# How to Compute the Fukui Matrix and Function for Systems with (Quasi-)Degenerate States

Patrick Bultinck,[†] Carlos Cardenas,*,[‡] Patricio Fuentealba,[‡] Paul A. Johnson,[§] and Paul W. Ayers[§]

[†]Ghent University, Department of Inorganic and Physical Chemistry, Krijgslaan 281 (S3), 9000 Gent, Belgium

[‡]Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile and Centro para el desarrollo de la Nanociencias y Nanotecnologia, CEDENNA, Av. Ecuador 3493, Santiago, Chile

[§]Dept. of Chemistry and Chemical Biology, McMaster University, Hamilton ON Canada L8S 4M1

**ABSTRACT:** A system in a spatially (quasi-)degenerate ground state responds in a qualitatively different way to a change in the external potential. Consequently, the usual method for computing the Fukui function, namely, taking the difference between the electron densities of the $N$- and $N \pm 1$ electron systems, cannot be applied directly. It is shown how the Fukui matrix, and thus also the Fukui function, depends on the nature of the perturbation. One thus needs to use degenerate perturbation theory for the given perturbing potential to generate the density matrix whose change with respect to a change in the number of electrons equals the Fukui matrix. Accounting for the degeneracy in the case of nitrous oxide reveals that an average over the degenerate states differs significantly from using the proper density matrix. We further show the differences in Fukui functions depending on whether a Dirac delta perturbation is used or an interaction with a true point charge (leading to the Fukui potential).

$$\Psi_1 \cdots \text{Degenerate states} \cdots \Psi_g$$
$$\text{Choose} \Downarrow \Delta\hat{v}$$
$$\begin{bmatrix} \langle \Psi_1 | \Delta\hat{v} | \Psi_1 \rangle & \langle \Psi_1 | \Delta\hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_1 | \Delta\hat{v} | \Psi_g \rangle \\ \langle \Psi_2 | \Delta\hat{v} | \Psi_1 \rangle & \langle \Psi_2 | \Delta\hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_2 | \Delta\hat{v} | \Psi_g \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_g | \Delta\hat{v} | \Psi_1 \rangle & \langle \Psi_g | \Delta\hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_g | \Delta\hat{v} | \Psi_g \rangle \end{bmatrix}$$
$$\text{Fukui function} \Downarrow \frac{\partial}{\partial N}$$
$$\text{Perturbation dependent} f^{\pm}(\mathbf{r}; \Delta\hat{v})$$

## I. INTRODUCTION

One reason why Density Functional Theory (DFT) has become so popular among chemists is that it has allowed many preexisting, yet often qualitative, concepts to be rationalized from a quantum chemical perspective. Many ideas such as the electronegativity equalization principle,[1−4] the maximum hardness principle[5−9] and the Hard and Soft Acids and Bases (HSAB)[10−16] principle found firm theoretical footing within what has become known as conceptual DFT.[17−19] Much of chemical reactivity can be rationalized using conceptual DFT tools. This is because just two, in principle, relatively simple, ingredients suffice to compute the energy of a system:[17] the number of electrons $N$ and the external potential $v(\mathbf{r})$ (abbreviated henceforth as $v$). The energy thus becomes a function of $N$ and a functional of $v$. Chemical interactions and reactions can be considered as processes where for each of the reacting partners, these ingredients change as a function of the progress of the reaction.[20] Starting from a number of electrons $N^0$ and external potential $v^0$, the energy of a system for a number of electrons $N$ and external potential $v$ is given by

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

(1)

In practice, this Taylor series is usually carried out no further than to the second order although explorative theoretical work has been performed on still higher order terms.[21,22] All derivatives in equation (eq 1) have been examined in detail[17,18] and are known respectively as the chemical potential, hardness, electron density, and the Fukui function for the terms shown explicitly. The Fukui function thus corresponds to the mixed second derivative in this expansion of the energy.[23−25] It quantifies the change in the functional derivative of the energy

with respect to the external potential to a change in the number of electrons in a molecule, that is,

$$f(\mathbf{r}) = \left( \frac{\partial \left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_{N=N^0}}{\partial N} \right)_{v=v^0} \tag{2}$$

The Fukui function is normalized, meaning that its integral over all space equals 1. Although the Fukui function is among the most popular conceptual DFT based reactivity indices, not all of its properties are well understood. For instance, the possibility of negative Fukui functions in some region(s) of space in a molecule has been debated (see Echegaray et al.,[26] Bultinck et al.[27−30] and references therein). Even more problems[31] appear when atom condensing Fukui functions as originally suggested by Yang and Mortier,[32] among other issues related to the commutation[33] of the different mathematical operations involved when going beyond the Mulliken approach.[34] In the present paper, we deal with the consequences of state degeneracy on the Fukui function. In order to state the problem, we must remember that eq 2 is not the most common representation of the Fukui function. The Fukui function is most often represented as

$$f(\mathbf{r}) = \left( \frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v=v^0} \tag{3}$$

meaning that it is the change in electron density upon changing the number of electrons under constant external potential $v^0$. The equality of eq 2 and eq 3 is based on equating $\left( \delta E/\delta v(\mathbf{r}) \right)_N$ to $\rho(\mathbf{r})$. Although this formula is generally valid, an often unspoken assumption is that it equals the difference in electron density of the system with $N^0$ electrons and charged states with $N \pm 1$ electrons. This assumption can be proven by taking the functional derivative of the energy with respect to a change in the external potential provided there is no spatial degeneracy in the system. It also assumes that the density is a piecewise linear function of $N$,[35−37] which is true in the exact theory but not for many approximate methods.[38−42] As Cardenas et al.[43] have shown, the presence of degeneracies means that one must use degenerate perturbation theory. The consequences of degeneracy and, by extension, quasi-degeneracy are quite significant, and the aim of this paper is to investigate these. To that end, section II derives the necessary expressions to obtain the Fukui matrix[29,30] and Fukui function in case of degeneracies and section IV gives a numerical example for the molecular radical NO, where the neutral state is doubly degenerate and the charged states are singly degenerate.

