

## Relation between the Fukui function and the Coulomb hole

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**Abstract.** By using a coarse-grain representation of the molecular electronic density, we demonstrate that the value of the condensed Fukui function at an atomic site is directly related to the polarization charge (Coulomb hole) induced by a test electron removed (or added) from (at) the atom. The link between the formation of an electron-hole pair and the condensed Fukui function provides insights on the possible negativity of the Fukui function which is interpreted in terms of two phenomena: overscreening and overstrengthening.

**Keywords.** Fukui function; Coulomb hole; electronegativity equalization method; chemical hardness.

### 1. Introduction

The Fukui function<sup>1,2</sup> is a reactivity index which measures the propensity of a region in a molecule to accept or donate electrons in a chemical reaction. It generalizes the concept of a frontier orbital<sup>3</sup> by including the relaxation of the orbital upon an electron transfer. More precisely, in Density Functional Theory (DFT), the Fukui function  $f(\mathbf{r})$  is the derivative of the density  $\mathbf{r}(\mathbf{r})$  relative to the total number of electrons  $N$  at constant external potential  $v_{ext}$ :<sup>1,2</sup>

$$f(\mathbf{r}) = [\partial \mathbf{r}(\mathbf{r}) / \partial N]_{v_{ext}} \quad (1)$$

The reactivity of a molecule is more easily discussed by using a discrete index, the condensed Fukui function  $f_k$ ,<sup>4</sup> which is obtained by partitioning the density of electrons between fragments:

$$f_k = [\partial N_k / \partial N]_{v_{ext}} \quad (2)$$

where  $N_k$  is the number of electrons in fragment  $k$  (most often an atom) of the molecule. In practise, the total number of electrons  $N$  is a discontinuous variable and the derivatives in (1) and (2) must be computed by using finite difference approximations<sup>2</sup> or by using a continuous model of the ground-state energy  $E(N)$  which extrapolates between integer numbers  $N$ .<sup>5,6</sup>

A large number of works have been devoted to the formulation and to practical calculations of the Fu-

kui function<sup>7–14</sup> and in particular of the corresponding condensed (atomic) reactivity index<sup>15–25</sup> for which the possible negativity of the function is debated. The interested reader may consult the following recent reviews of the enormous literature devoted to the reactivity indexes.<sup>26,27</sup>

The Fukui function is usually evaluated and interpreted from the computation of a change of the electronic density due to the removal (addition) of one electron from (to) *the whole molecule*. In the present paper, we develop a new *local* point of view by considering the removal of one electron *from an atom* in a molecule. Using this “gedanke” local ionization process, we demonstrate that the value of the condensed Fukui function of the atom is directly related to the (integrated) positive screening charge accompanying a test electron in the molecule.

In §2, the Fukui function is related to the charge induced by a hole or test electron in the framework of the electronegativity equalization method (EEM). In §3, we derive and discuss the conditions for which the condensed Fukui function might be negative and introduce two new concepts: overscreening and overstrengthening. In the last section, one briefly discusses the implications of the present results in exact DFT. Some details concerning the two-sites model used in the text are given in appendix A.

### 2. Fukui function and image charge

The relation between the Fukui function and the screening charge is derived in the framework of

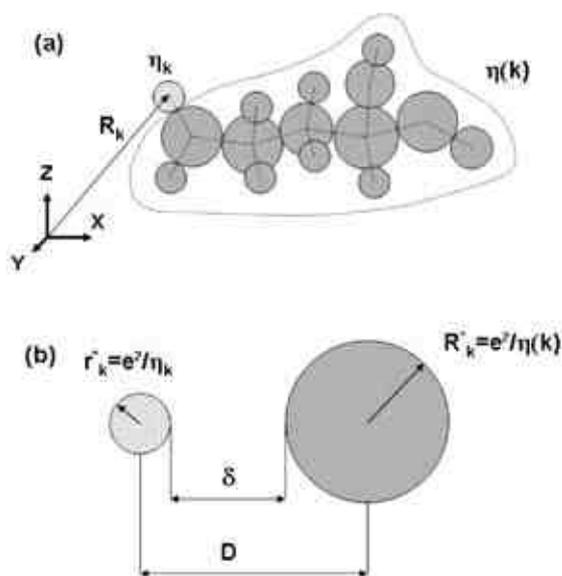
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EEM<sup>5</sup> where  $E(N)$  is a quadratic interpolation of the values of the energy at integer  $N$ . EEM uses a coarse-grain representation of the molecular electronic density in which  $\mathbf{r}(\mathbf{r})$  is represented by non-overlapping spherical atomic densities centered at the nuclei positions interacting with each other via the Coulomb interaction (Figure 1). Because the electrostatic potential outside the sphere confining the atomic density is exactly the potential which would be set up by the total charge placed at the center of the sphere, the molecular density is simply replaced in this model by a set of atomic charges  $N_k$  at the nuclei. The condensed Fukui function of the atom  $k$  is given by (2).

