

A naïve geometrical perspective of Fukui functions: definition of Fukui function skew symmetric matrices described on density function sets

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Abstract Recent description on density function (DF) sets of origin shifts is used in the present work to describe in a simple way Fukui functions. The present paper discusses first the possibilities and nuances of the origin shift in sets of three DF, formed by cation, neutral and anion functions; then uses quantum similarity techniques to analyze the resultant origin shifted DF sets. Extension of the origin shift in arbitrary sets of DF is also discussed, with a final application over the structure of a single DF itself in terms of the MO shape functions basis set.

Keywords Density functions (DF) · Origin shift of a DF set · Ionic states DF sets · Fukui functions · Quantum similarity · MO shape functions

1 Foreword

Since the times of the Fukui definition of frontier orbitals concept and the added relevance of such discovery in order to understand some aspects of chemical reactivity [1, 2], the interest about this remarkable quantum mechanical molecular characteristic has not disappeared in oblivion. The definition of Fukui functions due to Parr et al. [3] later on, based on the variation of the density function (DF) with the number of electrons, has generated a large volume of literature, see for example references [4–8]. Recently, we have also developed several papers producing some information on these interesting functions [10–12]. The present study tries to provide several aspects about the nature and behavior of Fukui functions from a geometrical perspective. The paper will be organized on the basis of some recently published [13–18] new insight about the manner of handling DF sets.

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The main tools to define Fukui functions on a specific DF set will consist in employing an origin shift, performing afterwards convex combinations of the resultant translated DF. First a DF set of the neutral, anion and cation states will be studied under the main origin shift possibilities; afterwards a general set of DF will be analyzed. The main conclusion is such that there can be defined not a Fukui function but a Fukui function skew symmetric (or antisymmetric) matrix, the dimension of it being related to the cardinality of the DF set.

2 Introduction

In this section will be briefly described the notation which will be employed thereafter and the nature of the geometrical point of view which will be adopted. This initial discussion will be mainly based on three DF sets made by the ground, cation and anion state DF. Also, the resulting geometrical scenario will be employed in order to apply the quantum similarity, see for example, the point of view of reference [18]. This simple scheme has been chosen as a prologue to set up the final analysis on DF sets of general cardinality, which will be performed later on in the present study.

It must be also pointed out that the fact that if such a ionic set is taken as basic example, this do not impede to consider other DF sets constructed by elements of non-ionic nature, like ground and excited states or several conformers. Within any DF set, the geometrical discussion which follows is completely valid, thus precluding that Fukui functions can be certainly be generalized to any known set of electronic DF.

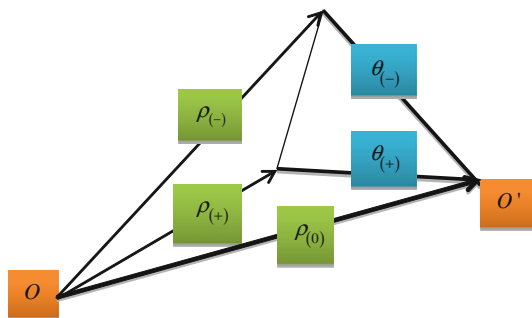
2.1 Neutral and ionic density functions (DF)

Suppose the ground state of any arbitrary electronic system and its anionic and cationic states as well, represented by their respective DF. The following symbols will be employed for the attached system states DF: neutral, $\rho_{(0)}$, cation, $\rho_{(+)}$ and anion, $\rho_{(-)}$. It can be supposed that a set containing the three DF, computed at any theoretical level is constructed and represented like: $P = \{\rho_I | I \in \{(0); (+); (-)\}\}$. It is a trivial matter to assume that Minkowski norms of these functions yield the respective number of electrons:

$$\begin{aligned}\langle \rho_{(0)} \rangle &= \int_D \rho_{(0)}(\mathbf{r}) d\mathbf{r} = \nu; \\ \langle \rho_{(+)} \rangle &= \int_D \rho_{(+)}(\mathbf{r}) d\mathbf{r} = \nu - 1; \\ \langle \rho_{(-)} \rangle &= \int_D \rho_{(-)}(\mathbf{r}) d\mathbf{r} = \nu + 1.\end{aligned}$$

When writing these three DF Minkowski norms, it is supposed that the set P is made of first order DF. Nothing opposes though that the following study can be generalized to any DF order, in this case just the Minkowski norms ought to be modified accordingly.

