

## FULL PAPER

## Structure of Fukui matrices

Roberto C. Bochicchio<sup>1,2</sup> <sup>1</sup>Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Física, Ciudad Universitaria, 1428, Buenos Aires, Argentina<sup>2</sup>CONICET - Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Ciudad Universitaria, 1428, Buenos Aires, Argentina

## Correspondence

Roberto C. Bochicchio, Universidad de Buenos Aires, Facultad de Ciencias exactas y Naturales, Departamento de Física, Pab. 1, Ciudad Universitaria, Buenos Aires, Argentina 1428.  
Email: rboch@df.uba.ar

## Funding information

UBA, Argentina, Grant/Award Number: 20020130100226BA; CONICET, Argentina Grant/Award Number: 11220090100061

## Abstract

Fukui matrices considered as the generalization of the concept of Fukui densities are decomposed into their pairing and unpairing contributions within the theory of the reduced density matrices. Their algebraic structure become clear from this decomposition providing their relationships with the spin density matrices and the irreducible part of the second-order reduced density matrix cumulant, that is, the explicit contributions of the many-body or correlation effects. The uncorrelated state function approximation is a simple way to emphasize the physical meaning of these matrices and represents the appropriate starting point for the treatment of a quasi-analytical model to denote the occurrence of correlation effects.

## KEYWORDS

Fukui matrices, pairing densities, reduced density matrices, unpairing densities

## 1 | THEORETICAL SCENARIO

Fukui densities (or Fukui functions) are central to the reactivity concept in chemical physics.<sup>[1]</sup> The natural scenario in which they have been properly defined as the first derivative of the electron density respect to the number of particles at fixed external potential is conceptual density functional theory (DFT).<sup>[1,2]</sup> Its matrix formulation has been reported by use of the first-order reduced density matrices at the DFT level of approximation<sup>[3]</sup> and also it has been generalized for any type of molecular state functions.<sup>[4–7]</sup> The aim of this report is to use the rigorous version of PPLB proposal<sup>[8,9]</sup> based on the representation of the grand-canonical ensemble to properly express these magnitudes from which the concept of systems with a non-integer number of particles  $\mathcal{N}$  ( $\mathcal{N}=N\pm v$ ) is introduced in a natural manner. Thus, it allows the number of particles to be a mathematically continuous variable to derive the Fukui like density matrices<sup>[7]</sup> from the first-order reduced density matrices  ${}^1D^{N\pm v}$  (1-RDM), with  $N \in \mathbb{N}_0$ ,  $v \in \mathbb{R}$ , and  $0 < v < 1$ .<sup>[9]</sup>  $\mathbb{N}_0$  and  $\mathbb{R}$  stand for the set of non-negative integer and real numbers, respectively. This type of systems may be identified with open systems, that is, an atom, a functional groups or a moiety, as a domain within a given molecular structure.<sup>[8]</sup> The convex structure of the energy in atomic or molecular systems driven by Coulomb interactions,<sup>[8]</sup> enables the ground state  ${}^1D^{N\pm v}$ , obtained by contraction mapping<sup>[10]</sup> of two integer  $M$ -particle system 1-RDMs, to be expressed by the simple convex expansion<sup>[8,9]</sup>

$${}^1D^{N\pm v} = v {}^1D^{N\pm 1} + (1-v) {}^1D^N \quad (1)$$

where  ${}^1D^N$  and  ${}^1D^{N\pm 1}$  stand for the 1-RDMs of the systems with  $N$  and  $N \pm 1$  particles, that is, the neutral and ionic species, respectively. During the course of this work, the states of the neutral species will be considered as singlet closed shells. Equation 1 is the meaningful physical expression for the 1-RDM of a system possessing a non-integer number of electrons that cannot be described neither by a pure nor a canonical ensemble state.<sup>[9]</sup> Its trace  $N \pm v$  may be interpreted as an average of the number of electrons of the systems involved in the expansion.<sup>[8,9]</sup>

The Fukui matrices are defined by the derivative of  ${}^1D^{N\pm v}$  respect to the number of particles  $\mathcal{N}$ , as it increases/decreases from  $N$  to  $N \pm v$  at constant external field  $v$ ,<sup>[1,7]</sup> by

$$\mathbb{F}^{\pm} = \pm \left( \frac{\partial}{\partial v} {}^1D^{N\pm v} \right)_v \quad (2)$$

which from Equation 1 straightforwardly leads to

$$\mathbb{F}^{\pm} = \pm ({}^1D^{N\pm 1} - {}^1D^N) \quad (3)$$

being the difference among the  $N \pm 1$  and  $N$  system 1-RDMs.<sup>[7]</sup> Equation 3 defines a 1-particle like density matrix (DM) associated to 1 extra (particle) or lacking electron (hole), that is, the cationic or anionic character, in reference to the neutral species. Consequently, it is of unit trace, that is,  $Tr(\mathbb{F}^{\pm})=1$ .

