Bond Fukui indices: comparison of frozen molecular orbital and finite differences through Mulliken populations

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Abstract

Bond Fukui functions and matrices are introduced for ab initio levels of theory using a Mulliken atoms in molecules model. It is shown how these indices may be obtained from first order density matrix derivatives without need for going to second order density matrices as in a previous work. The importance of taking into account the non-orthogonality of the basis in ab initio calculations is shown, contrasting the present results with previous work based on Hückel theory. It is shown how the extension of Fukui functions to Fukui matrices allows getting more insight into the nature of bond Fukui functions. All presently introduced indices respect the necessary normalization conditions and include the classical single atom condensed Fukui functions.

Keywords: Electronic-structure,reactivity,density functional theory,Fukui function   ∎

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$$A \neq B \rightarrow F_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} \left(\frac{\partial P_{\mu\nu}}{\partial N} \right)_{v(\mathbf{r})} S_{\nu\mu}$$

Chemical reactions are usually accompanied with a reorganization of the chemical bonds in the molecule. Here, Fukui functions are introduced to describe changes in chemical bonding under removal or addition of an electron using only first order density matrices and yielding atom condensed Fukui functions by straightforward integration.

INTRODUCTION

One of the main ambitions in chemistry is not only to be able to synthesize virtually any molecule and to be able to test its performance for some purpose, e.g. as a cure for a disease, but also to be able to predict the properties of a molecule prior to its synthesis. One of the most important properties of a molecule relates to its reactivity. Although many different categories of reactivity may be defined, depending on what property governs it, a particularly interesting approach to examining reactivity relies on studying the energy change of a molecule as a function of two main variables in Density Functional Theory (DFT): the number of electrons in a molecule and the external potential. This approach towards chemical reactivity lies at the basis of what has become known as conceptual or chemical Density Functional Theory (cDFT)[1,2]. Chemical reactions can be seen as processes where for each reaction partner both of these entities undergo changes through e.g., the approach of the other reactant leading to a change in external potential and charge transfer[3]. The energy of a molecule can be expressed as follows,

$$
\begin{aligned}
E\left[v, N\right] = E\left[v^0, N^0\right] & \\
+ \left(\frac{\partial E\left[v, N\right]}{\partial N}\right)_{\substack{v=v^0 \\ N=N^0}} \left(N - N^0\right) &+ \frac{1}{2}\left(\frac{\partial^2 E\left[v, N\right]}{\partial N^2}\right)_{\substack{v=v^0 \\ N=N^0}} \left(N - N^0\right)^2 + \cdots \\
+ \int \left(\frac{\delta E\left[v, N\right]}{\delta v\left(\mathbf{r}\right)}\right)_{\substack{v=v^0 \\ N=N^0}} \delta v\left(\mathbf{r}\right) d\mathbf{r} + \cdots & \\
+ \int \left(\frac{\partial \delta E\left[v, N\right]}{\partial N \delta v\left(\mathbf{r}\right)}\right)_{\substack{v=v^0 \\ N=N^0}} \left(N - N^0\right) \delta v\left(\mathbf{r}\right) d\mathbf{r} + \cdots &,
\end{aligned}
\tag{1}
$$

When modeling the reactivity of a molecule, this Taylor series is usually carried out no further than to second order. All derivatives in equation (1) have been examined in detail[1,2] and are known respectively as the chemical potential, hardness, electron density and the Fukui function for all terms shown explicitly. Note that in what follows, it is always assumed that no degenerate states exist for any of the charged states considered in the calculation of these quantities as otherwise, degenerate state perturbation theory has to be used[4].

The Fukui index[5–7] is one of the foremost used reactivity indices in cDFT[1,2]. It quantifies the response of the electron density to a change in the number of electrons in a molecule

through

$$f\left(\mathbf{r}\right) = \left(\frac{\partial\left(\frac{\delta E}{\delta v(\mathbf{r})}\right)_N}{\partial N}\right)_{v(\mathbf{r})}. \tag{2}$$

Its power lies in the fact that one can assess regioselectivity of a reaction without need for modeling the chemical reaction itself. That is, places in the molecule that have a large value for the Fukui function are more likely to undergo a reaction involving a change in the number of electrons. In the perturbative perspective on chemical reactivity within cDFT[3], it is the first $\mathbf{r}$ dependent term in the Taylor expansion (1) in terms of changes in the number of electrons and the external potential. Equation (2) clearly shows that it is a second order derivative and the first $\mathbf{r}$ dependent term beyond the electron density (assuming that the first order derivative of the energy versus the external potential is the electron density, i.e. a non-degenerate state[4]). The Fukui index has been used on numerous occasions and its properties have been scrutinized in detail. Several authors suggested different approaches towards their calculation beyond finite differences[8,9]. In finite differences, the Fukui function is computed using the electron density of a molecule with N electrons and that with $N \pm \delta$ electrons and the difference divided by δ is considered to be the Fukui function. Most often δ is simply taken to be one for computational convenience. This is usually approximate, although in an exact theory it is exact[10,11] and so we continue to use finite differences also in the present work (note: in Hartree-Fock and DFT theories, the theoretically expected and correct piecewise linear relation between energy and number of electrons is violated[12,13]). Several other approximations are also used to obtain different quality approximations to Fukui functions, including a frontier molecular orbital (FMO) approximation. This lies at the very heart of why this function was called the Fukui function by Parr and co-workers; it is the DFT extension of the FMO theory. There is no guarantee, however, that the FMO approximation is sufficiently good, and indeed, orbital relaxation may play an influential role in the Fukui function[14–17]. Moreover, even when the FMO plays the decisive role, the other orbitals play a key role in explaining why there is nothing unnatural about a region in space where the Fukui function is negative[14,15].

The Fukui function is clearly an $\mathbf{r}$ dependent function and as a consequence, every point in space has a specific value $f\left(\mathbf{r}\right)$. Most often, however, a coarse grained representation of

the Fukui function is used, in the sense that atom condensed values are reported[18]. This requires some model for the atom in the molecule (AIM) as one integrates over the domain of a single atom. Such atom condensed Fukui functions were originally introduced by Yang and Mortier[18] using the Mulliken population analysis method[19]. Besides the advantage of the easy implementation and computational efficiency of the Mulliken scheme, an important further advantage is that the differentiation of the electron density and the condensation to the AIM commute[18]. This alleviates the problem of having to choose between two possible schemes to compute atom condensed Fukui functions, known as the Fragment of Molecular Response and Response of Molecular Fragment approaches[20].

