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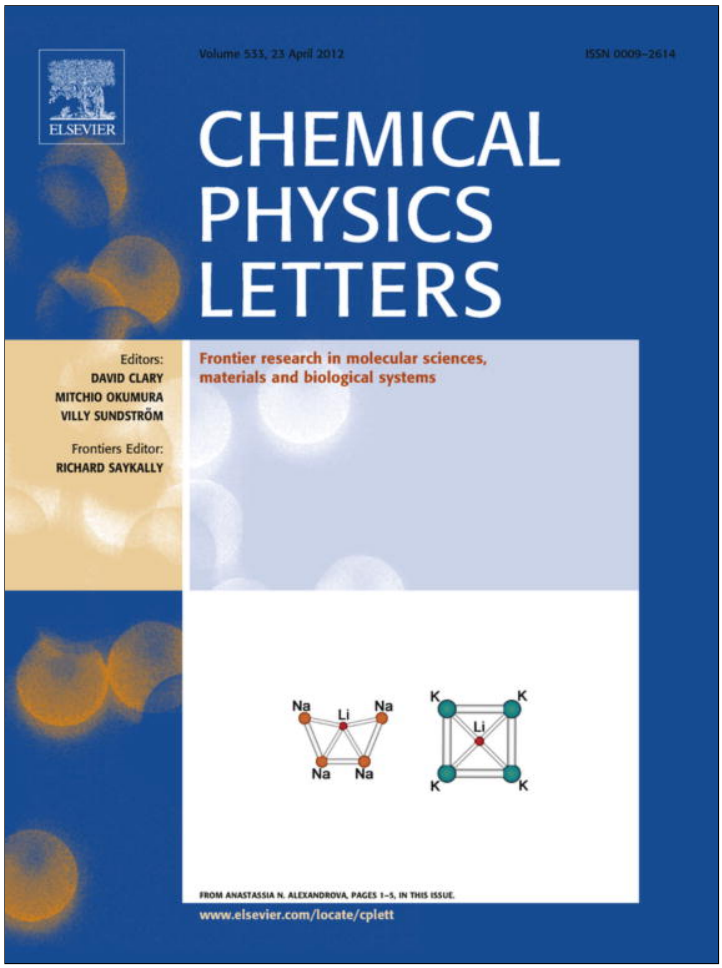


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# Fukui and dual-descriptor matrices in the basis-set representation: A spin-free approach

Diego R. Alcoba [a,*], William Tiznado [b,*], Ofelia B. Oña [c], Alicia Torre [d], Luis Lain [d]

[a] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina
[b] Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Av. República 275, Santiago de Chile, Chile
[c] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Diag. 113 y 64 (S/N), Sucursal 4, CC 16, 1900 La Plata, Argentina
[d] Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

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ABSTRACT

This Letter deals with matrix extensions of the Fukui and dual-descriptor functions which are represented in a basis set by means of a spin-free treatment. A study of the eigenvalues of these matrices and of the values of the coefficients which express their eigenvectors provides important information concerning molecular reactivity. Numerical determinations performed in selected closed- and open-shell systems at Hartree–Fock and configuration interaction levels of theory show the usefulness of this procedure. A comparison between these results and those arising from other approaches is analyzed in detail.

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## 1. Introduction

In conceptual density-functional theory [1,2], the chemical reactivity is quantified by means of changes in the energy and in the electron density corresponding to a canonical ensemble in response to an approaching reagent. Among the changes in the electron density, the Fukui functions [3–5] have proven to be powerful devices to describe the molecular reactivity and consequently they have become one of the most popular descriptors of the nucleophilic/electrophilic character of the regions within a determined $N$-electron system. As is well known, the Fukui functions are formulated as the derivative of the electron density with respect to a change in the number of electrons under constant external potential. Because the electron density is discontinuous versus the number of electrons one must distinguish between the right and left limits, giving rise to two different Fukui functions related with the electrophilic and nucleophilic molecular reactivity [3,6–9]. Likewise, the second derivative of the electron density function with respect to a change in the number of electrons, denominated dual descriptor [9–15], has also constituted another important indicator of the molecular reactivity. The dual descriptor has been proposed as a suitable tool to describe reagents that can act like electrophiles or nucleophiles depending on their reaction partners [16] as well as to describe reagents which simultaneously accept and donate electrons like in pericycle reactions [17].