One notes first that the condensed Fukui index of an atom in a molecule obeys the following equation in EEM:

$$\mathbf{h} = \mathbf{h}_{k'} f_{k'} + \sum_{k'' \neq k'} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_{k''}|} f_{k''}, \quad (3)$$

where the sum is over all the  $M$  atoms of the molecule but  $k'$ .  $\mathbf{R}_{k'}$  is the position of the atom  $k'$  and  $\mathbf{h}_{k'} \equiv [\partial^2 E / \partial N_{k'}^2]_{v_{ext}}$  is its chemical hardness.<sup>5</sup>  $\mathbf{h} \equiv [\partial^2 E / \partial N^2]_{v_{ext}}$ <sup>5</sup> is the molecular hardness and  $e$  is the charge of the electron. Equation (3) is the EEM discrete form of an exact property of  $f(\mathbf{r})$ .<sup>28</sup>



**Figure 1.** (a) Coarse-grain representation of the electronic density of an arbitrary molecule divided into an atom and a fragment. (b) The corresponding two-site model (see text).

One isolates next one atom  $k \neq k'$  from the sum in (3) as follows:

$$\mathbf{h} = \sum_{k'' \neq k} h_{k'k''} f_{k''} + \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|} f_k, \quad (4)$$

where  $h_{k'k''}$  is a square hardness matrix consisting of  $(M - 1)$  rows and columns defined by  $h_{k'k''} \equiv e^2 / |\mathbf{R}_{k'} - \mathbf{R}_{k''}|$  if  $k' \neq k''$  and  $h_{k'k'} \equiv \mathbf{h}_{k'}$ . This matrix represents the hardness kernel<sup>29</sup> of a fragment build from the molecule by removing the atom  $k$  (the molecular geometry is frozen as shown in figure 1a). The formal solution of (4) is

$$\mathbf{h} \sum_{k'' \neq k} h_{k'k''}^{-1} = f_{k''} + \sum_{k'' \neq k} h_{k'k''}^{-1} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|} f_k, \quad (5)$$

in which  $k''$  is any atom of the molecule but  $k$  and  $h_{k'k''}^{-1}$  is the inverse hardness matrix of the fragment. By summing the two sides of (5) over the  $M - 1$  atoms of the fragment we obtain the following expression:

$$\frac{\mathbf{h}}{\mathbf{h}(k)} = \sum_{k'' \neq k} f_{k''} + \sum_{k'' \neq k} \sum_{k' \neq k} h_{k'k''}^{-1} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|} f_k, \quad (6)$$

in which  $\mathbf{h}(k)$  is the chemical hardness of the fragment build from the molecule by excluding the atom  $k$ .  $\mathbf{h}(k)$  is related to the inverse hardness matrix of the fragment by the following relation:<sup>2</sup>

$$\mathbf{h}(k) = 1 / \left\{ \sum_{k'' \neq k} \sum_{k' \neq k} h_{k'k''}^{-1} \right\}. \quad (7)$$

Equation (6) has a profound physical meaning. The first term in right-hand side of (6) represents the fractional electron number  $q(k)$  carried out by the fragment when the molecule is charged with one electron. By using the definition of the Fukui function (2), and its normalization condition, one finds

$$q(k) \equiv \sum_{k'' \neq k} f_{k''} = 1 - f_k. \quad (8)$$

The second term in the right-hand side of (6) is *proportional* to the electronic polarization charge  $q_g(k)$  induced on the fragment by the potential set up by a test electron placed at the position of the atom  $k$ :

$$q_g(k) \equiv - \sum_{k'' \neq k} \left[ \sum_{k' \neq k} h_{k'k''}^{-1} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|} \right]. \quad (9)$$