## 2 | DENSITY MATRIX DECOMPOSITION

To reveal the nature of these response matrices  $\mathbb{F}^{\pm}$ , the decomposition of  ${}^1D^N$  into an effectively pairing and an effectively unpairing DM expressed by<sup>[11]</sup>

$${}^1D^N = P(N) + \frac{1}{2}u(N) \quad (4)$$

is introduced, where the  $P(N)$  and  $\frac{1}{2}u(N)$  matrices describe the paired and the unpaired electron distributions of an  $N$ -particle system and are defined by

$$P(N) = \frac{1}{2} ({}^1D^N)^2 \quad (5a)$$

and

$$u(N) = 2 {}^1D^N - ({}^1D^N)^2 \quad (5b)$$

respectively.<sup>[11]</sup> Thus, the matrix form in Equation 3 reads,

$$\mathbb{F}^{\pm} = \pm [P(N\pm 1) - P(N)] \pm \frac{1}{2}[u(N\pm 1) - u(N)] \quad (6)$$

This equation permits to appreciate the correlation effects in a natural form. For this goal, let us introduce the  $P(N)$  and  $u(N)$  matrices in terms of  ${}^1D^N$  (cf, Equations 5a and 5b) and the spin-free 2-particle DM  ${}^2D^N$  structure from which  ${}^1D^N$  is derived by contraction mapping. The matrix elements of  ${}^2D^N$  in an  $ij,kl,\dots$  orthogonal spin orbital basis set are given by<sup>[12]</sup>

$$({}^2D^N)_{kl}^{ij} = \frac{1}{2} ({}^1D^N)_k^i ({}^1D^N)_l^j - \frac{1}{4} ({}^1D^N)_l^i ({}^1D^N)_k^j - \frac{1}{4} {}^1D^{(s)j}_i {}^1D^{(s)k}_l + \frac{1}{2} (\Gamma^N)_{kl}^{ij} \quad (7)$$

where  $D^{(s)} = {}^1D^{\alpha} - {}^1D^{\beta}$  is the spin-free spin DM with  ${}^1D^{\alpha}$ , the spin up ( $\alpha$ ) and spin down ( $\beta$ ) 1-RDMs, respectively<sup>[13]</sup> and  $(\Gamma^N)_{kl}^{ij}$  stand for the matrix elements of the irreducible part of the spin-free 2-RDM cumulant matrix.<sup>[13]</sup> The first term in the rhs of Equation 7 is the direct or Coulomb term; the second and third terms represent the exchange effects, that is, particle and spin density exchange contributions, respectively. The fourth term is a nonfactorizable or irreducible term that segregates the many-body effects not present in the others.<sup>[12-14]</sup> Note that the sum  $(-\frac{1}{4} {}^1D^{(s)j}_i {}^1D^{(s)k}_l + \frac{1}{2} \Gamma_{kl}^{ij})$  is the spin-free version of the cumulant of  ${}^2D^N$ . This sum is independent of the spin substates of spin projection number  $S_z$  corresponding to the state. Then, the  $S_z$  invariance properties of the different contributions to the reduced density matrices<sup>[13,14]</sup> play the key role to establish and interpret the Fukui matrices.

The contraction mapping to obtain  ${}^1D^N$  from  ${}^2D^N$  is defined by  $({}^1D^N)_k^i = \frac{2}{N-1} \sum_j D_{kj}^{ij}$ .<sup>[15]</sup> Hence, the decomposition (cf, Equations 4, 5a, and 5b) permits to express the  $u(N)$  matrix,<sup>[12,14]</sup> as

$$[u(N)]_j^i = [(D^{(s)})_j^i]_{S_z=S} + \sum_k [(\Gamma^N)_{kj}^{ik}]_{S_z=S} \quad (8)$$