Recently, in Ref. [18], matrix generalizations of the Fukui functions have been introduced in the representation of the spin–orbitals of a given basis set. The diagonalization of these matrices has enabled to perform a study of their mathematical features which provides a useful information. The required task is to carry out a simple analysis of the magnitude and sign of their eigenvalues as well as to study the dominant coefficient of the eigenvector corresponding to the highest eigenvalue in a suitable basis set. The main aim of this Letter is to extend this kind of studies to a spin-free treatment for the Fukui matrices describing the features arising from this approach. Apart from the advantage that represents the use of the spin-free formulation within a computational point of view, another purpose of this Letter is to apply this procedure to the dual-descriptor function which, to our knowledge, has not yet been generalized to the matrix form neither in the spin–orbital representation nor in the spin-free one.

This Letter has been organized as follows. The second section describes the derivation of formulas which allow one to relate the Fukui matrices in the spin–orbital representation with those arising from the spin-free one as well as to define the dual-descriptor matrix within this technique. The third section reports the computational details and the results found for some selected closed- and open-shell systems described at the Hartree–Fock and correlated levels of theory. The discussion corresponding to these results and the comparison with those obtained from other

* Corresponding authors. Fax: +54 11 45763357 (D.R. Alcoba), +56 26618269 (W. Tiznado).
*E-mail addresses:* qfxaldad@lg.ehu.es (D.R. Alcoba), wtiznado@unab.cl (W. Tiznado).

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approaches is also reported in this section. Finally, in the last section we summarize the concluding remarks.

## 2. The spin-free Fukui and dual-descriptor matrices

The first-order reduced density matrix corresponding to an $N$-electron system $\rho(\mathbf{r},\sigma;\mathbf{r}',\sigma)$ will be expressed by means of its matrix elements $d_{ij}(\sigma)$

$$\rho(\mathbf{r},\sigma;\mathbf{r}',\sigma)=\sum_{i,j} d_{ij}(\sigma)\phi_i^*(\mathbf{r},\sigma)\phi_j(\mathbf{r}',\sigma) \tag{1}$$

In this notation $\phi_i,\phi_j,\ldots$ stand for the orbitals of an orthonormal basis set, $\mathbf{r}$ and $\mathbf{r}'$ are the spatial coordinates and $\sigma$ is the spin coordinate ($\sigma=\alpha,\beta$).

The Fukui matrix elements projected in this spin–orbital basis set are defined as [18]

$$f_{ij}(\sigma)=\left[\frac{\partial d_{ij}(\sigma)}{\partial N}\right]_v \tag{2}$$

where $v$ is the external potential that will be kept constant; it means that the molecular geometry and atom types are fixed for all the chemical species involved in this formulation. The derivative represented in Eq. (2) can be calculated making use of the finite difference approximation so that two Fukui matrices are obtained

$$f_{ij}^{+}(\sigma)=d_{ij}^{(N_\alpha+1,N_\beta)}(\sigma)-d_{ij}^{(N_\alpha,N_\beta)}(\sigma) \tag{3}$$

and

$$f_{ij}^{-}(\sigma)=d_{ij}^{(N_\alpha,N_\beta)}(\sigma)-d_{ij}^{(N_\alpha,N_\beta-1)}(\sigma) \tag{4}$$

where the superscripts $N_\alpha$ and $N_\beta$ are the number of electrons of type $\alpha$ and $\beta$ of the states of the chemical species that describe the corresponding first-order reduced matrices. According to Eq. (3) the traces of the matrices $f_{ij}^{+}(\alpha)$ and $f_{ij}^{+}(\beta)$ are 1 and 0, respectively and consequently the relevant information will be contained in the spin block $f_{ij}^{+}(\alpha)$. In the same way according to Eq. (4) the value of the traces of matrices $f_{ij}^{-}(\alpha)$ and $f_{ij}^{-}(\beta)$ is 0 and 1, respectively and the matrix $f_{ij}^{-}(\beta)$ will contain the relevant information. In this formulation, we have added an $\alpha$-electron and removed an $\beta$-electron so that the convention $N_\alpha\geqslant N_\beta$ is always kept, although other alternatives which fulfill that convention are also possible, e.g. removing an $\alpha$-electron in systems of high-spin doublet symmetry.