The purpose of the present paper is to examine whether and how a separate Fukui function condensed to both atoms and chemical bonds (or, more generally, sets of two atoms) can be obtained, such that the often used single atom condensed Fukui functions can be obtained from these two-atom Fukui functions. Furthermore, we require that the condensed Fukui functions always satisfy the normalization constraints. Moreover, it should be possible to extend the Fukui functions to Fukui matrices[14,15] such that atom and bond condensed Fukui functions are the traces of the corresponding matrices. In the first section, a theoretical development of the ideas is presented, including how the presently introduced bond Fukui functions fit into derivatives of the first order density matrix as opposed to earlier works[21–23] based on exchange-correlation densities and how it respects the required normalization conditions as opposed to the approach by Contreras and co-workers[24–26] when applied to calculations using overlapping basis functions. We also show how the newly introduced bond Fukui functions are closely related to the first order density matrix whereas other attempts[21,22], in fact, require the second order density matrix which is not always readily within reach. In the next section, results are presented for a set of ethylene derivatives used previously[25] and the newly introduced indices are compared to those obtained in other works. Finally, the new information contained in our indices is highlighted.

METHODOLOGY

Theoretical derivation

Let us consider a molecule with a non-degenerate ground state for the neutral system. From first order perturbation theory, the non-degenerate ground state allows us to write equation (2) in the form[2]

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} . \tag{3}$$

The Fukui function was recently extended to a matrix by Bultinck et al.[14,15] to give

$$f(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial \rho(\mathbf{r}, \mathbf{r}')}{\partial N}\right)_{v(\mathbf{r})} , \tag{4}$$

where $\rho(\mathbf{r}, \mathbf{r}')$ is the first order density matrix. Note that due to the discontinuity in the E versus N relationship, one needs to distinguish two Fukui functions, namely a limit to the left and to the right[2]. For the theoretical development, in order not to overload notation, we will not indicate this difference. We further assume real functions only as an extension to complex functions is simple, yet also overloads notation. When due, which side limit has been used for the Fukui function will be indicated by a superscript $+$ (adding an electron, producing a negative ion) or $-$ (removing an electron, producing a positive ion). Likewise, when considering spin separated Fukui functions, an α or β superscript will be added.

Following Gonzalez-Suarez et al.[25], we use a Mulliken type approach[19,27,28] for distinguishing the atom in the molecule. Introducing the density matrix $\mathbf{P}$ expressed in terms of the basis functions and using $\mathbf{S}$ to denote the overlap matrix over these same functions and

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\mu\nu} P_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}') , \tag{5}$$

$$N = \int_{\mathbf{r}=\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} = \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = Tr(\mathbf{PS}) , \tag{6}$$

where N denotes the total number of electrons in the molecule. We can divide the density matrix in position space in biatomic parts by restricting the summations in the following

way,

$$\rho\left(\mathbf{r}, \mathbf{r}'\right) = \sum_{AB} \sum_{\substack{\mu \in A \\ \nu \in B}} P_{\mu\nu} \phi_\mu\left(\mathbf{r}\right) \phi_\nu\left(\mathbf{r}'\right) \tag{7}$$

$$= \sum_{AB} \rho_{AB}\left(\mathbf{r}, \mathbf{r}'\right) .$$

The quantities

$$D_{AB} = \int_{\mathbf{r}=\mathbf{r}'} \rho_{AB}\left(\mathbf{r}, \mathbf{r}'\right) d\mathbf{r} , \tag{8}$$

are known as bond indices in the McWeeny-Mulliken sense [29,30].

One can define a bond index based Fukui matrix and function as

$$f_{AB}\left(\mathbf{r}, \mathbf{r}'\right) = \left(\frac{\partial \rho_{AB}(\mathbf{r}, \mathbf{r}')}{\partial N}\right)_{v(\mathbf{r})} . \tag{9}$$

Note that this means an arbitrary choice was made to first perform the condensation of the density matrix in basis function space to atoms in molecules, followed by integration. As shown by several authors [20,31,32], this is not automatically the same as when first considering the derivative for the entire molecule and then condensing it by application of weight functions. The effects of this difference, which were already hinted at by Yang and Mortier [18], were studied in detail by Bultinck et al. [20] where it was also pointed out that for Mulliken based quantities there is no difference between both approaches.

Combining equations (7) and (9), the Fukui matrix for a combination AB of atoms can be expressed as

$$f_{AB}\left(\mathbf{r}, \mathbf{r}'\right) = \left(\frac{\partial \sum_{\substack{\mu \in A \\ \nu \in B}} P_{\mu\nu} \phi_\mu\left(\mathbf{r}\right) \phi_\nu\left(\mathbf{r}'\right)}{\partial N}\right)_{v(\mathbf{r})} , \tag{10}$$

or in condensed form,

$$F_{AB} = \left(\frac{\partial \sum_{\substack{\mu \in A \\ \nu \in B}} P_{\mu\nu} S_{\nu\mu}}{\partial N}\right)_{v(\mathbf{r})} . \tag{11}$$

The overlap matrix $\mathbf{S}$ is independent on the number of electrons, however $\mathbf{P}$ is. Elementary calculus gives

$$F_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} \left(\frac{\partial P_{\mu\nu}}{\partial N}\right)_{v(\mathbf{r})} S_{\nu\mu} . \tag{12}$$

This is the point where the main difference occurs with the works of the Contreras group.[24–26] Their approach, originally developed at the Hückel level of theory[26], does not consider the effect of the overlap matrix, including when the basis set has a very clear non unit overlap matrix. This is due to the fact that, in their work, classical Coulson-Longuet-Higgings response function theory based on Hückel molecular orbital theory is directly merged with cDFT. As a consequence, they suggest as bond Fukui function $F_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} \left(\frac{\partial P_{\mu\nu}}{\partial N} \right)_{v(\mathbf{r})}$. This obviously results in problems with normalization.