Fig. 1 Schematic drawing where it is depicted the initial origin O , the three original DF set: $P = \{\rho_I | I \in \{(0); (+); (-)\}\}$, considered as vectors, the new origin O' (corresponding to the origin shift performed over $\rho_{(0)}$, the neutral DF) and the set of the two resultant ionic DF, origin shifted by the neutral DF, $Q = \{\theta_I | I \in \{(+); (-)\}\}$



In the same way it can be indicated now that the number of ionic DF can be also augmented. Such increase of the DF in the study will complicate the given arguments, but will lead to similar conclusions; although the electron variation will be in such other non-ionic situations null and generalized Fukui functions will correspond to other kind of processes, where the external potential could vary as well. As already commented, handling several DF from a geometrical point of view has been already described preliminarily in another context [18] using an indefinite number of DF.

2.2 Geometrical point of view

The set of the three DF of the set P , when observed from a geometric point of view, can be considered as a triangle: a simple geometric figure, supposedly drawn within an infinite dimensional Hilbert semispace [14] and referred to an arbitrary origin O . Keeping this triangular picture in mind, nothing opposes to shift the origin of this triangle made of DF defining its vertices. This can be done by using any of the three involved functions in turn or appropriate linear combinations of them. See Fig. 1 to have a visual example of this origin shift procedure in the case the translation is performed using the ground state function.

3 Origin shift with respect to the neutral DF

Among many choices, which will be studied later on, one can use first as translation origin shift the neutral DF $\rho_{(0)}$, producing a zero function,¹ which will substitute the neutral molecule, and will act as the origin O' of the new translated vertices (see Fig. 1). Thus, in this way it is generated a new set: $Q = \{\theta_I | I \in \{(+); (-)\}\}$ of two new origin shifted DF which represents now the ionic states:

$$\theta_{(+)} = \rho_{(+)} - \rho_{(0)} \wedge \theta_{(-)} = \rho_{(-)} - \rho_{(0)}. \quad (1)$$

¹ The zero function might be defined as: $\forall \mathbf{r} \in \mathbf{R}^3 : 0(\mathbf{r}) = 0$.

The Minkowski pseudonorm of the origin shifted DF provides:

$$\langle \theta_{(+)} \rangle = (\nu - 1) - \nu = -1 \wedge \langle \theta_{(-)} \rangle = (\nu + 1) - \nu = +1.$$

Such origin shifted DF constructed as in Eq. (1) have no longer the DF crucial property of being non-negative definite. Interesting enough, their Minkowski pseudonorms coincide with the number of electrons lost or gained through the ionization process.

As already commented in [18], one must be aware of the fact that sets of cardinality N made of linearly independent vectors, upon any origin shift, become sets of $N - 1$ linearly independent vectors, simply because a vector of the set becomes zero or is linearly dependent of the rest. In the present case involving three DF, the structure of the problem becomes coherent, as the initial DF set can be considered forming a planar triangle and the origin shifted DF set defines the basis set for a two-dimensional vector space.

3.1 Construction of a weighted shifted DF

Choosing a parameterized weight: $\alpha \in [0, 1]$, from the set of functions Q one can construct another function, which in terms of such a weight yields a continuous function, possessing a Minkowski pseudonorm varying in the interval: $[-1, +1]$. For such purpose it is only needed to define the function:

$$\begin{aligned} \phi &= \alpha \theta_{(+)} + (1 - \alpha) \theta_{(-)} = \alpha (\theta_{(+)} - \theta_{(-)}) + \theta_{(-)} = \alpha (\rho_{(+)} - \rho_{(-)}) + \theta_{(-)} \\ &\rightarrow \langle \phi \rangle = \alpha ((\nu - 1) - (\nu + 1)) + 1 = 1 - 2\alpha. \end{aligned} \quad (2)$$

The meaning of this convex construction is such that when:

$$\alpha = 1 \rightarrow \phi \equiv \theta_{(+)} \wedge \alpha = 0 \rightarrow \phi \equiv \theta_{(-)},$$

while the midpoint will produce:

$$\alpha = \frac{1}{2} : \phi = \frac{1}{2} (\theta_{(+)} + \theta_{(-)}) \rightarrow \langle \phi \rangle = 0.$$

Therefore, the function ϕ in terms of the weight α smoothly defines the transformation of the shifted DF from the cation to the anion, passing thru some composite state, which corresponds to an arithmetic mean of both charged states. In the same manner one can perform an equivalent convex linear combination using the reversed form of Eq. (2) instead:

$$\phi' = \alpha \theta_{(-)} + (1 - \alpha) \theta_{(+)}.$$

Thus, the behavior of ϕ' will be similar to ϕ but exchanging the two origin shifted DF roles.