$q_g(k)e$  is in fact the so-called *electric image charge*,<sup>30</sup> i.e. the net charge induced on the fragment by a test electron placed at  $\mathbf{R}_k$  when the fragment is grounded. Indeed, the charge  $dq^{k''}$  induced at site  $k''$  in the fragment due to the electric potential of a test electron at  $k$  is given by the following relation in a linear response theory:<sup>31</sup>

$$dq_{k''} = \sum_{k' \neq k} c_{k''k'} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|}, \quad (10)$$

in which  $\chi_{k''k'}$  is the condensed density-density response of the fragment.  $c$  is related to the fragment hardness kernel  $h$  by the so-called Berkowitz–Parr relation<sup>29</sup> which can be written in condensed form as follows:

$$c_{k''k'} \equiv -h_{k''k'}^{-1} + f_{k'} \sum_{k'' \neq k'} h_{k''k'}^{-1}. \quad (11)$$

In (11), the second term vanishes if the chemical potential of the fragment is kept constant (grounded molecule).<sup>6</sup> Therefore for a molecule in contact with an infinite electron reservoir, the charge induced at  $k''$  within the fragment due to the electric potential of a test electron at  $k$  is according to (10) and (11)

$$dq_{k''} = - \sum_{k' \neq k} h_{k''k'}^{-1} \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|}. \quad (12)$$

The net charge induced by the test electron at  $k$  is thus given by (9), obtained by summing (12) over all the atoms of the fragment. Of course, in a linear response theory, the charge  $q_g^h(k)$  induced by a *hole* created in the electronic density of the atom is

$$q_g^h(k) = -q_g(k). \quad (13)$$

Using (6), (8) and (9), we arrive at the following simple relation:

$$\begin{aligned} \frac{h}{h(k)} &= q(k) - q_g(k) f_k, \\ &\equiv q_{\text{eff}}(k). \end{aligned} \quad (14)$$

Equation (14) means that the ratio between the chemical hardness of a molecule and the chemical hardness of any fragment of this molecule obtained by removing an atom is equal to an effective electronic charge  $q_{\text{eff}}$ . This charge is the difference between the real charge on the fragment when the molecule is charged with one electron and the polarization charge induced on the fragment by a charge equal to the

Fukui function of the atom removed from the molecule. The fact that this property holds for any  $M - 1$  fragment is due to the variational principle (3). Equation (14) may be used iteratively. For instance, the ratio between the molecular hardness and the hardness of any atom  $h_k$  is

$$\frac{h}{h_k} = \prod_{\substack{i=1 \\ i \neq k}}^M q_{\text{eff}}(k_1, k_2, \dots, k_i), \quad (15)$$

in which in obvious notations  $q_{\text{eff}}(k_1, k_2, \dots, k_n)$  represents the effective charge of the fragment build from the molecule by removing the  $n$  atoms  $k_1, k_2, \dots, k_n$ .

A key, exact, formula for the condensed Fukui function of any atom of the molecule in EEM may be now deduced from (8), (9), (13), and (14)

$$f_k = [1 - \frac{h}{h(k)}] / [1 - q_g^h(k)]. \quad (16)$$

Equation (16) shows clearly that there are *two* factors governing the value of the condensed Fukui function of an atom  $k$  in the molecule: the charge induced (image charge) on the other atoms by the removal of *one electron at site  $k$*  (denominator of (16)) and the change of the molecular hardness due to the removal of *the atom  $k$*  (numerator of (16)). Alternatively, the denominator can be interpreted in terms of the screening charge  $q_g(k)$  accompanying a test electron of the atom  $k$ .

Using (16) the so-called local condensed softness  $s_k = f_k/h^{32}$  has also a simple form

$$s_k = \frac{S - S(k)}{1 - q_g^h(k)}, \quad (17)$$

where the softnesses  $S$  and  $S(k)$  are respectively  $1/h$  and  $1/h(k)$ . *The local softness of an atom is therefore proportional to the difference between the global softnesses of the molecule and of the molecular fragment obtained by excluding the atom from the molecule.* Analogous conclusions (16) and (17) could be derived in exact density functional theory instead of the discrete EEM framework as briefly discussed below.

