

Negative and infinite Fukui functions: The role of diagonal dominance in the hardness matrix

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The possible genesis of negative atom condensed Fukui functions is discussed based on hardness kernel matrix relationships. The recent hypothesis that diagonal dominance of the hardness matrix is a requirement for positive Fukui functions is proven, and general considerations also predict the possibility of regions with numerically unstable Fukui functions, including discontinuities.

KEY WORDS: electronegativity equalization method, Fukui function, hardness, conceptual DFT

1. Introduction

Fukui functions play a prominent role in the field known as conceptual Density Functional Theory (DFT). Based on the original ideas of Fukui [1,2], they are introduced as quantities that reflect the response of a molecular system towards a change in the number of electrons (N_e) of the molecular system under consideration [3]. They were introduced as a local quantity, that is, depending on r , the spatial coordinates:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N_e} \right)_V. \quad (1)$$

As is clear from equation (1), Fukui functions measure the response of the electron density at every point r , in front of a change in the number of electrons, under the constant external potential. The sites with the largest value for the Fukui functions are those with the largest response, and as such the most reactive sites within a molecule.

In chemistry, often chemical reactivity and molecular properties in general are preferably interpreted in terms of the atoms composing molecular structure. It is then logical to introduce the so-called atom condensed Fukui functions. This means that

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some way of calculating the change in the total atomic electron density of an atom α with respect to N_e is needed. Since the nuclear charge of an atom is a constant, one of the easiest ways is to use the concept of atomic charges, which introduces the following expression for atom condensed Fukui functions:

$$f_\alpha = -\left(\frac{\partial q_\alpha}{\partial N_e}\right)_V. \quad (2)$$

Yang and Mortier were the first to use such atom condensed Fukui functions, and used Mulliken charges to obtain values for the above defined atom condensed Fukui functions [4]. To mimic the actual analytical derivative, often finite difference approaches are used to calculate atom condensed Fukui functions. As in every numerical use of finite differences, many computational errors may be introduced, and when the framework of quantum chemistry is concerned many other difficulties may arise, for example, those connected with the way of considering the derivative with respect to an integer variable. Other examples can be found in the relaxation effects, and the assumption that the accuracy of the functional and basis set is equal for calculations on neutral molecules, which are often singlet states, and charged molecules, that are usually doublets.

An especially intriguing case is constituted by negative atom condensed Fukui functions. These indicate that, when an electron is added to or removed from the molecule, the electron density is reduced or respectively increased on some atoms in the molecule. This is counter intuitive, and heavily debated, as can be found in recent literature. In an interesting study Ayers et al. [5] hypothesized that negative Fukui functions may be the consequence of loss of diagonal dominance in the hardness matrix. For an N -atom molecule, the $(N \times N)$ hardness matrix holds the hardness kernels $\{\eta_{ij}\}$:

$$\mathbf{E} = \begin{bmatrix} \eta_{11} & \eta_{12} & \dots & \eta_{1N} \\ \eta_{21} & \eta_{22} & \dots & \eta_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \eta_{N1} & \eta_{N1} & \dots & \eta_{NN} \end{bmatrix}. \quad (3)$$

As has been shown using both the explicit matrix equations [6,7] and more concise algebraic equations [8], Fukui functions can be obtained from this hardness kernel matrix as

$$|\mathbf{f}\rangle = \langle \mathbf{E}^{-1} \rangle^{-1} \mathbf{E}^{-1} |\mathbf{1}\rangle \quad (4)$$

which also takes care of the normalization requirement.

The present study aims at supporting and proving the hypothesis of Ayers et al. [5] that diagonal dominance is the necessary condition for positive atom condensed Fukui functions. And, as will be shown, also indicates those areas where Fukui functions can not be obtained accurately, or may even go to infinity.

2. Results and discussion

Starting from equations (3) and (4) one can easily examine when negative or even infinite Fukui functions may be introduced. It should be noted that the same derivations can, *mutatis mutandis*, be made for the more classical EEM-based equation for the atom condensed Fukui functions [6,7]:

$$\begin{bmatrix} \eta_{11} & \eta_{12} & \dots & \eta_{1N} & 1 \\ \eta_{21} & \eta_{22} & \dots & \eta_{2N} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \eta_{N1} & \eta_{N1} & \dots & \eta_{NN} & 1 \\ 1 & 1 & \dots & 1 & 0 \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ \vdots \\ f_N \\ -\eta_{N,\text{mol}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}, \quad (5)$$

where $\eta_{N,\text{mol}}$ is the total molecular hardness for the N -atom molecule. This work will, however, be focused on the more elegant derivations, deduced using algebraic expressions, which on the other hand are also more instructive from a conceptual DFT point of view.

