (2) which is the most widely used one and

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consequently provides straightforward comparisons with other works.

On the other hand, the elements of the second-order reduced density matrix corresponding to the state  $\Psi$  will be denoted by  ${}^2D_{j\sigma}^{\sigma'k\sigma'}$  and their spin-free version by  ${}^2D_{jl}^{ik} = \sum_{\sigma,\sigma'} {}^2D_{j\sigma}^{\sigma'k\sigma'}$ . These elements  ${}^2D_{j\sigma}^{\sigma'k\sigma'}$  have been formulated as [14,15]

$${}^2D_{j\sigma}^{\sigma'k\sigma'} = \frac{1}{2} {}^1D_{j\sigma}^{\sigma'} {}^1D_{\sigma'}^{k\sigma'} - \frac{1}{2} {}^1D_{\sigma'}^{\sigma'} {}^1D_{j\sigma}^{k\sigma'} + \frac{1}{2} \Gamma_{j\sigma}^{\sigma'k\sigma'}, \quad (3)$$

where  $\Gamma_{j\sigma}^{\sigma'k\sigma'}$  are the elements of the cumulant matrix of the second-order reduced density matrix.

The substitution of  ${}^1D_{j\sigma}^{\sigma'} = \frac{1}{2} ({}^1D_j^{\sigma'} + {}^1D_j^{(s)\sigma'})$  and  ${}^1D_{\sigma'}^{\sigma'} = \frac{1}{2} ({}^1D_j^{\sigma'} - {}^1D_j^{(s)\sigma'})$  in the components  ${}^2D_{j\sigma}^{\sigma'k\sigma'}$ ,  ${}^2D_{j\sigma}^{\sigma'k\sigma'}$ , ... represented by Eq. (3) and the sum  $\sum_{\sigma,\sigma'}$  leads to [16]

$${}^2D_{jl}^{ik} = \frac{1}{2} {}^1D_j^i {}^1D_l^k - \frac{1}{4} {}^1D_l^i {}^1D_j^k - \frac{1}{4} {}^1D_l^{(s)i} {}^1D_j^{(s)k} + \frac{1}{2} \Gamma_{jl}^{ik} \quad (4)$$

in which  ${}^1D_j^{(s)i} = {}^1D_{j\sigma}^{\sigma'} - {}^1D_{j\sigma}^{\beta\sigma'}$  are the elements of the spin density matrix and  $\Gamma_{jl}^{ik} = \sum_{\sigma,\sigma'} \Gamma_{j\sigma}^{\sigma'k\sigma'}$ . In Eq. (4) the elements  ${}^2D_{jl}^{ik}$ ,  ${}^1D_j^i$  and  $[-\frac{1}{4} {}^1D_l^{(s)i} {}^1D_j^{(s)k} + \frac{1}{2} \Gamma_{jl}^{ik}]$  are independent of the  $S_z$  quantum number corresponding to the state  $\Psi$  but  ${}^1D_l^{(s)i} {}^1D_j^{(s)k}$  and  $\Gamma_{jl}^{ik}$  separately are  $S_z$ -dependent.

Eq. (4) provides the calculation of the expression

$$\sum_{i,k} {}^2D_{ki}^{ik} = \frac{1}{2} \sum_{i,k} {}^1D_k^i {}^1D_i^k - \frac{1}{4} N^2 - S^2 + \frac{1}{2} \sum_{i,k} \Gamma_{ki}^{ik}, \quad (5)$$

which has been obtained taking into account the values of the traces  $\sum_i {}^1D_i^i = N$  and  $\sum_i {}^1D_i^{(s)i}(S_z) = \frac{S_z}{S} \sum_i {}^1D_i^{(s)i}(S_z = S) = 2S_z$  [17].