The Fukui matrices $f_{ij}^{+}(\sigma)$ and $f_{ij}^{-}(\sigma)$ defined in Eqs. (3) and (4), which have already been reported in Ref. [18], are expressed in terms of spin–orbitals. However, a spin-free version of these matrices can be directly obtained summing over the spin coordinates

$$f_{ij}^{+}=\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha+1,N_\beta)}(\sigma)-\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha,N_\beta)}(\sigma) \tag{5}$$

$$f_{ij}^{-}=\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha,N_\beta)}(\sigma)-\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha,N_\beta-1)}(\sigma) \tag{6}$$

The summations $\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha+1,N_\beta)}(\sigma)$, $\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha,N_\beta)}(\sigma)$ and $\sum_{\sigma=\alpha}^{\beta} d_{ij}^{(N_\alpha,N_\beta-1)}(\sigma)$ are the spin-free first-order reduced matrix elements $d_{ij}^{N+1}$, $d_{ij}^{N}$ and $d_{ij}^{N-1}$, respectively, which are independent of the number of $N_\alpha$ and $N_\beta$ electrons [19]. They only depend on the total number of electrons $(N_\alpha+1+N_\beta)$, $(N_\alpha+N_\beta)$ and $(N_\alpha+N_\beta-1)$, respectively; Eqs. (5) and (6) can be expressed as

$$f_{ij}^{+}=d_{ij}^{N+1}-d_{ij}^{N} \tag{7}$$

$$f_{ij}^{-}=d_{ij}^{N}-d_{ij}^{N-1} \tag{8}$$

In these equations we have kept the superscripts $N+1$, $N$ and $N-1$ to point out the number of electrons of the systems which are described by the matrix elements $d_{ij}$. Accordingly, the spin-free Fukui matrices described in Eqs. (7) and (8) turn out to be independent of the procedure followed in the addition and removal of electrons in Eqs. (3) and (4). As has been mentioned in the Section 1 one of the purposes of this Letter is to study the behavior of the spin-free Fukui matrices described in Eqs. (7) and (8) versus those described in Eqs. (3) and (4) which contain spin coordinates. This aspect will be developed in the next section.

On the other hand, the second derivative of the first-order reduced density matrix elements, at constant external potential, projected in a spin–orbital basis set is

$$f_{ij}^{2}(\sigma)=\left[\frac{\partial^2 d_{ij}(\sigma)}{\partial N^2}\right]_v \tag{9}$$

that hereafter will be denominated as dual-descriptor matrix.

The calculation of this derivative applying again the finite difference approximation leads to

$$f_{ij}^{2}(\sigma)=f_{ij}^{+}(\sigma)-f_{ij}^{-}(\sigma) \tag{10}$$

or, alternatively

$$f_{ij}^{2}(\sigma)=d_{ij}^{(N_\alpha+1,N_\beta)}(\sigma)-2d_{ij}^{(N_\alpha,N_\beta)}(\sigma)+d_{ij}^{(N_\alpha,N_\beta-1)}(\sigma) \tag{11}$$

that allows one to formulate the elements of the dual-descriptor matrix by means of those of the first-order reduced density matrix; the chemical species with $N=N_\alpha+N_\beta$ is used as reference system. This formulation is in agreement with that of the spatial representation of the dual-descriptor function where $f^2(\mathbf{r})=f^{+}(\mathbf{r})-f^{-}(\mathbf{r})$ [12].

The summation of the matrices $f^2(\alpha)$ plus $f^2(\beta)$ provides to formulate the spin-free dual-descriptor matrix elements as

$$f_{ij}^{2}=\sum_{\sigma=\alpha}^{\beta} f_{ij}^{2}(\sigma)=f_{ij}^{+}-f_{ij}^{-}=d_{ij}^{N+1}-2d_{ij}^{N}+d_{ij}^{N-1} \tag{12}$$

In the next section we show the information that is possible to draw out from the dual-descriptor matrices, which is another purpose of this Letter.