Suppose one constructs an N -atom molecule step by step, starting from an arbitrarily chosen single atom. This first atom obviously has a Fukui function equal to unity, and the hardness matrix is given by

$$\mathbf{E}_1 = [\eta_{11}]. \quad (6)$$

It is straightforward to work out equation (4), which will show this Fukui function unity value. When proceeding to two atoms, it is needed to consider the (2×2) hardness matrix

$$\mathbf{E}_2 = \begin{bmatrix} \eta_{11} & \eta_{12} \\ \eta_{21} & \eta_{22} \end{bmatrix}. \quad (7)$$

Central to the further derivations is the way of writing the hardness matrix, after addition of the M th atom, containing the previous \mathbf{E}_{M-1} as submatrix:

$$\mathbf{E}_M = \begin{bmatrix} \mathbf{E}_{M-1} & |\boldsymbol{\eta}_M\rangle \\ \langle \boldsymbol{\eta}_M| & \eta_{MM} \end{bmatrix}. \quad (8)$$

In this definition, $|\boldsymbol{\eta}_M\rangle$ is a column vector holding as elements all the hardness kernels η_{iM} ($i = 1, M - 1$). $\langle \boldsymbol{\eta}_M|$ is the row vector related by transposition to the previous one. η_{MM} is the hardness kernel for atom M . Since equation (4) shows that for obtaining Fukui functions one needs the inverse of the hardness matrix, one can, using the symmetrical nature of the hardness matrix, write the inverse of the partitioned hardness matrix as

$$\mathbf{E}_M^{-1} = \begin{bmatrix} \mathbf{E}_{M-1}^{[-1]} & |\mathbf{e}^{[-1]}\rangle \\ \langle \mathbf{e}^{[-1]}| & e^{[-1]} \end{bmatrix}. \quad (9)$$

Suppose the associated linear system, in order to obtain the Fukui functions of an N -atom molecule, is solved step by step, starting with a single atom. This means that, when arriving at some atom M , \mathbf{E}_{M-1}^{-1} is known. One can now consider at every stage

in the construction of the molecule how the Fukui functions will change, obtaining the inverse elements by means of the following equality:

$$\begin{bmatrix} \mathbf{E}_{M-1}^{[-1]} & |\mathbf{e}^{[-1]}\rangle \\ \langle \mathbf{e}^{[-1]}| & e^{[-1]} \end{bmatrix} \begin{bmatrix} \mathbf{E}_{M-1} & |\boldsymbol{\eta}_M\rangle \\ \langle \boldsymbol{\eta}_M| & \eta_{MM} \end{bmatrix} = \begin{bmatrix} \mathbf{I}_{M-1} & |\mathbf{0}\rangle \\ \langle \mathbf{0}| & 1 \end{bmatrix}. \quad (10)$$

In equations (9) and (10), $|\mathbf{0}\rangle$ and $\langle \mathbf{0}|$ are N -dimensional column and row zero vectors. The inverse column $|\mathbf{e}^{[-1]}\rangle$ and row $\langle \mathbf{e}^{[-1]}|$ are $(M-1)$ -dimensional vectors, related by transposition. $e^{[-1]}$ is simply a scalar. Working out equation (10) the following four equations are obtained:

$$\mathbf{E}_{M-1}^{[-1]} \mathbf{E}_{M-1} + |\mathbf{e}^{[-1]}\rangle \langle \boldsymbol{\eta}_M| = \mathbf{I}_0, \quad (11)$$

$$\mathbf{E}_{M-1}^{[-1]} |\boldsymbol{\eta}_M\rangle + \eta_{MM} |\mathbf{e}^{[-1]}\rangle = |\mathbf{0}\rangle, \quad (12)$$

$$\langle \mathbf{e}^{[-1]}| \mathbf{E}_{M-1} + e^{[-1]} \langle \boldsymbol{\eta}_M| = \langle \mathbf{0}|, \quad (13)$$

$$\langle \mathbf{e}^{[-1]}| \boldsymbol{\eta}_M\rangle + e^{[-1]} \eta_{MM} = 1. \quad (14)$$

Equation (13) is readily transformed, and introducing the new parameter

$$\alpha_M = \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle - \eta_{MM} \quad (15)$$

one finds by substitution in equation (14):

$$e^{[-1]} = -\alpha_M^{-1}. \quad (16)$$

This result, back substituted in equation (13), gives an expression for the off-diagonal submatrix $\langle \mathbf{e}^{[-1]}|$:

$$\langle \mathbf{e}^{[-1]}| = \alpha_M^{-1} \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1}. \quad (17)$$