### 3. The decomposition of the number of effectively unpaired electrons

The value of the sum  $\sum_{i,k} {}^2D_{ki}^{ik}$  is [18]

$$\sum_{i,k} {}^2D_{ki}^{ik} = \frac{(4-N)N}{4} - S(S+1), \quad (6)$$

where  $S$  denotes the spin quantum number corresponding to the state  $\Psi$ . This expression can also be derived from the expectation value of the  $\hat{S}^2$  operator corresponding to the state  $\Psi$ ,  $\langle \Psi | \hat{S}^2 | \Psi \rangle$ , using the spin-free second-quantized expression of the operator  $\hat{S}^2$  [19].

The substitution of  $\sum_{i,k} {}^2D_{ki}^{ik}$  in Eq. (5) by the right hand side of Eq. (6), taking into account the expression (2) leads to

$$N_u = 2S + 2S^2 - 2S_z^2 + \sum_{i,k} \Gamma_{ki}^{ik}(S_z) \quad (7)$$

in which we have introduced the symbol ( $S_z$ ) to point out that the value of the  $\sum_{i,k} \Gamma_{ki}^{ik}$  quantity depends on the substate of quantum number  $S_z$ . Obviously, the quantities  $N_u$ ,  $2S$  and  $2S^2$  in Eq. (7) are  $S_z$ -independent and consequently the sum  $[-2S_z^2 + \sum_{i,k} \Gamma_{ki}^{ik}(S_z)]$  is also  $S_z$ -independent. If we focus our attention on the highest projection substate,  $S_z = S$ , Eq. (7) is transformed into

$$N_u = 2S + \sum_{i,k} \Gamma_{ki}^{ik}(S_z = S). \quad (8)$$

Eq. (8) provides a decomposition of the number of effectively unpaired electrons,  $N_u$ , into two terms with clear physical meaning.  $2S$  represents the number of net spin unpaired electrons whereas the term  $\sum_{i,k} \Gamma_{ki}^{ik}(S_z = S)$  accounts for the above mentioned number of unpaired electrons arising from the partial split of electron pairs in the case of multideterminantal correlated wave func-

tions. In inverse order, Eqs. (7) and (8) allow one to interpret physically the quantity  $\sum_{i,k} \Gamma_{ki}^{ik}(S_z = S)$ , which is identical to  $[2S^2 - 2S_z^2 + \sum_{i,k} \Gamma_{ki}^{ik}(S_z)]$  ( $\forall S_z$ ).

This interpretation of the two terms of the r.h.s. of Eq. (8) requires that  $\sum_{i,k} \Gamma_{ki}^{ik}(S_z = S) \geq 0$ . We will show, by means of an independent reasoning, that  $N_u \geq 2S$  and consequently that requirement is fulfilled. Let us consider the highest spin projection substate  $S_z = S$  corresponding to the spin  $S$  of the wave function  $\Psi$  which possesses  $N_\alpha = \frac{N}{2} + S$  electrons of type  $\alpha$  and  $N_\beta = \frac{N}{2} - S$  electrons of type  $\beta$  [20]. We will calculate the trace of the  ${}^1D^2$  matrix, that is  $\sum_{i,k} {}^1D_k^i {}^1D_i^k$ , through the basis set of the natural orbitals,  $I, J, \dots$ , which diagonalize the  ${}^1D$  matrix

$$\begin{aligned} \sum_{i,k} {}^1D_k^i {}^1D_i^k &= \sum_I ({}^1D_I^\alpha + {}^1D_I^\beta)^2 \\ &= \sum_I ({}^1D_I^\alpha)^2 + \sum_I ({}^1D_I^\beta)^2 + 2 \sum_I ({}^1D_I^\alpha) ({}^1D_I^\beta). \end{aligned} \quad (9)$$