### 3. On the negativity of the condensed Fukui function

#### 3.1 General conditions

The present approach provides new insights in the debate on the possible negativity of the condensed

Fukui function.<sup>19–22,24</sup> We expect the positivity of  $f(\mathbf{r})$  at all points in space if  $f(\mathbf{r})$  is interpreted as a probability density to find the electron added to (or removed from) the molecule in a volume element  $d\mathbf{r}$ . This interpretation is suggested by the approximation of the Fukui function by the HOMO and LUMO frontier orbital densities. The corresponding approximate Fukui index  $f_k$  is thus interpreted as a probability. We emphasize that it should therefore not only be positive but also smaller or equal to one (for a two-site model, because of the normalization condition  $f < 0$  on one site implies  $f > 1$  on the other one). On the other hand, no conclusions on the positivity of the Fukui function can be deduced if it is interpreted as differences of probabilities like in the finite difference approximation of  $f(\mathbf{r})$ . Some numerical computations of the Fukui function show that  $f_k$  may be negative.<sup>19</sup> One should note that the definition of the condensed Fukui function is not unique and that its precise value depends on the partitioning scheme used.

In the present approach (16), one deduces two *analytical* conditions for which the condensed Fukui function might be negative:

$$q_g^h(k) > 1 \quad \text{and} \quad \mathbf{h} < \mathbf{h}(k), \quad (18)$$

$$q_g^h(k) < 1 \quad \text{and} \quad \mathbf{h} > \mathbf{h}(k). \quad (19)$$

The first condition, (18), means an *overscreening* of the hole created at site  $k$ , i.e. an image charge  $q_g^h(k)$  larger than 1 (or an image charge  $q_g(k)$  larger than  $-1$  for an electron test at  $k$ ). The second condition, (19), means an *overstrengthening* which occurs if the addition of the atom  $k$  to the fragment *increases* the molecular hardness. Between these two conditions, one has the *perfect screening* condition:

$$q_g^h(k) = 1 \quad \text{and} \quad \mathbf{h} = \mathbf{h}(k), \quad (20)$$

where the equality of the hardnesses in (20) is required to maintain a finite Fukui index at site  $k$ . In EEM, we show now explicitly that for a two-site model the conditions (18) and (19) cannot be realized for *stable* systems.

### 3.2 Application to a two-site model

The hardness  $\mathbf{h}$  of the molecule can be evaluated analytically from the hardnesses of the atom  $\mathbf{h}_k$  and of the fragment  $\mathbf{h}(k)$  in a two-site model where we

replace all the atoms of the fragment by a single effective point entity as shown in figure 1b. The properties of such a model are derived in detail in appendix A. We obtain immediately a standard formula for the molecular hardness<sup>15</sup>

$$\mathbf{h} = [\mathbf{h}_k \mathbf{h}(k) - (\frac{e^2}{D})^2] / [\mathbf{h}_k + \mathbf{h}(k) - 2 \frac{e^2}{D}], \quad (21)$$

in which  $D$  is the distance between the atom  $k$  and a site of hardness  $\mathbf{h}(k)$  representing the fragment. The physical and chemical properties of the model depend in fact of the following dimensionless parameters:

$$\mathbf{I}_k \equiv \mathbf{h}_k D / e^2, \quad (22)$$

$$\mathbf{I}(k) \equiv \mathbf{h}(k) D / e^2, \quad (23)$$

$$\mathbf{I} \equiv \mathbf{h} D / e^2. \quad (24)$$

Using (21), we derive the following relation between these quantities (A12):

$$\mathbf{I} = \mathbf{I}(k) / [1 + \{(\mathbf{I}(k) - 1)^2 / (\mathbf{I}(k) \mathbf{I}_k - 1)\}]. \quad (25)$$

As required by the variational principle of DFT, we assume that the molecule is stable relative to charge fluctuations at fixed external potential. In other words, we choose a quadratic form  $E(N)$  which is positive definite. As shown in the appendix (A5–A7), this implies the following constraints on the model parameters:

$$\mathbf{I}_k > 0, \quad (26)$$

$$\mathbf{I}(k) > 0, \quad (27)$$

$$\mathbf{I}_k \mathbf{I}(k) > 1. \quad (28)$$

One deduces from (26) and (27) that the fragment and the atom must also be stable relative to charge fluctuations when separated. In a two-site model, the hardness kernel of the fragment and its inverse are reduced to the scalars  $\mathbf{h}(k)$  and  $1/\mathbf{h}(k)$  respectively. According to (9) and (13), the image charge induced on the fragment is therefore

$$q_g^h(k) = 1/\mathbf{I}(k). \quad (29)$$

From (16), one finds that the Fukui function of the atom is given by

$$f_k = \frac{\mathbf{I}(k) - \mathbf{I}}{\mathbf{I}(k) - 1}. \quad (30)$$

Perfect screening occurs for  $\mathbf{I}(k) = 1$  for which  $\mathbf{I} = 1$  as deduced from (21): The condition (20) is thus fulfilled and it is easily shown that the site  $k$  is forbidden to any additional electron and is never depopulated when an electron is removed because

$$f_k = \lim_{\mathbf{I}(k) \rightarrow 1} \frac{\mathbf{I}(k) - \mathbf{I}}{\mathbf{I}(k) - 1} = 0. \quad (31)$$