Application of these results in equation (11) provides an expression for $\mathbf{E}_0^{[-1]}$:

$$\mathbf{E}_{M-1}^{[-1]} = \mathbf{E}_{M-1}^{-1} - \alpha_M^{-1} (\mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1}). \quad (18)$$

It is found, finally, for \mathbf{E}_M^{-1} :

$$\mathbf{E}_M^{-1} = \begin{bmatrix} \mathbf{E}_{M-1}^{-1} - \alpha_M^{-1} \mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1} & \alpha_M^{-1} \mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle \\ \alpha_M^{-1} \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1} & -\alpha_M^{-1} \end{bmatrix}. \quad (19)$$

Using the previously derived algebraic relations for the Fukui functions [7], it is immediately found:

$$|\mathbf{f}\rangle = \eta_{M,\text{mol}} \mathbf{E}_M^{-1} |\mathbf{1}\rangle, \quad (20)$$

where $\eta_{M,\text{mol}}$ is the global molecular hardness for the M -atom molecule. The Fukui functions then become:

$$|\mathbf{f}\rangle = \eta_{M,\text{mol}} \alpha_M^{-1} \begin{bmatrix} (\alpha_M \mathbf{E}_{M-1}^{-1} - \mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1}) |\mathbf{1}'\rangle + \mathbf{E}_{M-1}^{-1} |\boldsymbol{\eta}_M\rangle \\ \langle \boldsymbol{\eta}_M| \mathbf{E}_{M-1}^{-1} |\mathbf{1}'\rangle - 1 \end{bmatrix}, \quad (21)$$

where $|\mathbf{1}'\rangle$ denotes a row vector holding $(M - 1)$ elements equal to the neutral multiplicative element 1.

It is, thus, clear that the above discussion sets up a recursive formula, in order to calculate Fukui functions incrementally during the atom-by-atom construction of the molecule. It might seem superfluous to do so, since it is a lengthy procedure, and more efficient implementations have been published [7–10]. It is, however, very illustrative to consider the case of a tri-atomic molecule. In this case the following form can be obtained for the inverse, which is shown below blocked:

$$\mathbf{E}_3^{-1} = \begin{bmatrix} \left[\begin{array}{cc} \mathbf{E}_1^{-1} - \alpha_2^{-1} \mathbf{E}_1^{-1} |\eta_2\rangle \langle \eta_2| \mathbf{E}_1^{-1} & \alpha_2^{-1} \mathbf{E}_1^{-1} |\eta_2\rangle \\ \alpha_2^{-1} \langle \eta_2| \mathbf{E}_1^{-1} & -\alpha_2^{-1} \end{array} \right] & \alpha_3^{-1} \mathbf{E}_2^{-1} |\eta_3\rangle \\ -\alpha_3^{-1} \mathbf{E}_2^{-1} |\eta_3\rangle \langle \eta_3| \mathbf{E}_2^{-1} & \\ \alpha_3^{-1} \langle \eta_3| \mathbf{E}_2^{-1} & -\alpha_3^{-1} \end{bmatrix}. \quad (22)$$

Considering now the atomic softnesses, which are given by

$$|\mathbf{s}\rangle = \mathbf{E}_M^{-1} |\mathbf{1}\rangle \quad (23)$$

then a great deal about the behavior of softness and Fukui functions can be learned. Equations (19) and (22) for the specific case of a tri-atomic molecule, show that not only negative Fukui functions are possible, but even infinite ones. Ayers et al. [5] hypothesized that negative Fukui functions may arise when the diagonal dominance of the hardness matrix is lost. But from the derivations presented above, it is clear that even worse cases may be present in well defined circumstances. Considering that, in the construction of the molecule, at some step one of the values α_i is zero, that is:

$$\alpha_i = \langle \eta_i | \mathbf{E}_{i-1}^{-1} | \eta_i \rangle - \eta_{ii} = 0 \quad \longrightarrow \quad \langle \eta_i | \mathbf{E}_{i-1}^{-1} | \eta_i \rangle = \eta_{ii}. \quad (24)$$

In such case, equation (21) clearly shows that atom-condensed Fukui functions may even go to infinity when condition (24) is met. Not only at the discontinuity itself, but also near this point, Fukui functions are very unlikely to be obtained with reasonable accuracy. In those cases negative Fukui functions can easily be observed. It should be further noted that, when some α_i approaches zero, not only Fukui functions become meaningless, but also the other EEM related concepts like atomic charges, equalized electronegativity, . . . are jeopardized in the same extent, since these molecular parameters are all of them related [8].