In any case, the elements of the shifted origin DF set Q constitute a simple example illustrating the property, which can be associated to vector sets, consisting in that a

set of an arbitrary number of DF can be origin shifted losing a dimension unit in their power to generating a function subspace [18].

4 A shifted Fukui function

Consequently, the derivative with respect to the parameter α of the weighted function ϕ , as defined in Eq. (2), can be written as:

$$F = \frac{d\phi}{d\alpha} = \theta_{(+)} - \theta_{(-)} = \rho_{(+)} - \rho_0 - (\rho_{(-)} - \rho_0) = \rho_{(+)} - \rho_{(-)}. \quad (3)$$

This derivative representing the origin shifted Fukui function, which can be associated to the corresponding origin shifted DF set: Q . In fact, the Fukui function as described here corresponds to the slope of the weighted function (2). Defined in this way the Fukui function, it is obvious that its Minkowski pseudonorm yields:

$$\langle F \rangle = \nu - 1 - (\nu + 1) = -2.$$

The minus sign of the Minkowski pseudonorm is a consequence of the definition associated to Eq. (2). This can be thought so, as exchanging the functions in the set $Q = \{\theta_I | I \in \{(+); (-)\}\}$ in their role within definition (2) will obviously yield a positive pseudonorm.

4.1 Approximate shifted Fukui function

One can use an approximate form for each ionic DF, taking into account the neutral HOMO, ρ_H and LUMO, ρ_L DF. Then, one can simply write:

$$\begin{aligned} \rho_{(+)} &\approx \rho_0 - \rho_H \wedge \rho_{(-)} \approx \rho_0 + \rho_L \\ \rightarrow F &\approx \rho_0 - \rho_H - (\rho_0 + \rho_L) = -(\rho_L + \rho_H) \rightarrow \langle F \rangle = -2 \end{aligned} \quad (4)$$

a result which is in accordance with the general Minkowski pseudonorm structure of the Fukui function and coincident with one of the original Fukui's definitions [1,2] of frontier orbital molecular reactivity, concretely the one providing reactivity indices for radical attack.

5 Comments

- (1) In the approximate expression (4), although one can observe that the sum of two DF possess the structure of a DF, and thus appears to be everywhere positive, the difference of state DF in Eq. (3) precludes the possible existence of negative regions in F .
- (2) Alternatively, the origin shift can be done using now the cation DF, yielding:

$$\theta_{(0)} = \rho_{(0)} - \rho_{(+)} \wedge \theta_{(-)} = \rho_{(-)} - \rho_{(+)},$$

which can be associated with the corresponding Minkowski pseudonorms:

$$\langle \theta_{(0)} \rangle = \nu - (\nu - 1) = 1 \wedge \langle \theta_{(-)} \rangle = \nu + 1 - (\nu - 1) = 2;$$

while now it is the cation shifted function which becomes a composite, therefore one can construct a weighted function like:

$$\begin{aligned} \phi &= \alpha \theta_{(0)} + (1 - \alpha) \theta_{(-)} = \alpha (\theta_{(0)} - \theta_{(-)}) + \theta_{(-)} \rightarrow \langle \phi \rangle \\ &= \alpha (\nu - (\nu + 1)) + (\nu + 1) - (\nu - 1) = 2 - \alpha \end{aligned}$$

which indicates that when $\alpha = 1 \rightarrow \phi = \theta_{(0)}$ and $\alpha = 0 \rightarrow \phi = \theta_{(-)}$ and at the midway value one has:

$$\alpha = \frac{1}{2} : \phi = \frac{1}{2} (\theta_{(0)} + \theta_{(-)}) \rightarrow \langle \phi \rangle = \frac{1}{2} (\nu + (\nu + 1)) = \nu + \frac{1}{2}.$$

Thus the origin shifted Fukui function in this case becomes:

$$F = \theta_{(0)} - \theta_{(-)} = \rho_{(0)} - \rho_{(-)} \rightarrow \langle F \rangle = -1.$$

The approximate Fukui function will be now:

$$F \approx \rho_{(0)} - (\rho_{(0)} + \rho_L) = -\rho_L,$$

which it is coincident with the reactivity in front of accepting an electron, that is: another of the original Fukui descriptions.