## 3. Computational details, results and discussion

The spin-free first-order reduced density matrix elements $d_{ij}^{N+1}$, $d_{ij}^{N}$ and $d_{ij}^{N-1}$, which enable us to calculate the matrix elements of the spin-free Fukui and spin-free dual-descriptor matrices according to Eqs. (7), (8) and (12), respectively, have been obtained from a modified version of the GAMESS package [20]. The counterpart matrix elements in the spin–orbital representation of these matrices have also been calculated with that code. In order to test this methodology we have chosen the simple neutral singlet systems $C_2H_4$, $CH_2O$ and NOF as well as the doublet allyl radical $C_3H_5$, all of them in their ground states, at the equilibrium geometries of the systems with $N$ electrons (neutral species) [21,22]. These geometries have also been kept for the corresponding systems possessing $N+1$ and $N-1$ electrons (ionic species). The calculations have been performed, using the basis sets 6-31G, at the levels restricted Hartree–Fock (HF) and configuration interaction with single and double excitations (CISD), which allows us to study the correlation effects. The matrix elements of the ionic species $d_{ij}^{N+1}$ and $d_{ij}^{N-1}$ corresponding to each one of these neutral systems have been transformed to the basis of the natural orbitals of the neutral species, that is, the eigenvectors of the matrices $d_{ij}^{N}$. This is a necessary requirement to be able to construct the Fukui and dual-descriptor matrices, which have been implemented through the well-known matrix algebra.

In Table 1 we have gathered the numerical results performed at HF level arising from the diagonalization of the Fukui matrices $f^{+}(\alpha)$, $f^{+}$(spin-free), $f^{-}(\beta)$ and $f^{-}$ (spin-free) for the above-mentioned species. Hereafter, the results refer to eigenvectors with eigenvalues above $10^{-4}$ or below $-10^{-4}$. In the case of the systems $C_2H_4$, $CH_2O$ and NOF, which are in singlet states, and their counterpart ionic

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**Table 1**
Number of positive (Pos) and negative (Neg) eigenvalues of the Fukui matrices and highest (High) and lowest (Low) eigenvalues found using 6-31G basis sets at the HF level. CF-H means the dominant coefficient in the eigenvectors of Fukui matrices with eigenvalue close to 1.

| | | $C_2H_4$ | $CH_2O$ | NOF | $C_3H_5$ |
|---|---|---|---|---|---|
| $f^+(\alpha)$ | Pos | 9 | 8 | 12 | 13 |
| | Neg | 8 | 7 | 11 | 12 |
| | High | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| | Low | −0.0671 | −0.1001 | −0.1200 | −0.0645 |
| | CF-H | 0.9985 | 0.9981 | 0.9982 | 0.9994 |
| $f^+$(spin-free) | Pos | 9 | 8 | 12 | 13 |
| | Neg | 8 | 7 | 11 | 12 |
| | High | 1.0000 | 1.0002 | 1.0068 | 1.0040 |
| | Low | −0.1341 | −0.2002 | −0.2400 | −0.1291 |
| | CF-H | 0.9985 | 0.9981 | 0.9964 | 0.9984 |
| $f^-(\beta)$ | Pos | 8 | 7 | 11 | 12[a] |
| | Neg | 7 | 6 | 10 | 11[a] |
| | High | 1.0000 | 1.0000 | 1.0000 | 1.0000[a] |
| | Low | −0.0696 | −0.1716 | −0.1666 | −0.0586[a] |
| | CF-H | 1.0000 | 0.9563 | 0.8055 | 1.0000[a] |
| $f^-$(spin-free) | Pos | 8 | 7 | 12 | 12 |
| | Neg | 8 | 7 | 12 | 11 |
| | High | 1.0050 | 1.0268 | 1.1060 | 1.0000 |
| | Low | −0.1392 | −0.3432 | −0.3720 | −0.1172 |
| | CF-H | 0.9988 | 0.9560 | 0.8391 | 1.0000 |

[a] Values obtained from the $f^-(\alpha)$ matrix with trace 1.