To investigate the role of the diagonal dominance, one can consider the following. Suppose again the positive definite nature of the hardness matrix from equation (8). The determinant of such a matrix is positive, as it can be computed by means of the product of the hardness matrix eigenvalues. Moreover, one has the Schur complement [11], so that the following relationship can be written:

$$\det(\mathbf{E}_M) = \det(\mathbf{E}_{M-1}) [\eta_{MM} - \langle \eta_M | \mathbf{E}_{M-1}^{-1} | \eta_M \rangle]. \quad (25)$$

Suppose again that one is constructing the molecule step by step, and that the procedure has reached the stage that $M = 2$. Suppose also that the i th atom is used as

starting point, bounded to atom j , as this choice is completely arbitrary from the computational point of view. Then equations (25) and (15) yield the inequality

$$0 < [\eta_{jj} - \eta_{ij}^2 \eta_{ii}^{-1}] = -\alpha_2. \quad (26)$$

This result sets up the requirement that the following relationship shall be present:

$$\eta_{ij} < \sqrt{\eta_{ii} \eta_{jj}}. \quad (27)$$

This is naturally an easily checked condition for a given hardness matrix, and may reveal cases where problems with negative or discontinuous Fukui functions may be ahead. Moreover, since it is of no importance which atoms are picked as starting points up for the construction of the molecule, one should check for all combinations i and j whether (27) is fulfilled. These requirements are not yet conclusive indications of diagonal dominance, but since α_2 is negative, equation (21) shows that, in order to have a positive-definite Fukui function for the second atom, the following condition shall be met:

$$\langle \boldsymbol{\eta}_2 | \mathbf{E}_1^{-1} | \mathbf{1}' \rangle - 1 < 0. \quad (28)$$

Applying the previous inequality one can easily find the following requirements for a positive-definite Fukui function on atoms i and j :

$$\eta_{ii} > \eta_{ij} \quad \text{and} \quad \eta_{jj} > \eta_{ij}. \quad (29)$$

Another interesting possibility, completely related and coherent to the previous results, which can be also applied to show diagonal dominance, can be found in the Gershgorin circles [11]. Using the fact that one needs to have positive-definite eigenvalues then, this is the same as that the following inequalities shall be fulfilled for the row or column elements of any hardness matrix:

$$\forall i: \eta_{ii} > \sum_{j \neq i} \eta_{ij}. \quad (30)$$

Such relationships constitute the diagonal dominance statements that needed to be shown to support the hypothesis of Ayers et al. These are quite strict requirements, and may be used to assess if problems are likely to arise in a specific molecule or not. Ayers et al. [5] used matrix perturbation theory to derive so called strong diagonal dominance. To derive this result, it is assumed that there is already near diagonal dominance in the hardness matrix. Their findings for a model system also point to the importance of diagonal dominance as the present work does in a general way.

In the case of EEM environment calculated atom condensed Fukui functions, it has been found that application over hundreds of organic molecules never resulted in any negative Fukui function [7,8].

Discontinuous and negative behavior of atom condensed Fukui functions has been described in greater detail [12] by the present authors in the case of Mortier's electronegativity equalization method [13,14], as implemented and extended by Bultinck et al. [7–10] for the calculation of other conceptual DFT quantities. In Mortier's EEM,

the hardness kernels: $\forall(i \neq j) \eta_{ij}$, are, in fact, r_{ij}^{-1} , the interatomic inverse distance between atoms i and j . Contrary to the general hardness kernel matrix used throughout the present study, in Mortier's EEM, one can actively seek to find the discontinuities in a systematic way (see Bultinck et al. [12]) by varying interatomic distances. Using such a procedure, actual numeric examples of infinite Fukui functions were found, together with areas where the Fukui functions become negative. In the context of Mortier's EEM, such cases were found to occur only in situations where much distorted geometries occurred, and in this way the diagonal dominance is entirely lost. In the same study, it was also shown that equivalent conclusions could be reached on the basis of employing the Cholesky decomposition of the hardness matrix.

3. Conclusions

Using algebraic considerations, derivations are presented which show the importance of diagonal dominance in the hardness matrix. Using an atom-by-atom molecule building approach and recursive relationships for the calculation of Fukui functions, it was found that not only negative Fukui functions may arise, but even infinite values. This situation is likely to affect the values of other hardness matrix related parameters, like electronegativities and charges. The identification of such situations, where hardness kernels will produce chemically irrelevant parameter values, is fairly straightforward, involving simple hardness matrix element manipulations. Negative values for Fukui functions were found to occur mainly near discontinuities, provoked by the occurrence of the departure of diagonal dominance of hardness matrix. Such discontinuities can, in the specific case of Mortier's EEM, be related to chemically less meaningful highly distorted molecular structures.

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