- (3) Of course, the origin shift provided by the anion DF, will be associated to the remnant Fukui reactivity definition. That is:

$$\theta_{(0)} = \rho_{(0)} - \rho_{(-)} \wedge \theta_{(+)} = \rho_{(+)} - \rho_{(-)}$$

with the corresponding Minkowski pseudonorms:

$$\langle \theta_{(0)} \rangle = \nu - (\nu + 1) = -1 \wedge \langle \theta_{(+)} \rangle = \nu - 1 - (\nu + 1) = -2;$$

while now it is the anion shifted function which becomes a composite, therefore one can construct a weighted function like:

$$\begin{aligned} \phi &= \alpha \theta_{(0)} + (1 - \alpha) \theta_{(+)} = \alpha (\theta_{(0)} - \theta_{(+)}) + \theta_{(+)} \\ &\rightarrow \langle \phi \rangle = \alpha (\nu - (\nu - 1)) + (\nu + 1) - (\nu - 1) = 2 + \alpha \end{aligned}$$

which when $\alpha = 1 \rightarrow \phi = \theta_{(0)} \wedge \alpha = 0 \rightarrow \phi = \theta_{(+)}$ and the situation at the midway gives:

$$\alpha = \frac{1}{2} : \phi = \frac{1}{2} (\theta_{(0)} + \theta_{(+)}) \rightarrow$$

$$\langle \phi \rangle = \frac{1}{2} (v - (v - 1)) + (v - 1) - (v + 1) = -\frac{3}{2}.$$

Thus, the origin shifted Fukui function in this case becomes:

$$F = \theta_{(0)} - \theta_{(+)} = \rho_{(0)} - \rho_{(+)} \rightarrow \langle F \rangle = v - (v - 1) = +1.$$

The approximate Fukui function will be now written as:

$$F \approx \rho_{(0)} - (\rho_{(0)} - \rho_H) = \rho_H,$$

coincident with the reactivity in front of the attack to give away an electron, another of the original Fukui descriptions.

- (4) One must conclude in front of the above results that, when considering the three DF associated to the cation, neutral and anion molecule, there is or can be not a uniquely defined Fukui function but three, according to the original Fukui prescription.
- (5) Another characteristic is the negative sign appearing in front of approximate Fukui functions, when shifting with respect the neutral state or the anion.

6 Origin shift using a centroid DF

6.1 Definitions

An alternative way to proceed in the origin shift of the original DF could be made by means of a centroid DF (CDF) construction, which can be defined in the three DF set P case by means of:

$$\theta_C = \frac{1}{3} (\rho_{(0)} + \rho_{(+)} + \rho_{(-)}) \rightarrow \langle \theta_C \rangle = \frac{1}{3} (v + (v - 1) + (v + 1)) = v,$$

constituting an alternative definition, which this time behaves as a DF.² The Minkowski norm of the CDF results in the number of electrons v , like in the neutral DF case. Using the CDF obtained in this way as origin shift, one can obtain three newly shifted DF namely:

² This has to be seen as a general property of vector semispaces. Convex linear combinations of their elements belong to the semispace. That is the same to say that vector semispaces are closed upon convex linear combinations.

$$\begin{aligned}
 {}^C\theta_{(0)} &= \rho_{(0)} - \theta_C = \frac{1}{3} (2\rho_{(0)} - (\rho_{(+)} + \rho_{(-)})) \\
 &\rightarrow \langle {}^C\theta_{(0)} \rangle = \frac{1}{3} (2\nu - (\nu - 1) - (\nu + 1)) = 0, \\
 {}^C\theta_{(+)} &= \rho_{(+)} - \theta_C = \frac{1}{3} (2\rho_{(+)} - (\rho_{(0)} + \rho_{(-)})) \\
 &\rightarrow \langle {}^C\theta_{(+)} \rangle = \frac{1}{3} (2(\nu - 1) - \nu - (\nu + 1)) = -1,
 \end{aligned}$$

and

$$\begin{aligned}
 {}^C\theta_{(-)} &= \rho_{(-)} - \theta_C = \frac{1}{3} (2\rho_{(-)} - (\rho_{(0)} + \rho_{(+)})) \\
 &\rightarrow \langle {}^C\theta_{(-)} \rangle = \frac{1}{3} (2(\nu + 1) - \nu - (\nu - 1)) = +1.
 \end{aligned}$$

The resultant centroid shifted DF have Minkowski pseudonorms which correspond to the associated ionization level. As it has been done previously, one can obtain a function which smoothly provides the centroid shifted DF at the extremal values, for instance:

$$\phi_{(+)} = \alpha {}^C\theta_{(0)} + (1 - \alpha) {}^C\theta_{(+)} = \alpha (\rho_{(0)} - \rho_{(+)}) + {}^C\theta_{(+)} \rightarrow \langle \phi_{(+)} \rangle = \alpha - 1$$

and

$$\phi_{(-)} = \alpha {}^C\theta_{(0)} + (1 - \alpha) {}^C\theta_{(-)} = \alpha (\rho_{(0)} - \rho_{(-)}) + {}^C\theta_{(-)} \rightarrow \langle \phi_{(-)} \rangle = 1 - \alpha$$

Both convex linear combinations deliver a similar picture as the one obtained earlier for Fukui functions, found in turn from origin shifted DF in comments (2) and (3).