The issue of degeneracies in Fukui functions has been addressed previously and a rather pragmatic approach is usually taken where, in case of degeneracy, the density entering in eq 3 is taken to be the average density over the degenerate states.[44−48] As will be shown below, such an approach is not in line with the results of the present derivation, which is based on the theoretical considerations of Cardenas et al.[43] and the study by Bultinck et al.[49] on the effect of degeneracy on the electrostatic potential and atomic charges.

## II. FUKUI MATRICES AND FUNCTIONS FOR DEGENERATE STATES

As mentioned above, eq 3 is a generally valid equation, but in case of degeneracies, one needs to carefully establish how the density $\rho(\mathbf{r})$ is to be computed. In order to show this, we first extend the Fukui function to a Fukui matrix,[29,30] as the latter is more directly related to a wave function. Despite the Fukui function being usually linked to purely DFT, it is more informative to work with a wave function based derivation because it facilitates accounting properly for degeneracy. The Fukui matrix corresponds to taking the derivative of the density matrix:[29,30]

$$f(\mathbf{r}, \mathbf{r}') = \left( \frac{\partial \rho(\mathbf{r}, \mathbf{r}')}{\partial N} \right)_{v=v^0} \tag{4}$$

It is thus an extension of eq 3 in the same sense as that the density matrix is an extension of the electron density. The density to be used in eq 3 depends on the functional derivative:

$$\left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_N \tag{5}$$

If no degeneracies appear, functional differentiation[17] allows us immediately to establish that it corresponds to the electron density of that nondegenerate state.

$$\lim_{\varepsilon \to 0} \frac{E(N, v + \varepsilon \Delta v) - E(N, v)}{\varepsilon} = \int \left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_N \Delta v(\mathbf{r}) d\mathbf{r}$$

$$= \int \rho(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \tag{6}$$

Here, $\varepsilon$ is a scalar taken to the zero limit and $\Delta v$ is a suitable change in the external potential ("suitable" reflecting that it must lie in the same function space as $v$). The same result is obtained from first order perturbation theory. In the remainder, the perturbation approach is used and we therefore introduce the external potential *operator* (assuming only nuclear attraction and thus no external fields):

$$\hat{v} = -\sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \tag{7}$$

for a system with $M$ nuclei located at positions $\{\mathbf{R}_\alpha\}$ with nuclear charges $\{\mathbf{Z}_\alpha\}$ and $N$ electrons located at positions $\{\mathbf{r}_i\}$. We further consider the perturbation operator, $\Delta \hat{v}$, which denotes the change in the external potential operator. We can then introduce the perturbation matrix to find the energy and wave function corrections. If the state is nondegenerate, the perturbation matrix has dimension $1 \times 1$ and the first-order change in energy, $E^{(1)}$, is simply $\int \rho(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r}$, where $\rho(\mathbf{r})$ is the electron density of the nondegenerate state. If degeneracies do exist, one needs to consider the perturbation matrix:

$$\begin{bmatrix} \langle \Psi_1 | \Delta \hat{v} | \Psi_1 \rangle & \langle \Psi_1 | \Delta \hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_1 | \Delta \hat{v} | \Psi_g \rangle \\ \langle \Psi_2 | \Delta \hat{v} | \Psi_1 \rangle & \langle \Psi_2 | \Delta \hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_2 | \Delta \hat{v} | \Psi_g \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_g | \Delta \hat{v} | \Psi_1 \rangle & \langle \Psi_g | \Delta \hat{v} | \Psi_2 \rangle & \cdots & \langle \Psi_g | \Delta \hat{v} | \Psi_g \rangle \end{bmatrix} \tag{8}$$

The eigenvectors of the above matrix, in case of $g$ degenerate states, correspond to the correct zeroth order wave functions accompanying each eigenvalue. So, there no longer is a one-to-one correspondence between the electron density obtained from that eigenvector and that from a single state. Each eigenvector is in general a linear combination of all degenerate wave functions where this linear combination depends in a

parametric way on the actual perturbation, $\Delta\hat{v}$, considered. The ansatz above is not only valid when considering the Fukui function but is much more general and was used recently to show the ill-defined nature of the electrostatic potential for degenerate states.[49] Once a specific eigenvalue of the perturbation matrix is chosen, one can use its eigenvector to compute a new density matrix which will in general not be a simple linear combination of density matrices of the different degenerate states but will also involve the transition density matrices between states. Each eigenvector is a linear combination of all (quasi-)degenerate states (real wave functions are assumed throughout):

$$\Phi_a = \sum_{i=1}^{g} c_{ai} \Psi_i \tag{9}$$

resulting in a density matrix composed of the density matrices of the states $\Psi_i$ and transition density matrices between states:

$$\rho_a(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{g} c_{ai}^2 \rho_{ii}(\mathbf{r},\mathbf{r}') + \sum_{i=1}^{g}\sum_{\substack{j=1 \\ j\neq i}}^{g} c_{ai}c_{aj}\rho_{ij}(\mathbf{r},\mathbf{r}') \tag{10}$$