The use of a finite difference scheme for the derivative with respect to N,

$$f^\pm \left(\mathbf{r}, \mathbf{r}' \right) = \pm \left(\rho_{N\pm 1} \left(\mathbf{r}, \mathbf{r}' \right) - \rho_N \left(\mathbf{r}, \mathbf{r}' \right) \right) , \tag{13}$$

leads to a simple expression for the derivative of matrix P,

$$\left(\frac{\partial P_{\mu\nu}}{\partial N} \right)_{v(\mathbf{r})}^\pm = \pm \left[\sum_i n_i^{N\pm 1} C_{\mu i}^{N\pm 1} C_{\nu i}^{N\pm 1} - \sum_i n_i^N C_{\mu i}^N C_{\nu i}^N \right] = \pm \left[P_{\mu\nu}^{N\pm 1} - P_{\mu\nu}^N \right] . \tag{14}$$

Here n_i^N and $C_{\mu i}^N$ are the natural occupation numbers and natural orbital expansion coefficients of the species with N electrons. Also it is assumed that the basis set is the same for both species. Substitution in equation (12) leads to

$$F_{AB}^\pm = \pm \sum_{\substack{\mu \in A \\ \nu \in B}} \left[P_{\mu\nu}^{N\pm 1} - P_{\mu\nu}^N \right] S_{\nu\mu} . \tag{15}$$

The set of F_{AB} gives rise to both diagonal and off-diagonal terms, i.e.,

$$A = B \rightarrow F_{AA} = \sum_{\substack{\mu \in A \\ \nu \in A}} \left(\frac{\partial P_{\mu\nu}}{\partial N} \right)_{v(\mathbf{r})} S_{\nu\mu} , \tag{16}$$

$$A \neq B \rightarrow F_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} \left(\frac{\partial P_{\mu\nu}}{\partial N} \right)_{v(\mathbf{r})} S_{\nu\mu} . \tag{17}$$

A single atom Fukui function may be obtained through summation,

$$F_A = \sum_B F_{AB} . \tag{18}$$

When reporting data in tabular form in the results and discussion, we will rather use as generic expression

$$F'_{AB} = (2 - \delta_{AB}) F_{AB} , \tag{19}$$

such that instead of F_{AB} and F_{BA} separately, only one value F'_{AB} is reported. The same applies to other quantities if an $'$ is added.

Simple algebraic manipulations reveal immediately that these single atom F_A are exactly the atom condensed Fukui functions originally introduced by Yang and Mortier[18]. A simple recovering of single atom condensed Fukui functions is possible from the bond Fukui functions of Contreras and co-workers although they will not equal the atom condensed Fukui functions of Yang and Mortier[18] (see below).

Obviously, other definitions for the atom in the molecule may be used, although for several of these methods significant issues appear related to the order in which operations have to be carried out[20]. Given these extra issues, an in-depth discussion of bond Fukui functions using 3D space based methods will be reported elsewhere.

Returning to the Fukui matrix for AB in equation (4), one can just, as for density matrices, express it in terms of Fukui orbitals $\Phi_a(\mathbf{r})$ and Fukui eigenvalues η_a[14,15],

$$f\left(\mathbf{r}, \mathbf{r}'\right) = \sum_a \eta_a \Phi_a(\mathbf{r}) \Phi_a(\mathbf{r}') \ . \tag{20}$$

The $\Phi_a(\mathbf{r})$ form an orthonormal set that can be again expressed in terms of basis functions, allowing again a Mulliken decomposition[27,28]. So, besides a total AB condensed Fukui function, it is possible to make one AB condensed Fukui function per (molecular) Fukui orbital. This gives rise to the values $_a\Phi'^{-;\alpha}_{AB}$ and analogs, where $_a\Phi'^{-;\alpha}_{AB}$ denotes the AB condensed Fukui function obtained from Fukui orbital a for removal of an electron and considering only the change in the α density matrix. For example:

$$_a\Phi'^{-;\sigma}_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} \left(\eta_a^{-;\sigma} d_{\mu a}^{-;\sigma} d_{\nu a}^{-;\sigma} \right) S_{\nu\mu} \ , \ (\sigma = \alpha, \beta) \ . \tag{21}$$

with $d_{\nu a}^{-;\sigma}$ the expansion coefficient of basis function ν in Fukui orbital a based on the α or β density matrix for removal of an electron. The Fukui orbital in itself is due to the diagonalization of a linear combination of natural orbitals of the neutral molecule and the charged species, if following Bultinck et al.[14], which therefore allows for trivial expression in terms of the basis functions.

Gonzalez-Suarez et al.[25] next introduce as an extra approximation a Frontier Molecular Orbital (FMO) approximation. This does exclude the possibility of regions with negative

Fukui functions, a necessity at single determinant level of theory as shown by one of the present authors[14,15] and confirmed by Alcoba et al.[33,34]. If, however, one considers only the relevant molecular orbital for the process (addition or removal of an electron), one obtains

$$\Theta_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} C^*_{\nu,FMO} S_{\nu\mu} C_{\mu,FMO} \ , \tag{22}$$

where $C_{\mu,FMO}$ is the coefficient of the basis function μ in the FMO. Note that at the single determinant level of theory, given that $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1}$, one also trivially finds that

$$\sum_{AB} \Theta_{AB} = 1 \ . \tag{23}$$

This is again not the case in the work by Contreras and co-workers at the DFT level of theory[24,25], due to the non-appearance of the overlap matrix $\mathbf{S}$. As we will show below, it is more informative to use as a single orbital the dominant Fukui orbital (the Fukui orbital with the highest eigenvalue) rather than the frontier molecular orbital of the neutral molecule. The reason is that, although in most cases this dominant Fukui orbital is nearly purely the frontier molecular orbital, one can capture easily also (part of) the relaxation effects[14,15].