6.2 A simpler picture

One can also combine the unshifted neutral state DF with the two ionic states in a convex manner, that is:

$$\begin{aligned}
 \zeta_{(+)} &= \alpha\rho_{(0)} + (1 - \alpha)\rho_{(+)} = \alpha(\rho_{(0)} - \rho_{(+)}) + \rho_{(+)} \rightarrow \langle \zeta_{(+)} \rangle = \nu + (\alpha - 1) \\
 \zeta_{(-)} &= \alpha\rho_{(0)} + (1 - \alpha)\rho_{(-)} = \alpha(\rho_{(0)} - \rho_{(-)}) + \rho_{(-)} \rightarrow \langle \zeta_{(-)} \rangle = \nu + (1 - \alpha)
 \end{aligned}$$

This choice permits to construct two functions, which according to the closed structure of vector semispaces can be also considered DF. The resultant Minkowski norms appear to be of the same nature as the ones defined above, using the centroid shifting, but with the number of electrons added. Such a characteristic provides functions, which

represent a fractionary number of electrons for values of the parameter in the middle of the interval.

6.3 Quantum similarity discussion

It might be interesting to use this simple geometrical picture, which can be constructed from the three DF of the set P , in order to obtain information on the three involved DF using quantum similarity formalism, see for example [19,20]. In fact, there are six possible quantum similarity measures between the pairs of the three considered DF, which can be collected into a symmetrical (3×3) quantum similarity matrix (QSM), with elements defined as the DF overlap integrals:

$$\forall I, J = \{(0), (+), (-)\} : \langle I|J \rangle = \langle \rho_I | \rho_J \rangle = \int_D \rho_I(\mathbf{r}) \rho_J(\mathbf{r}) d\mathbf{r}$$

then the SM can be structured as follows:

$$\mathbf{Z} = \begin{pmatrix} \langle 0|0 \rangle & \langle 0|+ \rangle & \langle 0|- \rangle \\ \langle +|0 \rangle & \langle +|+ \rangle & \langle +|- \rangle \\ \langle -|0 \rangle & \langle -|+ \rangle & \langle -|- \rangle \end{pmatrix}$$

and due that the QSM is symmetrical, the QSM elements will fulfill:

$$\langle 0|+ \rangle = \langle +|0 \rangle \wedge \langle 0|- \rangle = \langle -|0 \rangle \wedge \langle -|+ \rangle = \langle +|- \rangle .$$

The diagonal elements of the QSM: $Diag(\mathbf{Z}) = (\langle 0|0 \rangle \langle +|+ \rangle \langle -|- \rangle)$ are the quantum selfsimilarities, associated to the three DF of the set P . From there, one can obtain the usual dissimilarity and similarity indices, see for recent discussions [21,22], that is for instance:

(a) The squared Carbó similarity index:

$$\forall I, J = \{(0), (+), (-)\} : R_{IJ}^2 = \langle I|J \rangle^2 ((\langle I|I \rangle \langle J|J \rangle))^{-1} \rightarrow R_{II}^2 = 1$$

In this first case the similarity index R_{IJ}^2 corresponds to the squared cosine of the subtended angle between the involved functions. Obviously enough such an index is not invariant (see Fig. 1), if the DF underwent an origin shift. This kind of similarity index varies with respect of the considered origin.