Here, $\rho_{ij}(\mathbf{r},\mathbf{r}')$ denotes the spin summed density matrix obtained from $\int \Psi_i(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N)\Psi_j(\mathbf{x'}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N)d\mathbf{x}_2\cdots d\mathbf{x}_N$. Transition density matrices thus contribute, and this already establishes that approaches taken based on averages of density matrices[44,45,47,48] $\rho_{ij}(\mathbf{r},\mathbf{r}')$ will be subject to error. It is the diagonal of the density matrix in eq 10 that is the electron density to be used in eq 3 for the Fukui function. Another important observation is that the density, through the dependence of the eigenvector on the nature of the perturbation, does not exactly correspond to the functional derivative, as eq 6 is not linear anymore in the change in external potential, which means that the functional derivative does not exist. Finally, it must be stressed that in eq 9, the coefficients $c_{ai}$ depend on the nature of $\Delta\hat{v}$.

To compute the Fukui matrix, the derivative of the density matrix with respect to the number of electrons must be computed (see eq 4). This is usually done using a finite difference approach. Due to the discontinuity of the density with respect to the number of electrons,[17,23,24] two separate Fukui functions must be considered, namely one for the removal of an electron and one for adding an electron as follows respectively:

$$f^-(\mathbf{r},\mathbf{r}') = \rho^N(\mathbf{r},\mathbf{r}') - \rho^{N-1}(\mathbf{r},\mathbf{r}') \tag{11}$$

$$f^+(\mathbf{r},\mathbf{r}') = \rho^{N+1}(\mathbf{r},\mathbf{r}') - \rho^N(\mathbf{r},\mathbf{r}') \tag{12}$$

where the notation $\rho^N(\mathbf{r},\mathbf{r}')$ indicates the electron density of the $N$ electron system and these density matrices are obtained either via the nondegenerate density matrix or via eq 8 depending on whether the $N(\pm 1)$ system(s) exhibit(s) degeneracies.

The Fukui matrix exhibits many interesting properties.[29,30] Several of these are only manifest when separating the density matrix in an $\alpha$ and $\beta$ part depending on the electron spin (note that the Fukui matrix was originally introduced in spin specific form[29,30] and was studied in spin integrated and spin polarized form by Alcoba et al.[50,51]). The trace of the Fukui matrix always equals 1 for the spin for which the number of electrons effectively changes (here we consider the $\alpha$ electrons always in the majority for any system) and equals zero for the other. In

the specific case of idempotent density matrices, it has been shown that both the $\alpha$ and $\beta$ Fukui matrices have an interesting spectrum. All eigenvalues must always come in pairs $x$ and $-x$ except eigenvalues identical to zero or 1. This effect disappears when the density matrices are no longer idempotent, as is the case when introducing electron correlation. Another possibility, predicted by Bultinck et al.,[29,30] is degeneracy, and this paper indeed establishes this (see the following text).

It is important to note that, for degenerate systems, the Fukui matrix and Fukui function will, through eq 8, depend on the nature of $\Delta\hat{v}$. This is not the case for nondegenerate systems. If one considers as a perturbation a point charge $q_0 > 0$ located at position $\mathbf{R}_0$, $g$ negative eigenvalues are obtained because of the attraction between the negatively charged electrons and the positive point charge $q_0$.[49] Ordering these as $\lambda_{min}^{(+)} \leq ... \leq \lambda_{max}^{(+)} < 0$ (note the superscript (+) denoting that these values were obtained from the perturbation matrix for a positive point charge) but changing the sign of the point charge to $q_0 < 0$ results in positive eigenvalues of the same magnitude as previously, differing only in sign and such that $\lambda_{max}^{(-)} = -\lambda_{min}^{(+)} \geq ... \geq \lambda_{min}^{(-)} - \lambda_{max}^{(+)} \geq 0$. Seeking the lowest energy, the eigenvalue $E^{(1)} = \lambda_{min}^{(+)}$ is chosen for the positive point charge and $E^{(1)} = \lambda_{min}^{(-)} = -\lambda_{max}^{(+)}$ for a negative point charge, such that the limit differs depending on whether one approaches it from above or below.[49] There is thus no hope of finding a unique Fukui matrix or function even for a point charge at the same position and of the same magnitude, differing only in sign. As different eigenvectors are followed, different reactivity and regioselectivity may be expected.

All these effects are further enhanced when one then also considers that the point charges may be moved. The density matrices used in computing the Fukui function involving at least one species with degenerate states may change sometimes in a rather unpredictable way depending on the $\Delta\hat{v}$ considered. In case species are encountered that exhibit degeneracy, the only way forward is to obtain as good as possible a model for $\Delta\hat{v}$ and to carry out the degenerate perturbation theory. All these findings also hold for systems with quasi-degeneracy where it was previously found that these effects may even worsen.[49] Exact degeneracy is often a consequence of symmetry, and this puts extra constraints on the properties of the Fukui matrices, constraints that are relaxed in less symmetrical systems.