As mentioned earlier, other groups also introduced indices that relate more or less to what could be considered bond Fukui function alike. Fradera and Sola[21] called them second order Fukui functions which were later used again by Matito et al.[23]. Both studies relate second order Fukui functions to changes in bond orders upon ionization of a molecule. In 2012, Otero et al.[22] introduced chemical reactivity quantities in the framework of pair densities. Essentially, all three papers rely on exchange-correlation density matrices and the derivation[35] of shared electron distribution indices[36] (variably also described as bond indices, delocalization indices and bond orders). The essential difference is here that, whereas in our approach the Fukui function always relates to the first order density matrix, these second order or pair based bond Fukui indices rely on the second order density matrix. So the second order Fukui function for two atoms $A \neq B$ measures the change in the shared-electron distribution index between A and B upon addition or removal of an electron. On the other hand, the one atom condensed Fukui function, F^A can be extracted from their second order Fukui functions through summation over all atoms B by virtue of the orthonormality of the natural orbitals. Note that both Fradera and Sola[21] and Otero and Mandado[22] base their

derivations on $\mathbf{r}$ space based AIM methods although they can easily be rederived using a Mulliken method, affording for a single Slater determinant theory:

$$\Omega_{AB}^{\pm} = \pm(2 - \delta_{AB}) \sum_{\sigma=\alpha,\beta} \sum_{\substack{\mu \in A \\ \nu \in B}} \left[\left(P^{N\pm1,\sigma}S\right)_{\mu\nu} \left(P^{N\pm1,\sigma}S\right)_{\nu\mu} - \left(P^{N,\sigma}S\right)_{\mu\nu} \left(P^{N,\sigma}S\right)_{\nu\mu} \right] . \quad (24)$$

Note in the last equation, $P^{N\pm1,\sigma}$ is the σ spin density matrix, as for bond indices involving open shell systems, one needs to consider separately the exchange interaction of α and β electrons[37]. In other words, the second order Fukui function as in the above is the change in the Wiberg-Giambiagi-Mayer[38–40] bond order separated in the two spin parts. The essential difference between our method derived above and theirs is thus that we rely solely on the first order density matrix at any level of theory, whereas they invoke the second order density matrix. Alternatively, our approach is similar to the one by Contreras and co-workers, although that is derived differently and does not take into account overlap between basis functions when due and thus does not satisfy normalization conditions for the Fukui function. Below the different approaches will be compared and differences pointed out.

Computational methods

In order to test the above formulae, calculations have been performed, using Gaussian03[41], at the B3LYP[42–44] DFT level of theory with the Cartesian 6-31G(d)[45] basis set . Based on the data contained in the formatted checkpoint files, we computed the Fukui matrices (9) for the set of ethylene derivatives studied by Gonzalez-Suarez et al.[25]. All molecular geometries were optimized at the same level of theory starting from the geometries supplied by the authors. Diagonalization of the Hessian confirmed all structures to correspond to minima. In some cases the default initial guess for the DFT calculations did not result in the lowest energy singlet state. In that case, starting from a new guess, geometry optimization was performed followed by a renewed evaluation of the stability. For the molecular anions and cations the geometry of the neutral molecule was used. The stability of the resulting solution of the Kohn-Sham equations was checked and if necessary the lower solution sought within doublet spin. We used DFT density matrices based on the Kohn-Sham orbitals, despite the fact that the wave function does not have the same theoretical meaning as in e.g., Hartree-

Fock theory. Nevertheless, we opted for a level of theory also used by Gonzalez-Suarez et al.[25] to maintain maximal comparability with their data. We did not opt for Hartree-Fock calculations at the same level as those used by the authors as often the wave function was unstable and for e.g. nitroethene the Hartree-Fock level provides a particularly poor description of the electronic structure[46]. The bond Fukui functions were computed using a finite difference approach using both the entire density matrix according to equation (15) and for a FMO approximation as in equation (22). Fukui matrices were obtained as described earlier[14], expressing the density matrices for both the neutral and charged molecule in terms of the orthonormal set of molecular orbitals obtained from the neutral state calculation. This allows for an alternative way of computing bond Fukui functions, with the added advantage that one can establish in which Fukui orbital each bond AB has the biggest contribution. Using a Mulliken reformulation of the second order Fukui function[21–23] (see equation (24)), we also computed these values for comparison. Note that because of the integer discontinuity in the energy versus the number of electrons, one needs to considered two Fukui functions depending on whether it reflects an increase in the number of electrons or a decrease. When considering Fukui matrices, a further split is made between an α and β part.

RESULTS AND DISCUSSION

Bond Fukui functions

Using the data set of Gonzalez-Suarez et al.[25], albeit using the set of ethylene derivatives only, the bond Fukui functions were computed according to the different approaches presented above.

The set of molecules is shown in figure 1 and the computed data are shown in tables 1 and 2. F'_{AB} is the AB condensed Fukui function between atoms A and B as defined by in equation (19). F_A is the single atom condensed Fukui function as originally introduced by Yang and Mortier[18] and obtained here through equation (18). Θ'_{AB} and Θ_A are the FMO versions of the previous, i.e. those obtained through equation (22) and its analog for a single atom FMO condensed Fukui function. Θ'^G_{AB} and Θ^G_A are the values computed with the

formulae taken from[25], which are their counterparts for Θ'_{AB} and Θ_A as they are limited to FMO. The last column reports values for the second order Fukui function Ω_{AB}, defined as in equation (24). Tables 1 and 2 give respectively the data for removal of an electron and addition of an electron. Although all values for all A or AB are computed in one single run, we limit reporting the data to only those values reported in reference[25] as the focus lies on the study of the added information provided using the newly introduced indices.

The first set of data corresponds to equation (19), including all orbitals, so not just the frontier molecular orbitals. The need to include the latter is a consequence of the fact that, as shown previously by Bultinck et al., some more subtle aspects of reactivity are not well taken into account if restricting oneself to only the frontier molecular orbitals[14,15]. One of these aspects is, e.g., the possibility of regions in space with negative values for the Fukui function, and thus possibly negative values of bond Fukui functions. Tables 1 and 2 show that there is indeed a significant difference between the values F'_{AB} and Θ'_{AB}. The correlation coefficient R^2 is 0.895 which is not too bad but the remaining 10% may hold a lot of more subtle information such as the presence of the often debated negative values. Moreover, the other orbitals will prove to be important contributors for bond Fukui functions as will be discussed in detail below. Concerning the values F'_{AB}, in general the larger absolute values correspond those systems that have a more localized π system.