where  $S_z=S$  means that the spin projection  $S_z$  must be evaluated at its highest projection value  $S$  because of the spin projection independence of these magnitudes.<sup>[12]</sup> Then, the explicit structure of the Fukui like density matrices arise by replacement of Equations 5a and 8 into Equation 6, yielding

$$\begin{aligned} [\mathbb{F}^{\pm}]_j^i &= \pm \frac{1}{2} \left\{ [D^{(s)}(N\pm 1)]_j^i \right\}_{S_z=S} \pm [P(N\pm 1) - P(N)]_j^i \\ &\quad \pm \frac{1}{2} \sum_k \left\{ [(\Gamma_{kj}^{ik}(N\pm 1))]_{S_z=S} - [(\Gamma_{kj}^{ik}(N))]_{S_z=0} \right\} \end{aligned} \quad (9)$$

The first term in its rhs shows the net unpaired density contribution from the spin DM. It comes from the system with the odd number of particles, that is, the ionic specie; the second term stands for the difference of  $N \pm 1$  and  $N$  pairing densities between of the neutral and ionic systems;

and the third term measures the explicit correlation contribution as the difference of the spatial unpairing due to the nonuniform double occupancy of the natural (or molecular) orbitals.<sup>[16,17]</sup>

### 3 | HARTREE-FOCK MODEL: THE LIMITING CASE

We will make use of the noncorrelated mean field motion of a Hartree-Fock state to analyze the physical meaning of these matrices by inspection of each terms in Equation 9. For this goal, each of the 2 1-RDMs to build the Fukui matrices must be written within this approximation. The neutral  $N$  ( $N$  even) particle system is written in the restricted closed shell (RHF) form, while that of the ionic species, in the restricted open shell Hartree-Fock (ROHF) state. It is worthy to note that in this approximation, the irreducible part of the second-order reduced DM cumulant  $\Gamma$ , vanishes identically. Hence, the RHF closed shell 1-RDM is expressed by

$${}^1D^N = 2 \sum_{k=1}^{2-\text{occ}} |\varphi_k\rangle\langle\varphi_k|$$

while

$${}^1D^{N\pm 1} = 2 \sum_{k=1}^{2-\text{occ}} |\varphi_k\rangle\langle\varphi_k| + |\varphi_o\rangle\langle\varphi_o|$$

represent the 1-RDM of the ( $N\pm 1$ ) ionic systems,<sup>[15]</sup> and  $\{|\varphi_k\rangle\}$  stands for the set of orthonormal molecular orbitals of the RHF approximation (frozen orbitals or Koopmans approximation). The upper limit  $2-\text{occ}$  of the summations indicates the number of double occupied orbitals in the corresponding state, that is,  $\frac{N}{2}$  for the neutral and the anionic systems and  $\frac{N}{2}-1$  for the cationic ones. In the ROHF approximation,  $|\varphi_o\rangle$  refers to the open shell single occupied orbital for the ions in its ground state, that is, the highest occupied molecular orbital (HOMO)  $|\varphi_H\rangle$  for the cation, while  $|\varphi_L\rangle$ , the lowest unoccupied molecular orbital (LUMO) for the anion. The introduction of these expressions for each of the corresponding pairing and unpairing density matrices in Equation 9 show that for  $\mathbb{F}^+$ , both magnitudes contribute in the same amount,  $\frac{1}{2}|\varphi_o\rangle\langle\varphi_o|$ , while for  $\mathbb{F}^-$  both contribute in different amounts,  $\frac{3}{2}|\varphi_o\rangle\langle\varphi_o|$  and  $\frac{1}{2}|\varphi_o\rangle\langle\varphi_o|$ , respectively. Nevertheless, the same value for both branches of the Fukui matrices is obtained, and

$$\mathbb{F}^\pm = |\varphi_o\rangle\langle\varphi_o| \quad (10)$$

which is the spin DM  $D^{(S)}(S_z=S)$  in the ROHF case.<sup>[16,17]</sup> Hence, the differences between the pairing contributions for the  $N$  and  $N\pm 1$  systems are not similar for each of the Fukui matrices, however they properly contribute to build up the spin DM of the doublet state in its higher projection. Note that for this approximation as well as for any single determinant model approaches, Fukui matrices are positive semi-definite with all their values equal to zero, except for only one of unit value.<sup>[5]</sup> The present example will be helpful for the physical observations in the next section.