Besides a point charge, an often used perturbation in conceptual DFT is a Dirac delta type operator, which has the advantage of mathematical simplicity. It does, however, not correspond to a clear physical interaction as the point charge potential does. Both are, however, of interest in their own right. To show this, consider the eigenvalues of the perturbation matrix with a Dirac delta operator:

$$E^{(1)} = -\int \rho(r)\delta(r - R_0)dr = -\rho(R_0) \tag{13}$$

Taking the difference in these eigenvalues between the neutral molecule and an ion, results immediately in the Fukui function $f^{\pm}(\mathbf{R}_0)$ where the influence of degeneracy appears in $\rho(\mathbf{R}_0)$ for the degenerate system. On the other hand, with the point charge operator, one has

$$E^{(1)} = -\int q\frac{\rho(r)}{|r - R_0|}dr \tag{14}$$

Taking $q = 1$ and making the difference between the molecule with $N$ and $N \pm 1$ electrons, one finds that eq 14 leads to the

Fukui potential: a different, yet promising, reactivity descriptor[52−55]

$$v_f(R_0) = \int \frac{f(r)}{|r - R_0|} dr \tag{15}$$

Note that in both eq 13 and eq 14 a minus sign appears. This is due to the negative (stabilizing) interaction between an electronic charge density (the negative of the electron density) and a positive point charge.

## III. COMPUTATIONAL METHODS

The molecular radical NO is chosen as an example as it has a degenerate neutral state and nondegenerate ionic states and has been used previously to examine effects of degeneracy on Fukui functions.[45] Moreover, it is an interesting molecule in biomodelling (see for example recent work by Lee et al.[56]). All (degenerate) state(s) of all systems needed for computing Fukui functions were computed at the complete active space (CAS) level for all valence electrons in all valence orbitals using the cc-pvtz basis set. Throughout, the NO radical geometry optimized at that same level was used. The integrals needed in eq 8 were obtained using the Obara−Saika scheme,[57] and all required calculations are performed using our own software except for the CAS calculations, where Gamess (U.S.)[58] was used. All required density matrices were obtained directly from the Slater determinant expansion coefficients of the different states computed with the Gamess (U.S.) full CI code.[59] As a basis, the orthonormal Hartree−Fock orbitals are used although, where of interest, this basis was expressed in nonorthonormal basis function space. Both representations are naturally equivalent, as, where needed, nonzero overlap is taken into account.[60]

As perturbing operators, we opt for a point charge with charge $q_0$ at $R_0$. The operator $\Delta\hat{v}$ in eq 8 is thus given by

$$\Delta\hat{v} = -\sum_{i=1}^{N} \frac{q_0}{|r_i - R_0|} \tag{16}$$

In the following, only unit point charges $|q_0| = 1$ are considered. The eigenvalues and eigenvectors of eq 8 have the same magnitude for $q_0$ of the same magnitude, but in order to reach the lowest energy, the opposite eigenvector and eigenvalue pair is followed. So, the eigenvalue/eigenvector pair followed for $q_0 > 0$ for the ground state would be the one that brings the system with $q_0 < 0$ to an excited state and vice versa (note also that the sign of the eigenvalues changes depending on the sign of $q_0$ but the set of eigenvectors remains exactly the same, see above). We furthermore also consider both a positive and a negative Dirac delta operator. As a physically significant grid of $R_0$ values, we have chosen a set of points on the van der Waals surface of the molecule. To facilitate discussion, we have aligned the molecule along the $z$-axis with the origin in the geometrical center of the molecule and use the zenith angle $\theta$ and azimuthal angle $\phi$ to locate the source of the perturbation (see Figure 1). Note also that the choice for a point charge or a Dirac delta are just two specific cases and one could consider also other operators in eq 8 and eq 16, for example the "soft" potentials used by Besalu and Carbo-Dorca.[61] However, the point charge and Dirac delta perturbations suffice to illustrate the most important points.
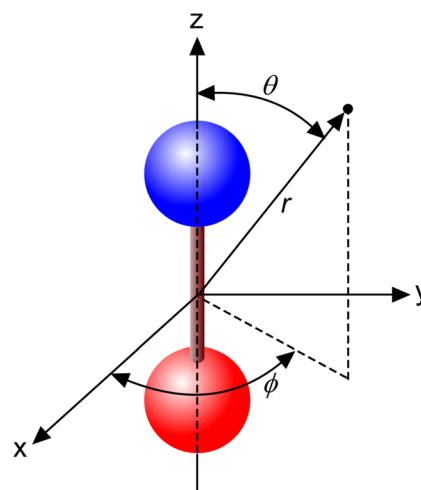