(b) The squared distance dissimilarity index:

$$\forall I, J = \{(0), (+), (-)\} : D_{IJ}^2 = \langle |\rho_I - \rho_J|^2 \rangle = \langle I|I \rangle + \langle J|J \rangle - 2 \langle I|J \rangle \rightarrow D_{II}^2 = 0$$

Contrarily to the Carbó similarity index, the squared distance dissimilarity indices become invariant with respect origin shifts. This can be easily seen considering

that an arbitrary origin shift, performed using some function $\xi(\mathbf{r})$ will transform the original DF set into a new one like:

$$\forall I = \{(0), (+), (-)\} : \zeta_I(\mathbf{r}) = \rho_I(\mathbf{r}) - \xi(\mathbf{r}).$$

Therefore the Euclidian norms of the differences between the shifted functions and those involving the original DF set become the same:

$$\forall I, J = \{(0), (+), (-)\} : \left\langle |\zeta_I - \zeta_J|^2 \right\rangle = \left\langle |\rho_I - \rho_J|^2 \right\rangle = D_{IJ}^2.$$

Both similarity-dissimilarity indices specific properties upon origin shift constitute general well-known geometrical properties which can be associated to vector spaces. Moreover, in both kinds of indices only three non-trivial and non-redundant index values as well are relevant. This is in obvious accordance of the triangular geometrical structure provided by the three original DF's considered.

In order to specify and characterize the similarity relationships between the involved DF, there is thus needed just to know, for example, the three indices: $\left\{ D_{(0)(+)}^2; D_{(0)(-)}^2; R_{(+)(-)}^2 \right\}$.

The similarity index $R_{(+)(-)}^2$ being defined for instance, as the squared cosine of the angle subtended by the origin shifted functions:

$$\left\{ \theta_{(+)} = \rho_{(+)} - \rho_{(0)}; \theta_{(-)} = \rho_{(-)} - \rho_{(0)} \right\} \\ \rightarrow R_{(+)(-)}^2 = \langle \theta_{(+)} | \theta_{(-)} \rangle^2 \left(\langle \theta_{(+)} | \theta_{(+)} \rangle \langle \theta_{(-)} | \theta_{(-)} \rangle \right)^{-1} = \cos^2 \left(\widehat{\theta_{(+)}, \theta_{(-)}} \right).$$

However, the two squared distances can be easily computed by using the same origin shifted DF as defined in the above squared cosine, because:

$$D_{(0)(+)}^2 = \left\langle |\theta_{(+)}|^2 \right\rangle = \langle \theta_{(+)} | \theta_{(+)} \rangle \wedge D_{(0)(-)}^2 = \left\langle |\theta_{(-)}|^2 \right\rangle = \langle \theta_{(-)} | \theta_{(-)} \rangle.$$

Consequently the set of quantum similarity integrals, constructing the following matrix:

$$\left\{ \langle \theta_{(+)} | \theta_{(-)} \rangle; \langle \theta_{(+)} | \theta_{(+)} \rangle; \langle \theta_{(-)} | \theta_{(-)} \rangle \right\} \\ \rightarrow \begin{pmatrix} \langle \theta_{(+)} | \theta_{(+)} \rangle & \langle \theta_{(+)} | \theta_{(-)} \rangle \\ \langle \theta_{(+)} | \theta_{(-)} \rangle & \langle \theta_{(-)} | \theta_{(-)} \rangle \end{pmatrix} = \begin{pmatrix} \alpha_{(+)} & \beta \\ \beta & \alpha_{(-)} \end{pmatrix} = \Theta$$

becomes sufficient in order to characterize the geometrical relationships between the three DF. The quantum similarity integrals can be reordered as a symmetrical (2×2) matrix. Furthermore, the eigensystem of the matrix: Θ , can provide interesting clues about the nature of the possible attached Fukui functions.

Indeed, one can suppose the construction of a function submitted to a normalization constraint:

$$\phi = a\theta_{(+)} + b\theta_{(-)} \wedge \langle |\phi|^2 \rangle = a^2 \langle \theta_{(+)} | \theta_{(+)} \rangle + 2ab \langle \theta_{(+)} | \theta_{(-)} \rangle + b^2 \langle \theta_{(-)} | \theta_{(-)} \rangle = \lambda$$

and perform afterwards the search of an optimal coefficient pair $\{a, b\}$. This is the same as to find out the eigenvectors of the matrix Θ . Dealing with a (2×2) matrix it is sufficient to consider an orthogonal transformation, which yields at the same time the eigenvalues and the eigenvectors. The (2×2) elementary Jacobi matrix:

$$J = \begin{pmatrix} c & -s \\ s & c \end{pmatrix} \leftarrow c^2 + s^2 = 1$$

transforms Θ into a diagonal matrix:

$$\begin{aligned} J^T \Theta J &= \begin{pmatrix} c & s \\ -s & c \end{pmatrix} \begin{pmatrix} \alpha_{(+)} & \beta \\ \beta & \alpha_{(-)} \end{pmatrix} \begin{pmatrix} c & -s \\ s & c \end{pmatrix} = \begin{pmatrix} c & s \\ -s & c \end{pmatrix} \begin{pmatrix} c\alpha_{(+)} + s\beta & c\beta - s\alpha_{(+)} \\ c\beta - s\alpha_{(-)} & c\alpha_{(-)} - s\beta \end{pmatrix} \\ &= \begin{pmatrix} c^2\alpha_{(+)} + 2cs\beta - s^2\alpha_{(-)} & (c^2 - s^2)\beta - cs(\alpha_{(+)} - \alpha_{(-)}) \\ (c^2 - s^2)\beta - cs(\alpha_{(+)} - \alpha_{(-)}) & c^2\alpha_{(-)} - 2sc\beta + s^2\alpha_{(+)} \end{pmatrix} \end{aligned}$$

The resultant diagonal elements permitting to obtain the eigenvalues:

$$\begin{aligned} \lambda_1 &= c^2\alpha_{(+)} + 2cs\beta - s^2\alpha_{(-)} \wedge \lambda_2 = c^2\alpha_{(-)} - 2sc\beta + s^2\alpha_{(+)} \\ \rightarrow \lambda_1 &= \alpha_{(+)} + 2cs\beta - s^2(\alpha_{(+)} + \alpha_{(-)}) \wedge \lambda_2 = \alpha_{(-)} - 2sc\beta + s^2(\alpha_{(+)} - \alpha_{(-)}) \end{aligned}$$

and the eigenvector components are readily computed from the off-diagonal null condition:

$$\begin{aligned} (c^2 - s^2)\beta - cs(\alpha_{(+)} - \alpha_{(-)}) &= 0 \rightarrow (c^2 - s^2) = cs(\alpha_{(+)} - \alpha_{(-)}) \\ \rightarrow T = \frac{S}{C} = \frac{2cs}{c^2 - s^2} = \frac{2\beta}{\alpha_{(+)} - \alpha_{(-)}} &\rightarrow \arctan\left(\frac{2\beta}{\alpha_{(+)} - \alpha_{(-)}}\right) = 2A \end{aligned}$$

being T the tangent of twice A , the Jacobi matrix rotation angle, and calling S and C the sine and cosine of twice this angle A too. Finally, the rotation pair $\{c, s\}$ can be easily computed by the well-known general Jacobi diagonalization result, see for example [23].

The new function pair possesses a set of Minkowski pseudonorms like:

$$\langle \phi_1 \rangle = s - c \wedge \langle \phi_2 \rangle = c + s,$$

and has selfsimilarities equal to the eigenvalues of the matrix: Θ . The transformed functions define a simple isosceles right triangle with the same kind of parameters as before, but possessing elementary values which can be written in general as: $\{\lambda_1 + \lambda_2, \lambda_1 + \lambda_2, 0\}$.

7 A general case involving an indeterminate number of DF

Until now, just the three functions associated to the neutral, anion and cation have been manipulated. But this has not to be considered the unique possibility one can

design for computing the Fukui functions. Suppose an indeterminate number of DF including the neutral state and a set of anions and cations. Constructing such a set as: $p = \{\rho_I(\mathbf{r}) \mid I \in \mathbf{I}\} \wedge \#p = N$, then it can be transformed by shifting with respect any of the elements into:

$$Q_J = \{\theta_{JI} = \rho_I - \rho_J \mid I \in \mathbf{I} \wedge I \neq J\} \wedge \#Q_J = N - 1.$$

One can use a convex set of coefficients:

$$A_J = \{\alpha_{JI} \mid I \in \mathbf{I} \wedge I \neq J\} \wedge \sum_I \alpha_{JI} = 1 \wedge \forall I : \alpha_{JI} \in \mathbf{R}$$

to obtain a linear combination like:

$$\lambda_J = \sum_{I \neq J} \alpha_{JI} \theta_{JI} \rightarrow \langle \lambda_J \rangle = \sum_{I \neq J} \alpha_{JI} \langle \theta_{JI} \rangle = \sum_{I \neq J} \alpha_{JI} (v_I - v_J) = \sum_{I \neq J} \alpha_{JI} \Delta_{IJ}$$

which as in the previous case of the three functions, with the appropriate choice of the coefficients, it can be used to smoothly transform one function subset into another. Also the DF Minkowski norms values of the original set might be defined by: $\forall I : \langle \rho_I \rangle = v_I$.