Clearly, the precise form of Fukui function for bonds has a prominent effect on the computed values. Our atom condensed Fukui functions, as defined in equation (18), coincide with the data reported in Gonzalez-Suarez et al.[25]. The reason is that these values are computed according to their equation (1)[25], which we expect to be based on a Mulliken model and to include the overlap terms in clear contradiction to the rest of their work where overlap is not considered. The problem with neglecting the overlap terms is easily demonstrated using ethene as an example. Based on symmetry, it is expected that $\Theta'^G_{1-1} = \Theta'^G_{2-2}$. For the calculation of both values, only the HOMO is needed. The non-zero coefficients for the HOMO atom C1 are $0.40144\phi_{p_x} + 0.28453\phi_{p'_x} - 0.01611\phi_{d_{xz}}$ and on atom C2: $0.40144\phi_{p_x} + 0.28453\phi_{p'_x} + 0.01611\phi_{d_{xz}}$. Given that the orbital is normalized and taking into account the overlap matrix, one immediately gets $\Theta'_{1-1} = \Theta'_{2-2} = 0.373$; but using their formulae (3) or (4) for a diagonal term (which ignores overlap) gives values of $\Theta'^G_{1-1} = (0.40144 + 0.28453 -$

$0.01611)^2 = 0.449$ and $\Theta'^G_{2-2} = (0.40144 + 0.28453 + 0.01611)^2 = 0.493$ for atoms 1 and 2 respectively, even breaking the symmetry. This is a consequence of not considering the overlap terms in their expressions, despite using a level of theory that takes into account the overlap matrix. It is therefore not allowed to simply transfer the Hückel level of theory formulae to a (post-)Hartree-Fock or DFT level of theory for the diagonal terms. The $\Theta^G_{1-2} = \Theta^G_{2-1}$ symmetry is respected, but other symmetries in the non-diagonal terms are also violated. For instance, their Θ'^G bond Fukui functions in molecule 8 between each of the two cyanide carbon atoms and the adjacent ethylene carbon atom differ. This is not the case for the Θ' values. Their bond Fukui functions do sometimes agree with the values obtained by us if we took the same level of theory and geometries (Hartree-Fock based, note that we chose DFT in order to reduce problems with non minimum SCF solutions and, in some cases, probably took different electronic states of the desired multiplicity if the default initial guess did not give a stable solution; see computational details), likely because by coincidence we sometimes took the same bond among symmetry equivalent ones or because there is only one bond of the type reported. A factor two difference is noticed because in reporting the data in tables 1 and 2 we made the sum $\Theta_{AB} + \Theta_{BA}$ and similar for other quantities when $A \neq B$ whereas Gonzalez-Suarez et al.[25] consider AB separately from BA. Note that, again in line with the reported on not considering the overlap, the sum over all bond Fukui functions Θ^G_{AB} differs from $\sum_{AB} \Theta_{AB} = 1$. It should be mentioned that we obtained the values in tables 1 and 2 as Θ^G_A as $\sum_B \Theta^G_{AB}$ to get a coherent picture on including or not the overlap. This is admittedly different from Gonzalez-Suarez et al.[25], where the formulae imply that for (non-diagonal) bond Fukui functions, one needs to use a Hückel type expression and a Mulliken type expression, as in equation (18), for atom condensed Fukui functions; for diagonal bond Fukui functions no equation is given. We stress that in our approach, the atom condensed and bond condensed Fukui functions follow the same philosophy with respect to overlap and, therefore, respect normalization. On the other hand, for e.g., ethene $\sum_{AB} \Theta^G_{AB} = 1.88$. For molecule 12 we find $\sum_{AB} \Theta^G_{AB} = 0.008$ and for molecule 3 $\sum_{AB} \Theta^G_{AB} = 3.391$. This behavior makes comparisons between molecules very problematic.

The second order Fukui functions exhibit the largely expected trends. The nature of the test set is such that in the majority of cases, the HOMO and LUMO correspond to π or

π^* orbitals. This entails that the cationic species have, compared to the neutral molecule, one electron less in a bonded orbital and that in the anionic species an electron ended up in the antibonding orbital. As second order Fukui functions are based on bond indices, which in turn are close to classical bond orders, one expects a positive value for the second order Fukui function for electron removal and a negative one for addition of an electron. This is indeed what is found in tables 1 and 2. In this sense, the second order Fukui function clearly performs as expected, although we stress again that it is not a Fukui function in the sense of being associated with the derivative of an electron density. It may well serve a purpose, however. From our point of view, only the bond Fukui functions defined here by us according to equation (11) can be considered truly in the spirit of equation (2), if an ab initio level of theory is considered in which non-orthonormal basis sets are used for which every basis function is located on only one single centre (one can obviously also work with an orthonormalized basis but, in the realm of atom centered Gaussian basis sets as used here, any orthonormalization procedure destroys the one-to-one attachment of every basis function to a single atom). Other methods may well (seem to) fulfill a purpose of e.g., explaining reactivity, but regression analysis or a possible explanation without thorough theoretical background and vast statistical evidence may render such reactivity analyses and predictions problematic. From a more fundamental point of view, the presently introduced bond Fukui functions can be considered to lie somewhat closer to DFT, as the other methods rely on pair densities or fail in other respects although admittedly, in the derivation of bond Fukui functions the Kohn-Sham density matrix is used whose significance is also still subject to discussion.

The comparison between the bond indices computed with equation (22) and those from González-Suárez et al. formula[25] shows a roughly linear trend for the bonds analyzed here. This behavior can be rationalized in a simple way. If one assumes that the overlap integrals depend exclusively on the distance among their respective centers, $S_{\mu\nu} = s_{AB}$ ($\mu \in A$, $\nu \in B$), then $\Theta_{AB} = s_{AB} \sum_{\substack{\mu \in A \\ \nu \in B}} C^{N*}_{\nu,FMO} C^N_{\mu,FMO} = s_{AB} \Theta^G_{AB}$. That is, for the same type of bond, if the bond distance shows small variations, both approaches must be roughly proportional. The linear fitting of the Fukui bond indices computed with both approaches for the C-C bond between atoms 1 and 2 shows similar slopes for both donor and acceptor Fukui indices, 3.47

and 3.25 respectively, with R^2 correlation coefficients 0.839 and 0.940. Similar results are obtained for the Fukui indices for the C-C bond between atoms 2 and 3. However, the slopes significantly increase for the bond index between atoms 1 and 3, 23.41 and 15.93, since the overlap integrals become smaller as a consequence of the longer distance among these atoms. When the bond lengths have a strong variation within a molecule, the overlap integrals are also affected and the Θ_{AB}^G bond indices will not be comparable along the molecule. A similar problem arises when diffuse basis functions are used, overlap integrals involving this type of functions significantly differ from the others and the proportionality is broken. In general, the bond Fukui indices from equation (15) should be preferred since relaxation effects are included.