**Figure 1.** Coordinate system for the $R_0$ points.

## IV. RESULTS AND DISCUSSION

The molecular radical NO has a degenerate ground state where the unpaired electron can occupy one of two equivalent molecular orbitals. The ions, on the other hand, are all nondegenerate. One could alternatively have chosen a molecule with degenerate ionized states or even both degenerate ground and excited states. The present case of degeneracy in the ground state, however, is of prime interest in the context of NO being a reactant of interest in biomodeling.[56] For the degenerate NO ground state, a point charge $q_0$ or a Dirac delta is placed at $R_0$ using the grid introduced in section III. For this operator, the lowest eigenvalue of eq 8 is sought, and the associated eigenvector is used to compute the corresponding density matrix. Using this density matrix, the Fukui matrix is computed as in eqs 11 and 12. This matrix is then diagonalized to examine the structure of its eigenvalues and its eigenvectors. The number of possible Fukui matrices, and thus Fukui functions, doubles for a given $R_0$ and interaction potential model. This is due to the fact that there are two Fukui functions to be considered according to eqs 11 and 12, and there is a parametric dependence on the nature of the perturbation (here a point charge or Dirac delta operator of two possible signs). Given the parametric dependence of the Fukui matrix on $q_0$ and $R_0$ and the fact that it is a function of $r$ and $r'$, the following notation will be used:

$$f_{\pm}^{\pm}(r, r'; R_0) \tag{17}$$

The superscript denotes removal or addition of an electron, the subscript $\pm$ denotes the sign of the point charge used in case of a point charge perturbation or the sign of the Dirac delta operator and ";$R_0$" denotes the parametric dependence on $R_0$. In the following, we present data illustrating the complexity of Fukui matrices and functions involving species with degenerate states and emphasize the symmetry in both the solutions of the perturbation matrix and the Fukui matrix.

**Properties of the Perturbation Matrix of NO.** NO is a somewhat special case in the sense that the neutral state of the molecule is degenerate whereas in most other cases it is the ionized systems that exhibit degenerate states. In line with eq 8, we find two solutions of the perturbation matrix. Depending on the location of the perturbation, $R_0$, the two associated eigenvalues and eigenvectors differ to a smaller or a larger extent, with a maximum difference of roughly 20 kcal/mol. This

is in line with the previous findings by Bultinck et al.[49] Figure 2 shows the difference between the eigenvalues for a positive unit point charge located at the different $\mathbf{R}_0$ grid points.
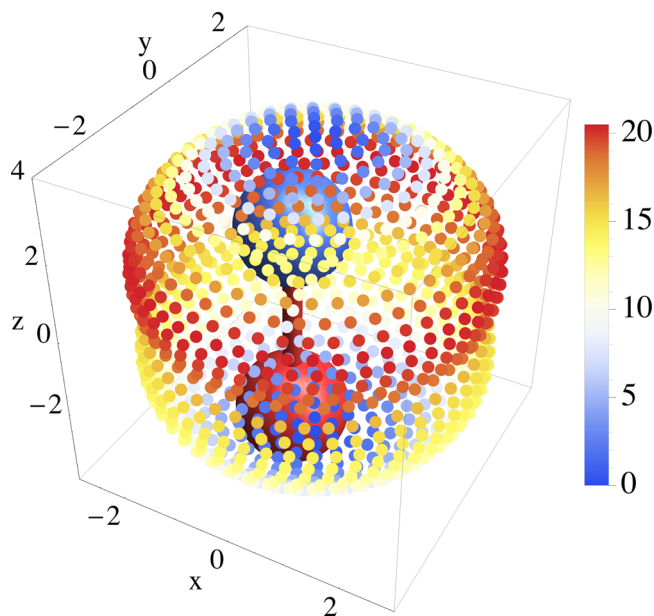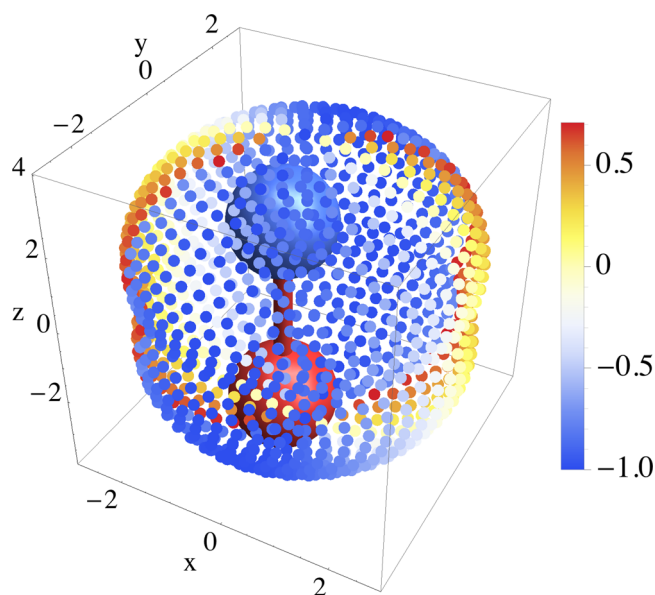


**Figure 2.** Difference between the two eigenvalues ($\lambda_{max}^{(+)} - \lambda_{min}^{(+)}$, in kcal/mol) of the perturbation matrix for the chosen grid for a positive unit point charge.