Then a Fukui function can be provided by the derivatives:

$$F_{JK} = \frac{\partial \lambda_J}{\partial \alpha_{JK}} = \sum_{I \neq J} \frac{\partial \alpha_{JI}}{\partial \alpha_{JK}} \theta_{JI} = \theta_{JK} = \rho_K - \rho_J$$

Thus generating an antisymmetric matrix whose elements are the pairs of DF differences: $\mathbf{F} = \{F_{IJ} = \rho_I - \rho_J\} \rightarrow \mathbf{F}^T = -\mathbf{F}$. Therefore according to this definition there is not under the specified procedure a unique Fukui function but, as already it has been discussed in the simpler case, a set of Fukui functions, which can be ordered into an antisymmetric matrix.

7.1 The case of any DF in MO theory

The previous discussion can be applied to the particular case of a specific DF expressed in the MO theoretical framework. The subject has been addressed in a previous paper [24], but here it will be resumed in some parts and enlarged in other aspects for the sake of completeness.

Whenever a set of MO is well defined as: $M = \{|I\rangle \mid I = 1, N\}$, a set of MO DF can be immediately deduced: $P = \{\sigma_I = |I\rangle \langle I| \mid I = 1, N\}$ with Minkowski norms given by: $\forall I : \langle \sigma_I \rangle = 1$. Providing a set of MO occupation numbers: $\Omega = \{\omega_I \mid I = 1, N\} \wedge \sum_I \omega_I = v$, then it is easily constructed a DF as a linear combination: $\rho = \sum_I \omega_I \sigma_I$.

One can also write the set of equalities:

$$\forall J : \omega_J = v - \sum_{I \neq J} \omega_I$$

and it can be readily written the set of equivalent DF:

$$\forall J : {}^J \rho = v \sigma_J + \sum_{I \neq J} \omega_I (\sigma_I - \sigma_J) = \rho,$$

which defines a vector, easily expressed like:

$$|{}^S \rho\rangle = v |\sigma\rangle + \mathbf{F} |\omega\rangle \tag{5}$$

where: $|\sigma\rangle = \{\sigma_I\} \wedge |\omega\rangle = \{\omega_I\} \wedge \mathbf{F} = \{F_{IJ} = \sigma_I - \sigma_J\}$.

Taking into account that the resulting vector will be:

$$|{}^S \rho\rangle = \rho |\mathbf{1}\rangle \rightarrow \forall I : {}^S \rho_I = \rho.$$

The curious, if not interesting, conclusion is that there are N possible equivalent ways to write a given DF.

Also, one can write a derivative with respect the number of particles applied over Eq. (5):

$$\frac{\partial}{\partial v} |{}^S \rho\rangle = |\sigma\rangle + \mathbf{F} \frac{\partial}{\partial v} |\omega\rangle = \frac{\partial \rho}{\partial v} |\mathbf{1}\rangle \rightarrow \mathbf{F} \frac{\partial}{\partial v} |\omega\rangle = \left(\frac{\partial \rho}{\partial v} \right) |\mathbf{1}\rangle - |\sigma\rangle$$

and as it can also be used the following derivative:

$$\frac{\partial \rho}{\partial v} = \left\langle \sigma \left| \frac{\partial}{\partial v} \right| \omega \right\rangle$$

it can be finally obtained:

$$\mathbf{F} \frac{\partial}{\partial v} |\omega\rangle = |\mathbf{1}\rangle \left\langle \sigma \left| \frac{\partial}{\partial v} \right| \omega \right\rangle - |\sigma\rangle \rightarrow \frac{\partial}{\partial v} |\omega\rangle = -[\mathbf{F} - |\mathbf{1}\rangle \langle \sigma|]^{-1} |\sigma\rangle = -\mathbf{G}^{-1} |\sigma\rangle.$$

And the problem is how to obtain the inverse appearing in the equation above. In fact it can be written:

$$\mathbf{F} = |\sigma\rangle \langle \mathbf{1}| - |\mathbf{1}\rangle \langle \sigma|$$

then:

$$\mathbf{G} = |\sigma\rangle \langle \mathbf{1}| - 2 |\mathbf{1}\rangle \langle \sigma|$$

and maybe the inverse of such a matrix whose elements are functions is not too difficult to obtain for simple structures.

8 Conclusions

In fact, in all the previous cases all the exposed elementary properties mean that, when handling three analytically different DF, there is the possibility to transform them into two linearly independent functions, the result being no longer necessarily positive definite, but leading to the easy definition of Fukui-like functions. Similar but extended properties can be set up in arbitrarily chosen sets of DF. Finally, a curious consequence of the present mathematical manipulation can be obtained when a simple application of the origin shift technique is carried out on the MO shape basis function set, resulting in the possible construction of a collection of equivalent DF forms.

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