From elementary electrostatics, one expects a perfect screening in EEM only for atoms embedded in the interior of large macromolecules as indeed observed in our recent *ab initio* calculations.<sup>33</sup> For a two-site model, a perfect screening would correspond to an atom  $k$  with no (effective) size. Indeed, we can give a geometrical interpretation of the hardnesses using Born's model.<sup>34</sup> In Born's model, we define the following effective radii:

$$r_k^* \equiv e^2/h_k, \quad (32)$$

$$R_k^* \equiv e^2/h(k), \quad (33)$$

$$R^* \equiv e^2/h, \quad (34)$$

which can be interpreted as electrostatic "compliances" or "capacitances".<sup>35,36</sup> In these notations, one has

$$\mathbf{I}_k = D/r_k^*, \quad (35)$$

$$\mathbf{I}(k) = D/R_k^*, \quad (36)$$

$$\mathbf{I} = D/R^*. \quad (37)$$

The distance between the two-sites is set by the parameter  $\mathbf{d} \equiv D - (R_k^* + r_k^*)$  (see figure 1b). For  $\mathbf{I}(k) = 1$ ,  $\mathbf{d} = -r_k^*$  and the nucleus of the atom is at the surface of the sphere of radius  $R_k^*$  representing the fragment. Such a large overlap of the spheres is not consistent with a multipole representation of the density of the electrons if the effective Born radii are interpreted as the actual sizes of the fragment and of the atom. Perfect screening is not expected unless the effective size of the atom  $r_k^*$  is vanishing which means that the atom is replaced by a point charge on site  $k$  with  $h_k = +\infty$ . For a point charge, (29) is nothing else than the classical expression of the image charge<sup>30</sup>

induced by a point charge at a distance  $\mathbf{d}$  from the surface of a metallic sphere of radius  $R_k^*$ , that is

$$q_g(k) = -\frac{1}{1 + \mathbf{d}/R_k^*},$$

and perfect screening is indeed reached when the point charge is exactly at the surface of the sphere.

Overstrengthening occurs for  $\mathbf{I}(k) < 1$ . Using the definitions of the Born radii (36) and (37), this means that the overstrengthening occurs as soon as the atom nucleus enters in the fragment sphere:  $D < R_k^*$  or in other words  $\mathbf{d} < -r_k^*$ . Again this situation is not consistent with the present multipole representation if the Born radii represent the actual sizes of the atom. We note that  $f_k$  will be negative if *in addition*  $\mathbf{I}(k) > \mathbf{I}$ , (18). As shown in the appendix, (A14), this last condition is always true for a stable system. Therefore, for a stable system for which  $E(N)$  is positive definite, the Fukui function becomes negative as soon as the overstrengthening appears, i.e. as soon as the atom nuclei enters in the density of the spherical fragment: A large overlap of the densities of the atom and of the fragment is not possible if the Born radii are interpreted strictly as the *actual* sizes of the atom and of the fragment but cannot be totally excluded as the radii are *effective*.

Overstrengthening occurs for  $\mathbf{I}(k) < \mathbf{I}$ . Using the definitions of the Born radii (36), this means that the size of the fragment is *larger* than the molecular size:  $R^* < R_k^*$  which is impossible for the geometrical interpretation of the radii represented in figure 1.  $f_k$  is negative if we have in addition  $\mathbf{I}(k) > 1$ , (19). However as shown in appendix (A15), the condition  $\mathbf{I}(k) < \mathbf{I}$  is not compatible with a stable system. The negativity of  $f_k$  in case of overstrengthening indicates that the system is unstable or in other words that  $E(N)$  is not positive definite.