Besides this difference in eigenvalues, an important requirement for the method described is that it must fulfill all symmetry requirements imposed by the lowering from the $C_{\infty\nu}$ symmetry in the unperturbed case to $C_s$ symmetry. Physically, for a specific zenith angle $\theta$, the eigenvalues of the perturbation matrix should remain the same independent of the azimuthal angle $\phi$ (see Figure 1). Our results indeed reveal that this symmetry is fully respected, as is shown in Figure 3. Figure 3 shows the minimum eigenvalue of the perturbation matrix for a
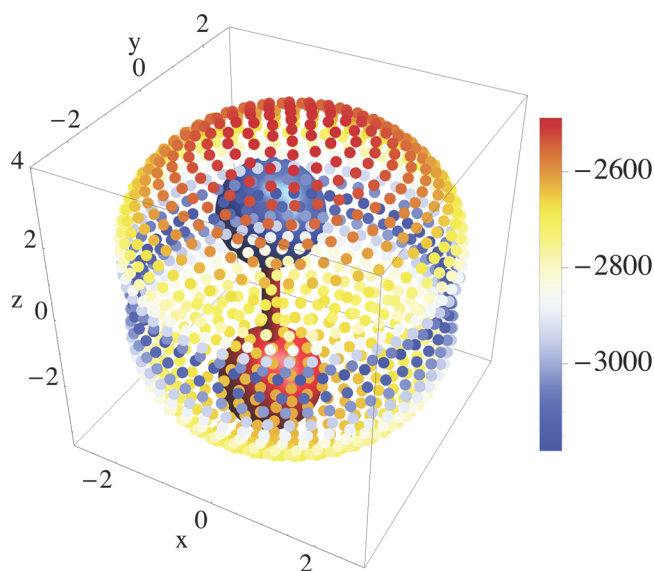


**Figure 3.** Minimal eigenvalue $\lambda_{min}^{(+)}$ of the perturbation matrix for the chosen grid for a positive unit point charge (in kcal/mol). Each point corresponds to the location of the point charge.

positive unit point charge located in each of the grid points for the neutral molecule. The maximum eigenvalue exhibits the same symmetry. Another symmetry is that in the eigenvector. Taking the same perturbation but considering now the eigenvector symmetry for the lowest eigenvalue and plotting the coefficient of the first state, we find that the coefficient is independent of the zenith angle but depends on the azimuthal angle. Figure 4 illustrates this. This symmetry is expected. In



**Figure 4.** Coefficient of the first degenerate state in the eigenvector corresponding to the minimal eigenvalue $\lambda_{min}^{(+)}$ of the perturbation matrix for the chosen grid for a positive unit point charge. Each point corresponds to the location of the point charge.

NO the HOMO is of $\pi^*$ type and doubly degenerate. The corresponding orbitals are denoted $\pi_x^*$ and $\pi_y^*$. For the double degeneracy encountered here, one expects that for a positive point charge in, for example, the $xz$ plane, the entire response comes from the $\pi_y^*$ orbital whereas for a point in the $yz$ plane with the same zenith angle, one expects it to correspond to the $\pi_x^*$ orbital (see below for a detailed analysis), accounting for the dependence on the azimuthal angle. The independence with respect to the zenith angle is also expected. This is illustrated in Figure 4. For every point in the $xz$ plane, the entire response comes from the $\pi_y^*$ orbital, revealing constancy of the coefficient for the corresponding state. Other points outside this plane can be rationalized in the same way. Symmetry-wise, the important things are that the eigenvalues are constant for a given zenith angle and independent of the azimuthal angle, while the eigenvectors are constant for a given azimuthal angle and independent of the zenith angle.

An interesting question is to what extent the eigenvalues differ between different forms of the perturbation; e.g., a unit positive point charge versus a Dirac delta perturbation. It turns out that these are also significant differences, as is clear from comparison between Figure 3 and Figure 5. We refer in this context to the meaning of the eigenvalues (eq 13 and eq 14). In case of a point charge, the eigenvalues correspond to electrostatic potentials whereas in the case of a Dirac delta operator, they are simply electron densities.

**Properties of the Fukui Matrix.** If one were to consider only one state of NO and compute the Hartree−Fock Fukui
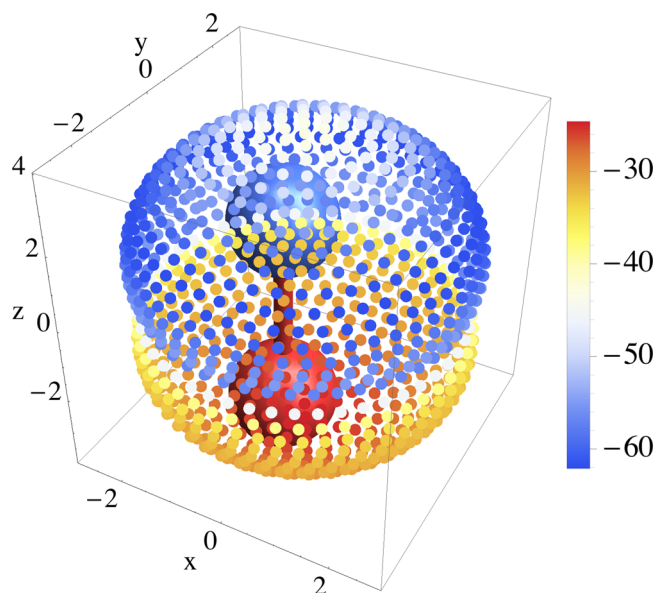
**Figure 5.** Lowest eigenvalue $\lambda_{min}^{(+)}$ of the perturbation matrix for the chosen grid for a positive Dirac delta operator.

matrix $f_{\pm}^{-}$ $(\mathbf{r},\mathbf{r}';\mathbf{R}_0)$ but for the $\beta$-spin density matrices only, it would have one strict unit eigenvalue because all density matrices are then idempotent.[29,30] This effect is, however, lost upon proper introduction of electron correlation and is further lost when one uses the true density matrix based on the eigenvector of the perturbation matrix, as was shown previously.[30] The effect is very similar for all other Fukui matrices.