Since  $0 \leq {}^1D_I^\alpha \leq 1$  and  $0 \leq {}^1D_I^\beta \leq 1$  ( $\forall I$ ) and taking into account that  $\sum_I {}^1D_I^\alpha = \frac{N}{2} + S$  and  $\sum_I {}^1D_I^\beta = \frac{N}{2} - S$  it follows that  $\sum_I ({}^1D_I^\alpha)^2 \leq (\frac{N}{2} + S)$ ,  $\sum_I ({}^1D_I^\beta)^2 \leq (\frac{N}{2} - S)$  and  $\sum_I ({}^1D_I^\alpha) ({}^1D_I^\beta) \leq (\frac{N}{2} - S)$ . Consequently,  $\sum_{i,k} {}^1D_k^i {}^1D_i^k \leq 2(N - S)$ . Introducing these relationships into Eq. (2) it results that  $N_u \geq 2S$ . Although in this proof we have utilized the substate  $S_z = S$  the result is fulfilled  $\forall S_z$  since the trace  $\sum_{i,k} {}^1D_k^i {}^1D_i^k$  is a  $S_z$ -independent quantity. According to this result, it follows from Eq. (8) that  $\sum_{i,k} \Gamma_{ki}^{ik}(S_z = S) \geq 0$ . Moreover, according to Ref. [5] the  $N_u$  quantity lies in the interval  $0 \leq N_u \leq 2N$ . However, in view of the relationship found  $N_u \geq 2S$ , a reformulation of that interval is required in terms of  $2S \leq N_u \leq 2N$ . Obviously, both intervals are coincident in the singlet state case. If the wave function is a spin eigenfunction which is a single Slater determinant the elements of the cumulant matrix  $\Gamma_{ji}^{ik}$  are zero and consequently  $N_u = 2S$ , which is the lower bound of that interval.

To check the correctness of the partitioning described in Eq. (8), we have performed numerical determinations in several systems corresponding to singlet, doublet and triplet spin symmetries. The results, shown in Table 1, have been obtained at configuration interaction level (single and double excitations) using 6-31G basis sets and experimental geometries with the PSI 3.3 program package [21]. The calculations have been performed using as reference the RHF states (singlets) and ROHF ones (doublets and triplets) and their corresponding molecular orbitals as orthonormal basis sets. The values written in column 3 have been directly obtained by means of Eq. (2) while those described in column 4 arise from Eq. (4). As can be observed taking into account Eq. (8), the concordance between the results arising from both independent procedures is perfect. It is worthy to point out the significant

**Table 1**

Decomposition of the number of the effectively unpaired electrons according to Eq. (8) for selected species at configuration interaction level (single and double excitations) with the 6-31G basis sets.

System	State	$N_u$	$\sum_{i,k} \Gamma_{ki}^{ik}(S_z = S)$
H <sub>2</sub>	${}^1\Sigma_g^+$	0.1138	0.1138
HF	${}^1\Sigma^+$	0.2372	0.2372
H <sub>2</sub> O	${}^1A_1$	0.3081	0.3081
NH <sub>3</sub>	${}^1A_1$	0.3520	0.3520
CH	${}^2\Pi$	1.3499	0.3499
CH <sub>3</sub>	${}^2A_2''$	1.3118	0.3118
NO	${}^2\Pi$	1.5480	0.5480
H <sub>2</sub> NO	${}^2B_1$	1.5080	0.5080
CH <sub>2</sub>	${}^3B_1$	2.2414	0.2414
C <sub>2</sub>	${}^3\Sigma_g^+$	2.5043	0.5043
HBBH (linear)	${}^3\Sigma_g^-$	2.3981	0.3981
O <sub>2</sub>	${}^3\Sigma_g^-$	2.5036	0.5036