Divergent hardness is another special case corresponding to  $\mathbf{I} = \pm \infty$  for which the Fukui function diverges and may be negative. Using the definitions of the Born radii (37), this occurs for a molecule with a zero effective radius. According to (21), the divergence appears when the following condition is true:

$$\mathbf{I}_k + \mathbf{I}(k) = 2, \quad (38)$$

and  $\mathbf{I}_k \mathbf{I}(k) \neq 1$ . As shown in the appendix, (A16), the Fukui function  $f_k$  is then equal to  $-\infty(+\infty)$  for  $\mathbf{I}(k) > 1(\mathbf{I}(k) < 1)$ . This very pathological case is precisely the condition of divergence of the con-

densed Fukui function of a two-site model discussed recently.<sup>24</sup>

#### 4. Summary and discussion

The Fukui function describes a response to the global transfer or removal of an electron to a molecule and is widely used to analyze the chemical reactivity. In the present work, the Fukui function is related to a local property: the screening charge induced on the rest of the molecule by the local ionization of the molecule in the framework of EEM. Alternatively, this screening charge (with the sign changed) can be viewed as the positive hole accompanying a test electron in the molecule when the molecule is connected to an infinite reservoir. This establishes therefore, although in a very simple model, a link between the local Coulomb hole and the Fukui function. Further works would be needed to clarify this relation in the framework of exact DFT. However some elements of generalization can be already derived as follows. Indeed, although the EEM model used here is mainly an electrostatic model, the conclusions are easily generalized to a coarse-grain model including non-diagonal hardness matrix elements representing non Coulomb interactions. Equation (9) can be indeed generalized as

$$q_g(k) \equiv - \sum_{k'' \neq k}^M \sum_{k' \neq k}^M h_{k''k'}^{-1} v_{k''k}, \quad (39)$$

where we define an electronic “pseudopotential” as follows:

$$v_{k'k} = \sum_{\substack{k'=1 \\ k' \neq k}}^M \left[ \frac{e^2}{|\mathbf{R}_{k'} - \mathbf{R}_k|} + h_{k'k}^T + h_{k'k}^{xc} \right], \quad (40)$$

in which  $h_{k'k}^T$  and  $h_{k'k}^{xc}$  are the *non-diagonal* kinetic and exchange-correlation hardness kernels (a discrete form of the second functional derivative of the exact kinetic and exchange-correlation functionals).<sup>6,37</sup>

In EEM, the kinetic and exchange-correlation energies are only represented by their contributions to the diagonal elements of the hardness kernel (atomic hardness  $\mathbf{h}_k$ ). As mentioned above, these diagonal elements can be formulated in terms of *effective* atomic radii  $r_k^*$ . By analogy with electrostatics (Born’s model<sup>34</sup>), these radii would represent the size of the atoms if they were metallic spheres.

Chemical reactivity concerns addition and removal of atoms or fragments. We believe therefore that it is particularly interesting that an electronic reactivity index like the Fukui function can be related to chemical hardness of a molecular fragment as demonstrated by (16). This equation shows clearly that the value of the condensed Fukui function of an atom is related to the addition/removal of the atom from the molecule and simultaneously to the addition/removal of an electron from this atom. We hope that this point of view will stimulate further works and numerical applications.

Using (16), we have shown that the condensed Fukui function  $f$  can be negative for two cases: *overscreening* and *overstrengthening*. For a simple two-site model, the negativity of the Fukui function in the case of *overstrengthening* is not compatible with a stable molecular system. Indeed, the negativity of  $f$  would violate the minimum variational principle of DFT which forces  $E(N)$  to be positive definite. On the other hand, it is the relative importance of the non-diagonal elements of the non-Coulomb hardness kernels  $h_{k'k}^T$  and  $h_{k'k}^{xc}$  compared to the self-energies (atomic hardnesses) which determine in which extent the Born radii used in §3 represent really the atom sizes and thus in which extent *overscreening* could occur in a real system. We are presently exploring the relative role of these diagonal and non-diagonal contributions of the kinetic and exchange contributions in the present new local description of the Fukui function.