### 4 | SIMPLE CORRELATED MODEL BEYOND HARTREE-FOCK

Let us introduce a simple correlated model to go beyond the Hartree-Fock level of approximation shown in the previous section. Thus, we state the idea of the physical essence of the extra/lacking electron distribution in the system as a response function contained in the Fukui matrices. These responses are interpreted as changes in the pairing and unpairing distributions as a consequence of the correlation effects. For that purpose, we will concentrate in the  $\mathbb{F}^-$  case (the result for  $\mathbb{F}^+$  is obtained in a similar way).

To make the example as analytical as possible, we will consider the correlated state function as a configuration interaction (CI) type expanded only by 2 configurations, that of the neutral  $N$ -particle ( $N$  even) closed shell Hartree-Fock ground state determinant system  $|\Phi_H\rangle$  and its double excited determinant  $|\Phi_L\rangle$  formed from the promotion of the 2 electrons in  $|\varphi_H\rangle$  (HOMO) to the LUMO  $|\varphi_L\rangle$ , that is,

$$|\Phi\rangle = c_H|\Phi_H\rangle + c_L|\Phi_L\rangle \quad (11)$$

where  $c_H$  and  $c_L$  stand for the CI expansion coefficients of the ground and the double excited determinant, respectively, fulfilling the normalization condition,  $|c_H|^2 + |c_L|^2 = 1$ . The ( $N-1$ )-particle system is represented by the ROHF approximation in its high spin state, as in the previous section, to retain the same state function scheme. The  ${}^1D^N$  obtained by the contraction mapping procedure<sup>[15]</sup> of the DM defined by  ${}^N D = |\Phi\rangle\langle\Phi|$  is diagonal and is expressed by

$${}^1D^N = |c_H|^2 {}^1D_H^N + |c_L|^2 {}^1D_L^N \quad (12)$$

where  ${}^1D_H^N$  and  ${}^1D_L^N$  represent the spin-free 1-particle reduced density matrices for the ground and the double excited determinant states, respectively. Thus, explicitly

$${}^1D^N = 2 \sum_k^{\frac{N}{2}-1} |\varphi_k\rangle\langle\varphi_k| + 2 |c_H|^2 |\varphi_H\rangle\langle\varphi_H| + 2 |c_L|^2 |\varphi_L\rangle\langle\varphi_L| \quad (13)$$

and the corresponding  $(N - 1)$  particle 1-RDM simply reads

$${}^1D^{N-1} = 2 \sum_k^{\frac{N}{2}-1} |\varphi_k\rangle\langle\varphi_k| + |\varphi_H\rangle\langle\varphi_H| \quad (14)$$

Hence, introducing these expressions in Equation 3, the expression for  $\mathbb{F}^-$  which contains correlation information is

$$\mathbb{F}^- = (2 |c_H|^2 - 1) |\varphi_H\rangle\langle\varphi_H| + 2 |c_L|^2 |\varphi_L\rangle\langle\varphi_L| \quad (15)$$

We can then by virtue of this result, look for the interpretation of both contributions to the Fukui matrices, that is, the difference of pairing and unpairing matrices as a function of the level of correlation as it is shown in Equation 6. Therefore, the pairing and unpairing density matrices defined by Equations 4, 5a, and 5b are read,

$$P(N) - P(N-1) = \left( 2 |c_H|^4 - \frac{1}{2} \right) |\varphi_H\rangle\langle\varphi_H| + 2 |c_L|^4 |\varphi_L\rangle\langle\varphi_L| \quad (16)$$