The above-discussed symmetry aspects also have a large impact on the eigenvalues and eigenvectors of the Fukui matrix. Take, for example, $f_{+}^{-}$ $(\mathbf{r},\mathbf{r}';\mathbf{R}_0)$, which reflects a positively charged perturbation removing an electron from the system, an archetypical electrophilic attack on the system. For a given zenith angle, based on cylindrical symmetry, we expect the same eigenvalues of the Fukui matrix for every value of the azimuthal angle. Our calculations indeed reveal that this is the case. On the other hand, we also expect that for a given azimuthal angle irrespective of the zenith angle the same

eigenvalues be obtained. This is due to the fact that the eigenvectors of the perturbation matrix are also required to respect symmetry and that the physics of the interaction requires that for every zenith angle, the same zero-th order wave function gives the first-order energy correction. Combining these two effects, it is clear that in all cases the same Fukui matrix eigenvalues must be found. The $f_{+}^{-}$ $(\mathbf{r},\mathbf{r}';\mathbf{R}_0)$ matrix has as dominant (most positive) eigenvalue 0.9455 with negative eigenvalues as low as −0.1363. With such large negative eigenvalues, regions with negative Fukui functions appear with high probability. Although negative eigenvalues already appear for systems lacking degenerate states,[29,30] the need to treat degeneracy makes them more significant. As expected, the existence of two roots in eq 8 implies that the Fukui matrix $f_{-}^{+}$ $(\mathbf{r},\mathbf{r}';\mathbf{R}_0)$ has different eigenvalues. This is indeed what is found. The most positive eigenvalue equals 0.9360. The two remaining Fukui matrices also have mutually different spectra for the Fukui matrix. As a consequence, there are not two Fukui functions to be considered but four per model potential (unit point charge or Dirac delta or other models). Although within one type of Fukui function the eigenvalue spectrum of the Fukui matrix remains the same for every $\mathbf{R}_0$, this does not apply to the eigenvectors. These must also obey symmetry and indeed, as expected, the eigenvector adapts to the location of the point charge perturbation. If, for example, a positive point charge lies in the $xz$ plane, the entire response comes from the $\pi_x^*$ molecular orbital and the eigenvector of the Fukui matrix reflects this.

Given the above-described effects, one readily understands that also the Fukui functions differ significantly depending on the model of the perturbing operator and of $q_0$ and, in general, on its position $\mathbf{R}_0$. It would be far too lengthy to plot every possible Fukui function; hence, we limit ourselves largely to a numerical comparison of the so-called Fukui orbitals $\phi_i(\mathbf{r})$.[49] These correspond to the eigenvectors of the Fukui matrix, for the present purpose expressed in terms of the nonorthogonal real Gaussian basis functions referred to using Greek symbols. The Fukui function is the diagonal of the Fukui matrix, such that it corresponds to

$$f_{\pm}^{\pm}(r, r; R_0) = \sum_{\mu,\nu} \phi_\mu(r) F_{\mu\nu} \phi_\nu(r)$$

(18)

**Table 1. Fukui Orbital Coefficients for $f_{\pm}^{-}$ $(\mathbf{r},\mathbf{r}';\mathbf{R}_0)$ for a Number of Positions $\mathbf{R}_0$ and Positive and Negative $q_0$ for the Perturbation Treatment versus the Average Density Approach (For the Latter No $\mathbf{R}_0$ or $q_0$ Are Shown, See Text)[a]**

| $\mathbf{R}_0$ | $(x,0,z)$ | | $(0,x,z)$ | | $(x,y,z)$ | | | |
|---|---|---|---|---|---|---|---|---|
| $q_0$ | 1 | −1 | 1 | −1 | 1 | −1 | avg | |
| eigenvalue | 0.9455 | 0.9455 | 0.9455 | 0.9455 | 0.9455 | 0.9455 | 0.4744 | 0.4744 |
| N $p_x(1)$ | −0.3069 | 0.0000 | 0.0000 | −0.3069 | −0.2170 | 0.2170 | 0.3026 | 0.0000 |
| N $p_x(2)$ | −0.4281 | 0.0000 | 0.0000 | −0.4281 | −0.2170 | −0.2170 | 0.4290 | 0.0000 |
| N $p_x(3)$ | −0.3479 | 0.0000 | 0.0000 | −0.3479 | −0.3027 | 0.3027 | 0.3623 | 0.0000 |
| N $p_y(1)$ | 0.0000 | −0.3069 | −0.3069 | 0.0000 | −0.3027 | −0.3027 | 0.0000 | 0.3026 |
| N $p_y(2)$ | 0.0000 | −0.4281 | −0.4281 | 0.0000 | −0.2460 | 0.2460 | 0.0000 | 0.4290 |
| N $p_y(3)$ | 0.0000 | −0.3479 | −0.3479 | 0.0000 | −0.2460 | −0.2460 | 0.0000 | 0.3623 |
| O $p_x(1)$ | 0.2816 | 0.0000 | 0.0000 | 0.2816 | 0.1991 | −0.1991 | −0.2702 | 0.0000 |
| O $p_x(2)$ | 0.3645 | 0.0000 | 0.0000 | 0.3645 | 0.1991 | 0.1991 | −0.3589 | 0.0000 |
| O $p_x(3)$ | 0.3196 | 0.0000 | 0.0000 | 0.3196 | 0.2578 | −0.2578 | −0.3465 | 0.0000 |
| O $p_y(1)$ | 0.0000 | 0.2816 | 0.2816 | 0.0000 | 0.2578 | 0.2578 | 0.0000 | −0.2702 |
| O $p_y(2)$ | 0.0000 | 0.3645 | 0.3645 | 0.0000 | 0.2260 | −0.2260 | 0.0000 | −0.3589 |
| O $p_y(3)$ | 0.0000 | 0.3196 | 0.3196 | 0.0000 | 0.2260 | 0.2260 | 0.0000 | −0.3465 |