#### Appendix A

In this appendix, we derive the properties of the model represented in figure 1. This two-site model has the following (2x2) hardness matrix  $h_{kk'}$

$$h = \frac{e^2}{D} \begin{pmatrix} \mathbf{I}(k) & 1 \\ 1 & \mathbf{I}_k \end{pmatrix}, \quad (A1)$$

in which we make use of the definitions of (22)–(24). The  $E(N)$  quadratic form is positive definite if all the eigenvalues of  $h$  are positive. The two eigenvalues  $\mathbf{I}_1$  and  $\mathbf{I}_2$  of  $h$  (in units of  $e^2/D$ ) are the roots of the following equation:

$$\mathbf{I}_n^2 - (\mathbf{I}(k) + \mathbf{I}_k)\mathbf{I}_n + (\mathbf{I}(k)\mathbf{I}_k - 1) = 0. \quad (A2)$$

From (A2), one deduces immediately

$$\mathbf{I}_1 \mathbf{I}_2 = \mathbf{I}(k) \mathbf{I}_k - 1, \quad (\text{A3}) \quad \text{from which we deduce}$$

$$\mathbf{I}_1 + \mathbf{I}_2 = \mathbf{I}(k) + \mathbf{I}_k. \quad (\text{A4}) \quad \mathbf{I}(k) \mathbf{I}_k > 1. \quad (\text{A14})$$

The positivity of both the eigenvalues implies therefore the following constraints

$$\mathbf{I}_k > 0, \quad (\text{A5})$$

$$\mathbf{I}(k) > 0, \quad (\text{A6})$$

$$\mathbf{I}_k \mathbf{I}(k) > 1, \quad (\text{A7})$$

which are (26)–(28) in the text.

The inverse of the hardness matrix (A1) is easily deduced

$$h^{-1} = \frac{D}{e^2} \begin{pmatrix} \frac{1}{\mathbf{I}(k) \mathbf{I}_k - 1} & \\ & \end{pmatrix} \begin{pmatrix} \mathbf{I}_k & -1 \\ -1 & \mathbf{I}(k) \end{pmatrix}, \quad (\text{A8})$$

The global softness  $S$  of the molecule is obtained from the inverse hardness kernel, (A8), by applying the following relation<sup>2</sup>

$$S = \sum_k \sum_{k'} h_{kk'}^{-1}, \quad (\text{A9})$$

which gives immediately

$$S = \frac{D}{e^2} \left( \frac{\mathbf{I}_k + \mathbf{I}(k) - 2}{\mathbf{I}(k) \mathbf{I}_k - 1} \right). \quad (\text{A10})$$

Using  $\mathbf{h} = 1/S$  and (24), one obtains

$$\mathbf{I} = \frac{\mathbf{I}(k) \mathbf{I}_k - 1}{\mathbf{I}_k + \mathbf{I}(k) - 2}. \quad (\text{A11})$$

Equation (25) in the text can be deduced by multiplying the numerator and denominator of (A11) by  $\mathbf{I}(k)/(\mathbf{I}(k) \mathbf{I}_k - 1)$ , which yields

$$\mathbf{I} = \mathbf{I}(k) / \left[ 1 + \frac{(\mathbf{I}(k) - 1)^2}{(\mathbf{I}(k) \mathbf{I}_k - 1)} \right]. \quad (\text{A12})$$

Now one demonstrates that the condition  $\mathbf{I}(k) > \mathbf{I}$  is always true if the system is stable, i.e. when the conditions (A5)–(A7) are valid. Using (A12),  $\mathbf{I}(k) > \mathbf{I}$  implies that

$$1 + \frac{(\mathbf{I}(k) - 1)^2}{(\mathbf{I}(k) \mathbf{I}_k - 1)} > 1, \quad (\text{A13})$$

Equation (A14) is always true for a stable system. In case of overstrengthening, i.e.  $\mathbf{I}(k) < \mathbf{I}$ , the  $E(N)$  form ceases to be positive definite because following the same reasoning one finds

$$\mathbf{I}(k) \mathbf{I}_k < 1. \quad (\text{A15})$$

One ends this appendix by noting that the Fukui function can be written as follows

$$f_k = \frac{\mathbf{I}(k) - 1}{\mathbf{I}_k + \mathbf{I}(k) - 2}, \quad (\text{A16})$$

which is easily deduced by applying the formula<sup>2</sup>

$$f_k = \mathbf{h} \sum_{k'} h_{kk'}^{-1}, \quad (\text{A17})$$

and by using the explicit form of  $h^{-1}$ , (A8). According to (A16), when (38) is fulfilled,  $f_k$  is thus equal to  $-\infty(+\infty)$  for  $\mathbf{I}(k) > 1$  ( $\mathbf{I}(k) < 1$ ) as announced in the text.

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