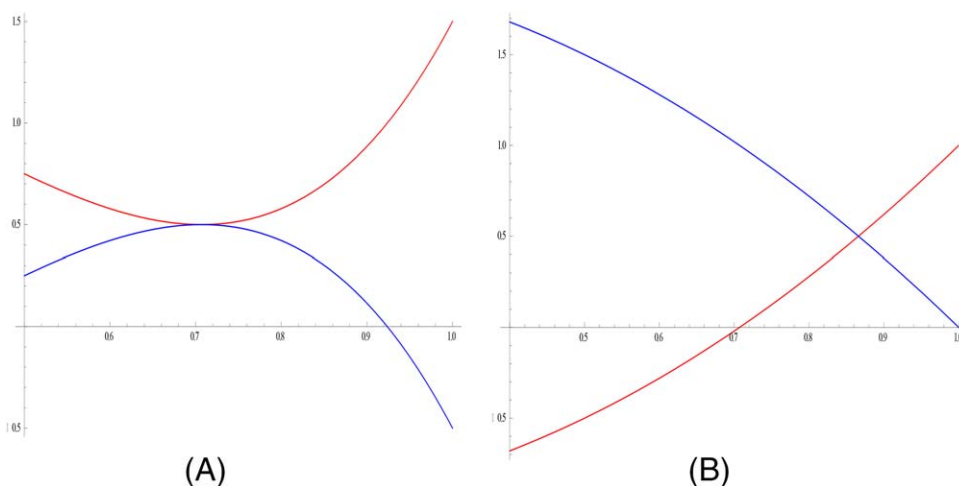
and

$$\frac{1}{2} [u(N) - u(N-1)] = \left( 2 |c_H|^2 |c_L|^2 - \frac{1}{2} \right) |\varphi_H\rangle\langle\varphi_H| + 2 |c_H|^2 |c_L|^2 |\varphi_L\rangle\langle\varphi_L| \quad (17)$$

Thus, these results enable us to discuss the changes in the difference electron distribution,  $\mathbb{F}^-$ , that is, the flux or change in the character of the electron population fraction from paired to unpaired and vice versa, under the correlation strength governed by the CI coefficients. To achieve this purpose, let us observe the trace of each of the contributions to  $\mathbb{F}^-$  coming from the paired and the unpaired density matrices (Equations 16 and 17). To feature the changes in the population character of the electron difference distribution, it is useful to write the populations by the trace of the paired and unpaired difference distributions,  $\mathbb{F}_p^- = P(N) - P(N-1)$  and  $\mathbb{F}_u^- = \frac{1}{2} [u(N) - u(N-1)]$ , respectively. These are  $2(|c_H|^4 + |c_L|^4) - \frac{1}{2}$  and  $4|c_H|^2|c_L|^2 - \frac{1}{2}$ , respectively. Two trivial cases of interest arise immediately in the present model, those where the coefficients are  $|c_H|=1$  and  $|c_L|=0$ , (or  $|c_H|=0$  and  $|c_L|=1$ ). Nevertheless, only the first of them is physically reliable because although the second has the same mathematical structure, the  $N$ -particle state function represents an excited determinant and not a ground state required for the Fukui function definition. For this reason, we will only concentrate in the first of these configurations. In this context, the  $N$ -particle system is described by only 1 closed shell determinant (cf, Equation 11) and the  $(N - 1)$  system is a high spin projection determinant. It should be noted that each of the population difference between two states, one of  $N$  and  $(N - 1)$ -particles, contribute to build the spin DM as shown in the previous section (cf, Equation 10). Thus, the negative sign is admitted and means that there are more paired or unpaired electron fraction in one of the states. These results reveal the difference in pairing and unpairing between the  $N$  and  $(N - 1)$ -particle distributions which in this case only comes from the net particle difference because no correlation is considered. Let us now inspect for the cases in which correlation effects are taken into account, that is, those where both coefficients do not vanish, that is,  $0 < |c_H| < 1$  and  $0 < |c_L| < 1$ . Figure 1 shows  $Tr(\mathbb{F}_p^-)$  and  $Tr(\mathbb{F}_u^-)$  contributions to the difference electron DM and the HOMO and LUMO orbital populations (Equation 15), as a functions of  $|c_H|$ . It may be observed in Figure 1A (red line), that the pairing contribution to the 1 electron Fukui density is positive for any value of the coefficient  $|c_H|$  with  $\max(\mathbb{F}_p^-) = \frac{3}{2}$  for a Hartree-Fock state ( $|c_H|=1$ ) while the unpairing population fraction may change its sign as shown in Figure 1A (blue line) with  $\min(\mathbb{F}_u^-) = -\frac{1}{2}$  (see text in the previous section). Note that also it is negative for decreasing values of the coefficient and its sign change, that is, the unpaired population difference becomes to be positive and continue increasing its value until reaching its maximum. The pairing population is greater than the unpaired one for all range of  $|c_H|$ . As the pairing contribution grows, the unpairing decreases even to be negative to preserve the particle conserving principle,  $Tr(\mathbb{F}^-) = 1$ .