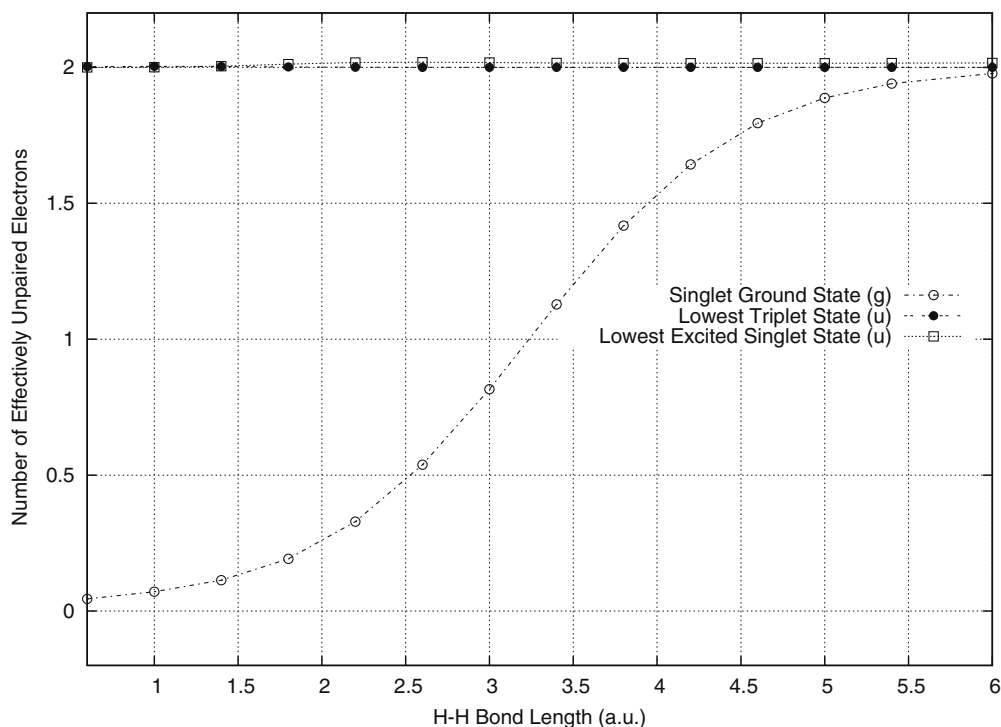


Fig. 1. The number of effectively unpaired electrons in the  $H_2$  molecule (singlets and triplet) as a function of the internuclear separation.

numerical values obtained as in closed- as in open-shell systems for the unpaired electron contribution arising from the multideterminantal character of the wave functions. In order to more comprehensively illustrate the physical meaning of the  $N_u$  number and its dependence on the environment geometry, we have studied the variation of the cumulant part with the internuclear distance for the hydrogen molecule in its singlet ground state  $^1\Sigma_g^+$ , its lowest triplet state  $^3\Sigma_u^+$  and its lowest excited singlet state  $^1\Sigma_u^+$ . The calculations have also been performed using the 6-31G basis set, at RHF/ROHF CISD level of approximation (FCI level in this case), respectively. The results are shown in Fig. 1. In the case of the singlet states, the  $N_u$  value obviously coincides with the value of the cumulant part. These singlet states are represented by strongly-correlated multideterminantal wave functions, while the triplet state wave function turns out to be practically a single determinant during the whole dissociation process. As can be observed, for the singlet state cases the cumulant part is always significant, pointing out the importance of the correlation effects; its value in the ground state increases with the internuclear distance approaching to the value 2 at the dissociation limit (one unpaired electron for each hydrogen atom) while it is almost constant in the excited singlet state. For the triplet state the  $N_u$  value also remains almost constant during the dissociation process being always only slightly higher than  $2S$ , which must be interpreted in terms of low correlation effects. The results for these states confirm the lower bound value for the  $N_u$  quantity reformulated in this work. Determinations of the  $N_u$  quantity have been performed in other systems [5] which could now be regarded in terms of cumulants.

#### 4. Concluding remarks

In conclusion, in this report we have performed a partitioning of the number of effectively unpaired electrons corresponding to an  $N$ -electron system into two contributions. A suitable management the cumulant of the second-order reduced density matrix allows us to show that one of these terms describes the number of unpaired electrons associated with the spin, while the other one corresponds

to the partial split of electron pairs that appear when the system is described by a multideterminantal correlated wave function. Moreover, our treatment also allows us to formulate the lower bound of the number of effectively unpaired electrons in a more precise manner.

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