Bond Fukui matrices

Despite that DFT does itself not attach meaning to density matrices based in a Kohn-Sham sense on orbitals from an (exact) single Slater determinant for a system of non-interacting electrons, we report for the first time atom and bond Fukui matrices as the same reasoning can be applied to other ab initio levels of theory, including those where the wave function does carry a deeper meaning. As described previously[14,15], one can introduce a Fukui matrix as the derivative of the first order density matrix. Expressing this in terms of an orthonormal basis, the resulting matrix can be diagonalized and eigenvectors and eigenvalues examined. As described previously[14,15] and independently confirmed later by Alcoba et al.[33,34,47], the spectrum of this matrix at the single determinant level of theory has only one eigenvalue exactly equal to 1 and any other eigenvector with a different eigenvalue must be accompanied by another with exactly the opposite eigenvalue, except if the eigenvalue is exactly zero. The Fukui orbitals (eigenvectors of the Fukui matrix) may be expressed in basis function space and the Mulliken operator applied for each Fukui orbital separately. Applied to the eigenvector with unity eigenvalue (the so-called dominant Fukui orbital), this mostly gives results quite close to those based on a FMO view, except that the dominant Fukui orbital is not exactly the same as the FMO due to the orbital relaxation. Moreover, although at the molecular level, the pairing of eigenvalues $\pm x$ is manifest, this is no longer the case at

the atom and bond level. Table 3 shows results for $_a\Phi'^{-;\alpha}_{1-2}$ and $_a\Phi'^{-;\beta}_{1-2}$ for all Fukui orbitals, Φ_a, of ethene alongside the Fukui eigenvalues $\eta_a^{-;\alpha}$ and $\eta_a^{-;\beta}$, for removal of an electron (see equation (20) and following). We limit the discussion to only one small molecule as the Fukui matrices for such a small molecule have a number of eigenvalues equal to the dimension of the basis set (38 here) and all eigenvalues are important in the discussion below. The table clearly shows that:

- In agreement with previous results[14,15], the non-zero Fukui eigenvalues η_a come in pairs $\pm x$ with the exception of one unity β eigenvalue(in the ions we assume that there is one α electron more than the β electrons).

- As the electron removed has β spin, the sum of $\eta_a^{-;\alpha}$ equals zero whereas the set $\eta_a^{-;\beta}$ sums to 1 exactly.

- The values $_a\Phi'^{-;\alpha}_{1-2}$ are not zero and do not show any special structure, as opposed to the Fukui eigenvalues. Moreover, the sum $\sum_a {}_a\Phi'^{-;\alpha}_{1-2}$ does not equal zero either. This means that the α block contributes significantly. In the present molecule, it contributes roughly one third of the total, which is certainly significant.

- The signs of $_a\Phi'^{-;\alpha}_{1-2}$ and $_a\Phi'^{-;\beta}_{1-2}$ show no structure.

- Due to the multiplication with the eigenvalues $\eta_a^{-;\sigma}$ with $\sigma = \{\alpha, \beta\}$, there is a tendency that $_a\Phi'^{-;\sigma}_{AB}$ is bigger for Fukui orbitals with higher $\eta_a^{-;\sigma}$, however it cannot be claimed in general that the highest $_a\Phi'^{-;\sigma}_{AB}$ always occur for a pair AB in the dominant Fukui orbital. This may be somewhat counterintuitive but is simply the nature of the underlying algebra. As an example, the most positive values in the set of data occur for the dominant Fukui orbital (the orbital with unity eigenvalue) and for the fifth most negative α Fukui orbital.

- All traces are respected and $\sum_{\sigma=\alpha,\beta} \sum_a {}_a\Phi'^{-;\sigma}_{1-2} = F'^{-}_{1-2}$. The α contribution is not negligible.

- The value $_d\Phi'^{-;\beta}_{1-2}$ where d is the dominant Fukui orbital in the set of β Fukui orbitals is approximately equal to Θ_{1-2}. This is expected because, in this molecule, the dominant

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Fukui orbital comes mainly from the HOMO of the neutral species. However, this is not universally the case and it will be evident when there is a strong orbital relaxation. This case will automatically be clear from inspection of the eigenvectors of the Fukui matrix.

All this shows a lot of extra structure and signals that sometimes care must be taken in assuming certain, albeit intuitive, properties of Fukui functions. Table 3 also shows that using a frontier molecular orbital approximation for bond Fukui functions is still more cumbersome than for the molecular Fukui function. Whereas all Fukui orbitals except for the dominant Fukui orbital have usually small eigenvalues that moreover sum to zero, for an individual bond Fukui function, no such zero sum is obtained making the frontier molecular orbital approximation for bond Fukui functions disregard a bigger part of the net effect of the existence of Fukui orbitals beyond the dominant one. Given the simplicity of the algebra involved in generating Fukui matrices and from there descending to Fukui orbitals, bond and atom Fukui functions, we advocate to always use this path to obtain Fukui functions, especially since it is universally applicable and gives much additional insight and at the same time respects the required normalizations. Future work will be devoted to extending the present derivations to other methods for atoms in molecules, with the associated caveats, and testing it in practice.

CONCLUSIONS

We have shown that a bond Fukui function may be introduced starting from the first order density matrix without neglect of basis function overlap and allowing for the usual atom condensed Fukui functions to be retrieved through simple summation from the bond Fukui functions. A simple set of algebraic manipulations suffices to obtain all these quantities and it is suggested to always follow this path. Instead of using a frontier molecular orbital approximation, it is suggested that, if it is desired to base the reasoning on a single orbital, to base all reasoning on an analysis of the dominant Fukui orbital.

Contrary to earlier works, the presently introduced bond and atom condensed Fukui functions respect all normalization conditions. Moreover, atom and bond Fukui matrices

can be obtained and their analysis provides more insight into the nature of Fukui functions.