Inasmuch the above remark, the changes due to the variation of the CI coefficients are crucial to depict the effects of the correlation in the electron difference distribution. Thus, it is worthy to note two important cases according the values of the CI coefficients which correspond to strong correlated electronic configurations. The first one is that in which both difference populations are equal, that is,  $\frac{1}{2}$  at  $|c_H| \approx 0.7$  (see Figure 1A) which reveals a case of strong correlation and represent the equalization of  $\min(\mathbb{F}_p^-)$  and the  $\max(\mathbb{F}_u^-)$ . The second case of interest may be mentioned as an electronic diradical situation (both electron configurations are dominant),<sup>[8]</sup> that is,  $|\Phi^{dirad}\rangle = \frac{1}{\sqrt{2}} \{ |\Phi_H\rangle - |\Phi_L\rangle \}$ ; the difference populations are  $\approx 0.75$  and  $\approx 0.25$ , respectively.

Let us finish the discussion in this section analyzing the Figure 1B. This shows the difference populations for the HOMO ( $\mathbb{F}_{HH}^-$ ) (red line) and LUMO (blue line) ( $\mathbb{F}_{LL}^-$ ) for the orbitals (Equation 15), as a functions of  $|c_H|$ . For  $|c_H|=1$ , that is, the Hartree-Fock case, the  $\mathbb{F}^- = |\varphi_H\rangle\langle\varphi_H|$  equals the corresponding spin DM (see previous section) ( $\mathbb{F}_{HH}^- = 1$ ,  $\mathbb{F}_{LL}^- = 0$ ). According to the introduction of the correlation effects, namely, when  $|c_H|$  decreases,  $\mathbb{F}_{HH}^-$  also decreases, and  $\mathbb{F}_{LL}^-$  begins to growth. Thus, close to the interval in which  $|c_H| \approx 1$ ,  $\mathbb{F}^-$  is close to the spin DM. For other values of  $|c_H|$ ,  $\mathbb{F}_{LL}^-$  begins to be important and  $\mathbb{F}_{HH}^-$  departs from the spin DM. At  $|c_H| \approx 0.866$ , both difference populations equalize and for the diradical state are very distant from each other and very different of a spin DM, even with negative HOMO difference population.



**FIGURE 1** A,  $Tr(\mathbb{F}_p^-)$  (red line) and  $Tr(\mathbb{F}_u^-)$  (blue line) contributions to the difference electron DM; B, populations for the HOMO (red line) and LUMO (blue line) orbitals (Equation 15), as a functions of  $|c_H|$

## 5 | FURTHER REMARKS

The simple quasi-analytic model example used in the present report permitted to introduce the correlation effects, although qualitatively, into the concept of the nature of the Fukui density matrices showing that these effects are supported by the change of part of the electron cloud character between paired and unpaired electron densities.

It is interesting to make some observations about the significance of Fukui matrices and the consequences to which they lead. The first aspect we want to mention is that for systems with low correlation, that is, those systems for which the Hartree–Fock approach is a good one, the  $\Gamma^N$  ( $\Gamma^{N\pm 1}$ ) matrix is close to the zero matrix and fulfills the norm matrix condition,  $\|\Gamma^N\| \ll \|\mathbb{1}^N\|^2$ . Consequently, the last term of Equation 9 approaches zero. Then, the term  $P(N\pm 1) - P(N)$  approaches  $\frac{1}{2}$  and  $-\frac{3}{2}$  times the spin DM, respectively. Therefore, one is finally tempted to write, without any loss of rigorousness, as it has been discussed above from the point of view of the electron populations in the frontier orbitals, that

$$[\mathbb{F}^\pm]_j^i = \{ [D^{(s)}(N\pm 1)]_j^i \}_{S_z=S} + \Omega_j^i \quad (18)$$

where  $\Omega$  may be interpreted as a measure of the deviation (distance) of the difference of pairing between the two systems. Therefore, for systems of low correlation, the Fukui matrices are no more than the spin density of the ionic state (net unpairing) plus a correction from the spatial unpairing due to the difference in the double occupancy of the orbitals as a consequence of the correlation effects.<sup>[16,17]</sup> Nevertheless, as shown in the discussion section of above, for high correlated systems, Equation 18 is no longer valid.