species of $(N+1)$ and $(N-1)$ electrons, which are in doublet states, we have used the matrices $f^+(\alpha)$ and $f^-(\beta)$ possessing trace 1. This means that we have constructed these matrices adding an $\alpha$-electron and removing an $\beta$-electron and consequently these are the matrices containing the relevant information instead of the matrices $f^+(\beta)$ and $f^-(\alpha)$. However, in the allyl radical we have used the matrix $f^-(\alpha)$ with trace 1 (removing an $\alpha$-electron) to compute the sequence doublet/singlet states for the species with $N$ and $(N-1)$ electrons. The matrices $f^+(\alpha)$ and $f^-(\beta)$ (that $f^-(\alpha)$ for the allyl radical) present an eigenvector with eigenvalue 1 and the others with much smaller eigenvalues which come in pairs with values of equal magnitude and opposite sign. A survey of the coefficients in the eigenvector with eigenvalue 1 reveals a clear dominance of a single value which corresponds to either the lowest unoccupied frontier molecular orbital of the neutral compound or the highest occupied one, depending on the Fukui matrix analyzed. This behavior has already been reported in Ref. [18]. Consequently, an analysis of these coefficients provides information on the quality of the frontier molecular orbital approximation. Thus, one can conclude from Table 1 that this approximation is quite good for all the systems except for the NOF one, where the dominant coefficient corresponding to the frontier molecular orbital in the $f^-(\beta)$ Fukui matrix is 0.81, meaning that it only accounts for the contribution 65% to the Fukui matrix. As can be observed in Table 1 the spin-free version of those Fukui matrices do not present significant changes in relation with their counterparts represented in the spin–orbital set. The dominant coefficients in the eigenvector corresponding to the highest eigenvalue are similar although in the spin-free case this eigenvalue slightly deviates from 1 and the other eigenvalues are not grouped in pairs with opposite sign. This loss of the pairing property should be attributed to the lack of idempotency of the reduced density matrices in the spin-free treatment. In fact, the spin-free Fukui matrices, expressed in Eqs. (7) and (8), are not a difference of two idempotent density matrices; the influence of this property has been described in Ref. [18].

The results shown in Table 2 have been obtained with the dual-descriptor matrices in both spin–orbital and spin-free representations, performed at HF level. In the case of closed-shell systems, $C_2H_4$, $CH_2O$ and NOF, we have used the sequence doublet/singlet/

**Table 2**
Number of positive (Pos) and negative (Neg) eigenvalues of the dual-descriptor matrices and highest (High) and lowest (Low) eigenvalues found using 6–31G basis sets at the HF level. CD-H and CD-L mean the dominant coefficients in the eigenvectors of the dual-descriptor matrices with eigenvalues close to 1 and −1.

| | | $C_2H_4$ | $CH_2O$ | NOF | $C_3H_5$ |
|---|---|---|---|---|---|
| $f^2(\alpha)$ | Pos | 12 | 13 | 14 | 17 |
| | Neg | 7 | 7 | 10 | 12 |
| | High | 1.0000 | 1.0517 | 1.0028 | 1.0045 |
| | Low | −0.0325 | −0.0764 | −0.3854 | −1.0001 |
| | CD-H | 0.9985 | 0.9866 | 0.9976 | 0.9983 |
| | CD-L | | | | 1.0000 |
| $f^2(\beta)$ | Pos | 11 | 11 | 14 | |
| | Neg | 7 | 7 | 11 | |
| | High | 0.0118 | 0.1619 | 0.2294 | |
| | Low | −1.0006 | −1.0112 | −1.0182 | |
| | CD-L | 1.0000 | 0.9548 | 0.8163 | |
| $f^2$(spin-free) | Pos | 12 | 13 | 15 | 18 |
| | Neg | 7 | 7 | 11 | 12 |
| | High | 1.0000 | 1.1389 | 1.0142 | 1.0254 |
| | Low | −1.0034 | −1.0275 | −1.2212 | −1.0001 |
| | CD-H | 0.9985 | 0.9632 | 0.9944 | 0.9903 |
| | CD-L | 1.0000 | 0.9598 | 0.8417 | 1.0000 |

doublet for the species of $(N+1)$, $N$ and $(N-1)$, respectively in Eqs. (11) and (12). The spin blocks, $f^2(\alpha)$ and $f^2(\beta)$, have trace values 1 and −1, respectively and both contain relevant information. However, in the case of the allyl radical, $C_3H_5$, we have used the sequence triplet/doublet/singlet adding and removing an $\alpha$-electron to the neutral species and consequently only the matrix $f^2(\alpha)$ (with trace zero) has relevant information. Hence, we have omitted in Table 2 the values corresponding to the $f^2(\beta)$ matrix for that radical. The results gathered in this table indicate that both formulations predict similar numerical values for the significant eigenvalues and the dominant coefficients in their corresponding eigenvectors. The eigenvectors with eigenvalues close to 1 and −1 present dominant coefficients associated with the lowest unoccupied frontier orbitals and the highest occupied ones, respectively, which is similar to the behavior of the Fukui matrices. The spin-free results show simultaneously the information contained in the $f^2(\alpha)$ and $f^2(\beta)$ matrices requiring a less computational cost.