Although all derivations have been performed using a Mulliken setup for the atom in the molecule, the entire procedure can also be performed using other AIM methods, provided judicious choices of the order of different mathematical operations. Such derivations will be reported elsewhere.

We stress that although other Fukui function like quantities may, at first glance or even beyond, serve to explain some observed reactivity, the presently introduced indices stay closest to the original perturbative approach to explain chemical reactivity based on a Taylor expansion of the energy, using as little as the number of electrons and external potentials as variables, and optionally using a Kohn-Sham density matrix when not working in a wave function based theory.

ACKNOWLEDGMENTS

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Figure 1: Ethylene derivatives considered in the present work with explicit indication of atoms 1 and 2. Atom 3 corresponds to the atom shown in boldface.
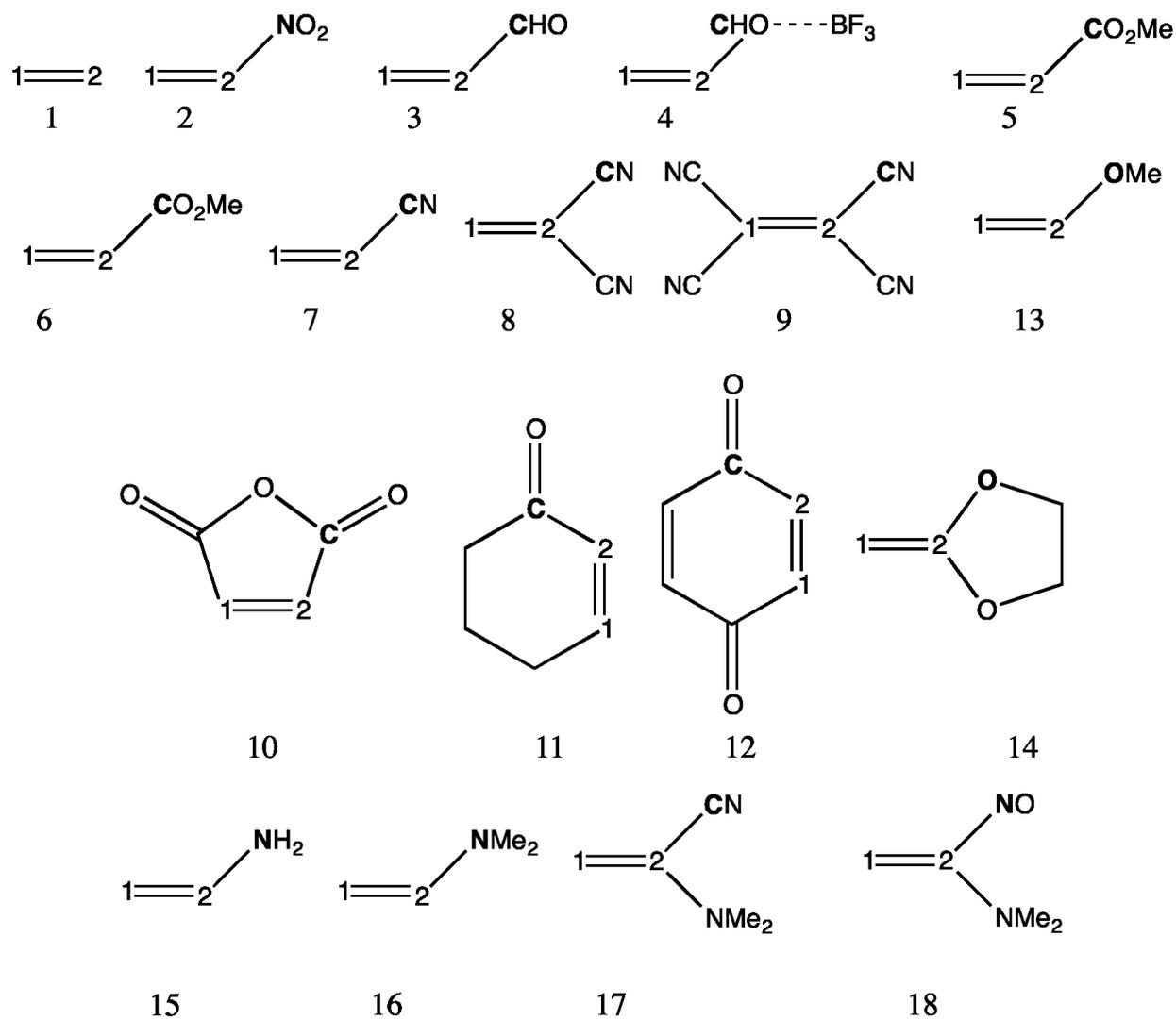
Figure 1
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	F'^-_{1-2}	F'^-_{2-3}	F^-_1	Θ'^-_{1-2}	Θ'^-_{2-3}	Θ^-_1	$\Theta'^{G,-}_{1-2}$	$\Theta'^{G,-}_{2-3}$	$\Theta^{G,-}_1$	Ω^-_{1-2}	Ω^-_{2-3}
1	0.517	0.022	0.170	0.255	0.000	0.500	0.941	0.000	0.919	0.590	0.058
2	0.038	0.022	0.072	-0.008	-0.003	0.006	0.030	0.002	-0.120	0.229	-0.010
3	0.055	-0.127	0.071	-0.061	-0.028	0.011	-0.048	-0.018	-0.287	0.182	-0.079
4	0.270	0.039	0.104	0.192	0.002	0.366	0.725	0.019	0.513	0.384	0.009
5	0.052	-0.115	0.057	-0.053	-0.033	0.010	-0.246	-0.148	-0.397	0.151	-0.041
6	0.197	0.004	0.079	-0.019	0.016	0.005	0.025	-0.003	0.006	0.319	-0.006
7	0.313	-0.084	0.135	0.172	-0.066	0.366	0.649	-0.295	0.172	0.436	-0.169
8	0.257	-0.076	0.133	0.149	-0.046	0.336	0.569	-0.242	-0.166	0.356	-0.105
9	0.143	-0.074	0.085	0.114	-0.037	0.177	0.439	-0.189	-0.607	0.228	-0.084
10	-0.211	-0.009	0.044	-0.146	0.024	0.040	-0.491	0.022	0.543	-0.014	0.027
11	-0.075	-0.025	0.056	-0.085	0.020	0.011	-0.076	0.032	0.205	0.109	-0.027
12	-0.237	0.038	0.034	-0.152	0.036	0.054	-0.008	0.033	-0.004	-0.043	0.048
13	0.319	-0.188	0.133	0.176	-0.115	0.466	0.830	-0.615	0.633	0.399	-0.532
14	0.351	-0.066	0.187	0.185	-0.066	0.555	0.796	-0.402	0.447	0.471	-0.192
15	0.338	-0.054	0.156	0.169	-0.115	0.472	0.682	-0.584	0.243	0.420	-0.294
16	0.229	0.013	0.136	0.119	-0.089	0.410	0.341	-0.279	0.317	0.298	-0.159
17	0.174	-0.004	0.139	0.094	0.000	0.370	0.217	-0.039	-0.099	0.238	-0.012
18	0.156	0.107	0.132	0.052	0.017	0.307	0.148	-0.108	0.132	0.204	0.032