Following the same line of reasoning, an interpretive aftermath worthy of mention is its relation with the spin-entanglement contribution to the correlation.<sup>[18,19]</sup> The  $\mathbb{F}^\pm$  matrices describe the electron difference among the  $N$  and  $N\pm 1$  particle electron distributions, namely what we called difference electron distribution. Hence, its associated density integrates to the unit trace (number of electrons in the distribution) and may be written as

$$\begin{aligned} Tr(\mathbb{F}^\pm) &= \mathbf{1} = \pm \frac{1}{2} \pm Tr[P(N\pm 1) - P(N)] \\ &\pm \frac{1}{2} \sum_{i,k} \{ [\Gamma_{ki}^{ik}(N\pm 1)]_{S_z=S} - [\Gamma_{ki}^{ik}(N)]_{S_z=0} \} \end{aligned} \quad (19)$$

Thus, regarding the fact that the first two terms in the rhs of Equation 9 may be related to the net spin density contributions as shown above for the Hartree–Fock approach, the last term is clearly related to the correlation effects and states the difference among the cumulant crossed traces of the spin-free 2-RDM,  $\epsilon_M = \sum_{i,k} \Gamma_{ki}^{ik}(S_z=S)$ .<sup>[20]</sup> Consequently, as it has been shown, it represents a measure of the spin-entanglement of the  $M$ -particle system<sup>[20]</sup> and then, this term expressed by the  $\pm(\epsilon_{N\pm 1} - \epsilon_N)$  means the contribution of the spin-entanglement difference among the neutral and the ionic states of the system.

The present results open the possibility of the local topological study of these densities expressed by Equation 6 which implies the numerical determination of them and their physical consequences, including other than the correlation effects, the orbital relaxation effects which needs numerical calculations and are out of the scope of present theoretical work. These topics are being considered in our laboratories.

## ACKNOWLEDGMENT

Financially supported by Projects 20020130100226BA (UBA, Argentina) and 11220090100061 (CONICET, Argentina)

## REFERENCES

- [1] P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793.
- [2] R. G. Parr, W. Yang, *J. Am. Chem. Soc.* **1984**, *106*, 4049.
- [3] P. Bultinck, D. Clarisse, P. W. Ayers, R. Carbo-Dorca, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6110.
- [4] D. R. Alcoba, W. Tiznado, O. B. Oña, A. Torre, L. Lain, *Chem. Phys. Lett.* **2012**, *533*, 114.
- [5] P. Bultinck, D. Van Neck, G. Acke, P. W. Ayers, *Phys. Chem. Chem. Phys.* **2012**, *14*, 2408.
- [6] D. R. Alcoba, L. Lain, A. Torre, O. B. Oña, E. Chamorro, *Phys. Chem. Chem. Phys.* **2013**, *15*, 9594.
- [7] R. C. Bochicchio, *Theor. Chem. Acc.* **2015**, *134*, 138.
- [8] J. P. Perdew, R. G. Parr, M. Levy, J. Balduz, Jr., *Phys. Rev. Lett.* **1982**, *49*, 1691.
- [9] R. C. Bochicchio, D. Rial, *J. Chem. Phys.* **2012**, *137*, 226101.
- [10] R. C. Bochicchio, R. A. Miranda-Quintana, D. Rial, *J. Chem. Phys.* **2013**, *139*, 199101.
- [11] R. M. Lobayan, R. C. Bochicchio, L. Lain, A. Torre, *J. Chem. Phys.* **2005**, *123*, 144116.
- [12] D. R. Alcoba, R. C. Bochicchio, L. Lain, A. Torre, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5144.
- [13] R. McWeeny, Y. Mizuno, *Proc. Roy. Soc. (London)* **1961**, *A259*, 554.
- [14] L. Lain, A. Torre, D. R. Alcoba, R. C. Bochicchio, *Theor. Chem. Acc.* **2011**, *128*, 405.
- [15] E. D. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, NY **1976**.
- [16] R. C. Bochicchio, *J. Mol. Struct. (THEOCHEM)* **1998**, *429*, 229.
- [17] V. N. Staroverov, E. R. Davidson, *Chem. Phys. Lett.* **2000**, *330*, 161.
- [18] G. C. Ghirardi, L. Marinatto, *Opt. Spectrosc.* **2005**, *99*, 388.
- [19] T. Juhász, D. A. Mazziotti, *J. Chem. Phys.* **2006**, *125*, 174105.
- [20] D. R. Alcoba, R. C. Bochicchio, L. Lain, A. Torre, *J. Chem. Phys.* **2010**, *133*, 144104.

How to cite this article: Bochicchio RC. Structure of Fukui matrices. *Int J Quantum Chem.* 2017;e25440. <https://doi.org/10.1002/qua.25440>