We have collected in Table 3 the results arising from the diagonalization of the spin-free matrices $f^+$, $f^-$ and $f^2$ (Eqs. (7), (8) and (12), respectively) in order to study the influence of the electron correlation within this methodology. These results refer to eigenvectors with eigenvalues above $10^{-4}$ or below $-10^{-4}$. As can be observed the comparison between the values found at the correlated and uncorrelated levels only shows slight differences in the highest and lowest eigenvalues as well as in the dominant coefficients, which in the correlated case correspond to frontier natural orbitals of the neutral compounds. Likewise, a survey of the results shown in Table 3 indicates that the dual-descriptor matrix retains the information contained in the Fukui matrices in agreement with the relationship among them, that is $f^2 = f^+ - f^-$. At correlated level the dominant coefficients in the systems $CH_2O$ and NOF are lower than in the other systems showing a lower contribution of the natural frontier orbitals to their Fukui and dual-descriptor matrices.

## 4. Concluding remarks

In this Letter we have described the Fukui matrices by means of a spin-free treatment showing the ability of this version to draw out information within the frontier molecular orbital approximation. Likewise, we have introduced the dual-descriptor matrices in both spin–orbital and spin-free representations. The results indicate that the dual-descriptor matrices provide so suitable

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**Table 3**
Number of positive (Pos) and negative (Neg) eigenvalues of the spin-free Fukui and dual-descriptor matrices and highest (High) and lowest (Low) eigenvalues found using 6-31G basis sets at the CISD and HF levels. CF-H and CD-H/(CD-L) mean the dominant coefficients in the eigenvectors of the Fukui and dual-descriptor matrices with eigenvalues close to 1/(−1).

| | | $C_2H_4$ | | $CH_2O$ | | NOF | | $C_3H_5$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | CISD | HF | CISD | HF | CISD | HF | CISD | HF |
| $f^+$(spin-free) | Pos | 14 | 9 | 12 | 8 | 14 | 12 | 20 | 13 |
| | Neg | 11 | 8 | 9 | 7 | 10 | 11 | 15 | 12 |
| | High | 0.9478 | 1.0000 | 0.9527 | 1.0002 | 0.9615 | 1.0068 | 0.9472 | 1.0040 |
| | Low | −0.1272 | −0.1341 | −0.1897 | −0.2002 | −0.1998 | −0.2400 | −0.1215 | −0.1291 |
| | CF-H | 0.9530 | 0.9985 | 0.9470 | 0.9981 | 0.9613 | 0.9964 | 0.9603 | 0.9984 |
| $f^-$(spin-free) | Pos | 15 | 8 | 10 | 7 | 12 | 12 | 19 | 12 |
| | Neg | 11 | 8 | 10 | 7 | 12 | 12 | 14 | 11 |
| | High | 0.9512 | 1.0050 | 0.9977 | 1.0268 | 1.0084 | 1.1060 | 0.9611 | 1.0000 |
| | Low | −0.1368 | −0.1392 | −0.2354 | −0.3432 | −0.1367 | −0.3720 | −0.1133 | −0.1172 |
| | CF-H | 0.9990 | 0.9988 | 0.8053 | 0.9560 | 0.9054 | 0.8391 | 1.0000 | 1.0000 |
| $f^2$(spin-free) | Pos | 17 | 12 | 11 | 13 | 15 | 15 | 21 | 18 |
| | Neg | 7 | 7 | 8 | 7 | 11 | 11 | 12 | 12 |
| | High | 0.9094 | 1.0000 | 1.0246 | 1.1389 | 0.9732 | 1.0142 | 0.9203 | 1.0254 |
| | Low | −0.9139 | −1.0034 | −1.0057 | −1.0275 | −1.0890 | −1.2212 | −0.9541 | −1.0001 |
| | CD-H | 0.9495 | 0.9985 | 0.9289 | 0.9632 | 0.9605 | 0.9944 | 0.9572 | 0.9903 |
| | CD-L | 0.9997 | 1.0000 | 0.8089 | 0.9598 | 0.8875 | 0.8417 | 1.0000 | 1.0000 |

information as the Fukui matrices do. In a computational point of view the spin-free version of these matrices requires a less cost and consequently its utilization must be preferred. The numerical determinations reported reveal that the electron correlation effects may be important in this treatment.

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