Table 1: B3LYP 6-31G* Bond Fukui Functions between the indicated atoms and the atom condensed Fukui Function on atom 1 for removal of an electron for each molecule.

	F'^{+}_{1-2}	F'^{+}_{2-3}	F^{+}_{1}	Θ'^{+}_{1-2}	Θ'^{+}_{2-3}	Θ^{+}_{1}	$\Theta'^{G,+}_{1-2}$	$\Theta'^{G,+}_{2-3}$	$\Theta^{G,+}_{1}$	Ω^{+}_{1-2}	Ω^{+}_{2-3}
1	-0.607	-0.056	0.140	-0.755	0.000	0.500	-2.208	0.000	0.054	-0.508	-0.003
2	-0.228	0.212	0.111	-0.167	0.124	0.278	-0.575	0.551	0.591	-0.273	0.215
3	-0.192	0.265	0.127	-0.240	0.170	0.373	-0.706	0.592	0.302	-0.302	0.267
4	-0.115	0.249	0.126	-0.160	0.142	0.371	-0.465	0.446	0.338	-0.233	0.237
5	-0.204	0.249	0.122	-0.270	0.176	0.372	-0.894	0.724	0.244	-0.314	0.263
6	-0.271	0.260	0.123	-0.352	0.179	0.415	-1.119	0.651	0.568	-0.252	0.117
7	-0.386	0.167	0.132	-0.447	0.147	0.469	-1.348	0.532	0.451	-0.437	0.224
8	-0.341	0.076	0.138	-0.382	0.077	0.499	-1.203	0.234	0.743	-0.411	0.103
9	-0.277	0.019	0.118	-0.259	0.040	0.257	-0.939	0.114	0.003	-0.293	0.051
10	-0.242	0.175	0.084	-0.256	0.131	0.237	-0.864	0.505	-0.010	-0.337	0.203
11	-0.231	0.244	0.097	-0.245	0.160	0.352	-0.990	0.802	0.285	-0.304	0.258
12	-0.138	0.086	0.040	-0.084	0.072	0.097	-0.279	0.301	0.002	-0.170	0.112
13	-0.585	-0.168	0.194	-0.718	-0.192	0.444	-2.877	-0.958	0.368	-0.186	-0.014
14	-0.446	-0.146	0.108	-0.697	-0.186	0.392	-2.352	-0.907	0.492	-0.363	-0.087
15	-0.408	0.021	0.096	-0.715	-0.177	0.408	-2.243	-0.480	0.661	-0.389	-0.050
16	-0.462	-0.147	0.096	-0.677	-0.225	0.400	-2.171	-0.417	0.316	-0.388	-0.108
17	-0.315	0.176	0.111	-0.355	0.174	0.365	-0.701	0.289	0.608	-0.301	0.216
18	-0.076	0.205	0.098	-0.062	0.079	0.184	-0.037	0.056	0.129	-0.042	0.172

Table 2: B3LYP 6-31G* Bond Fukui Functions between the indicated atoms and the atom condensed Fukui Function on atom 1 for addition of an electron for each molecule.

Orbital	$\eta_a^{-,\alpha}$	$\eta_a^{-,\beta}$	$_a\Phi'^{-,\alpha}_{1-2}$	$_a\Phi'^{-,\beta}_{1-2}$
1	-0.0766	-0.0660	0.104	0.087
2	-0.0754	-0.0628	-0.034	-0.027
3	-0.0623	-0.0537	-0.020	-0.020
4	-0.0607	-0.0382	-0.006	0.140
5	-0.0586	-0.0209	0.225	-0.001
6	-0.0189	-0.0006	0.002	0.002
7	-0.0007	-0.0004	0.000	0.000
8	-0.0004	0.0000	0.000	0.000
9	0.0000	0.0000	0.000	0.000
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
30	0.0000	0.0000	0.000	0.000
31	0.0004	0.0004	0.000	0.000
32	0.0007	0.0006	0.000	-0.002
33	0.0189	0.0209	0.005	0.005
34	0.0586	0.0382	-0.127	-0.081
35	0.0607	0.0537	0.021	0.031
36	0.0623	0.0628	0.025	0.003
37	0.0754	0.0660	0.004	-0.034
38	0.0766	1.0000	-0.041	0.255
	$\sum \eta_a^{-,\alpha} = 0.0000$	$\sum_a \eta_a^{-,\beta} = 1.0000$	$\sum_a {}_a\Phi'^{-,\alpha}_{1-2} = 0.159$	$\sum_a {}_a\Phi'^{-,\beta}_{1-2} = 0.358$

Table 3: B3LYP 6-31G* Fukui matrix eigenvalues, $\eta_a^{-,\alpha}$ and $\eta_a^{-,\beta}$, and bond contributions, $_a\Phi'^{-,\alpha}_{1-2}$ and $_a\Phi'^{-,\beta}_{1-2}$, along with relevant traces for electron removal of molecule 1. $\cdots$ denotes orbitals with only zero contributions. Note that $\sum_{\sigma=\alpha,\beta} \sum_a {}_a\Phi'^{-,\sigma}_{1-2} = 0.517 = F'^{-}_{1-2}$.