[a]The row Eigenvalue gives the largest eigenvalue of the Fukui matrix.

Note that in eq 18 on the right-hand side, the explicit and parametric dependencies remain hidden not to overload notation. Restricting ourselves to just $f_{\pm}^{-}$ $(\mathbf{r}, \mathbf{r}'; \mathbf{R}_0)$ using a point charge model, the dominant eigenvalue/vector pair, the $p_x$ and $p_y$ basis functions and a small set of symmetrically important positions of $\mathbf{R}_0$, we can infer the differences in Fukui functions. Table 1 illustrates many important points.

Using a set of admittedly special points $\mathbf{R}_0$, the first two columns with numerical data illustrate important physics: if a positive point charge is placed in the nodal plane of the $\pi_y^*$ orbital (denoted as a point with coordinates $(x,0,z)$), the point charge attracts the electron in an orbital pointed toward it, hence the significant coefficients for the $p_x$ basis functions. A negative point charge in the same location drives the electrons into the $\pi_y^*$ orbital such that they escape the repulsion. Similar findings apply to point charges in a point $(0,y,z)$. Putting a point charge on a bisecting line (denoted here $(x,y,z)$) mixes these extremes to make sure at every possible position $\mathbf{R}_0$ all symmetries are respected. Figure 6 shows the Fukui function $f_+^-$ $(\mathbf{r}; \mathbf{R}_0)$ for a point charge interaction originating from the $\mathbf{R}_0$ indicated.
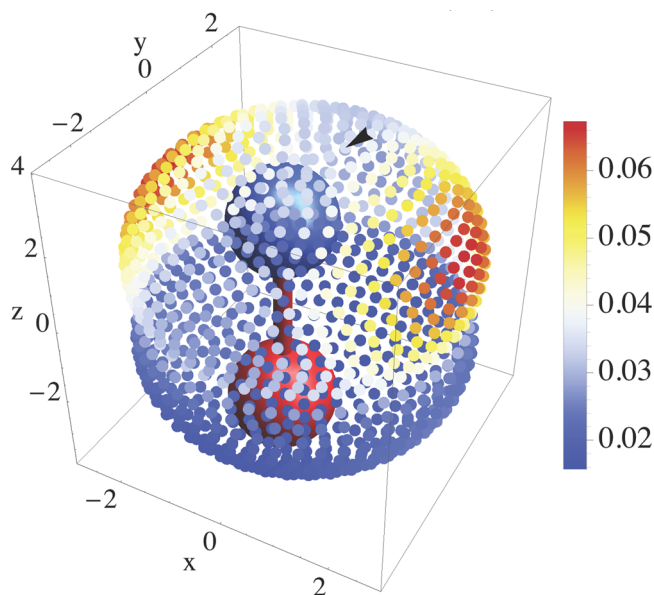


**Figure 6.** Fukui function $f_+^-$ $(\mathbf{r}; \mathbf{R}_0)$ originating from a positive unit point charge located at the point (arrow) indicated.

**Properties of the Average Density Approximation for NO: Derivative with Respect to the External Potential.** Using average densities does not lead to different responses as in the proper treatment based on eq 8. This shows this approximation to be flawed. Consistent with having only one "eigenvalue" is that that approach also leads to only one "eigenvector". Fundamentally, this is because in the average density approach, one disregards the importance of the transition density matrix. An interesting question is whether there is a significant difference between the two eigenvalues from a degenerate perturbation treatment versus an average density treatment. Figure 7 shows, as a function of the Z-coordinate, the difference between the minimum and maximum eigenvalue for a unit point charge (note again that the eigenvalues are independent of the azimuthal angles). The unique "eigenvalue" from the average density is chosen as
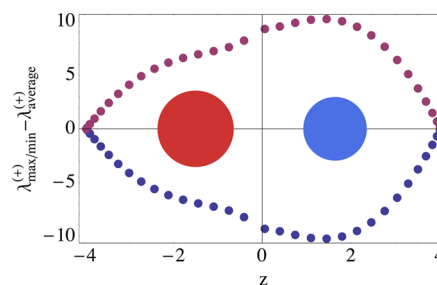


**Figure 7.** Minimal $\lambda_{\min}^{(+)}$ and maximal $\lambda_{\max}^{(+)}$ eigenvalues (in kcal/mol) of the perturbation matrix as a function of the $z$-coordinate (in bohr) of the unit positive point charge with respect to the energetic response of a density average ($\lambda_{\text{average}}^{(+)}$, used as baseline to emphasize the differences).

baseline. The differences are obviously significant and not uniform over all zenith angles.

**Properties of the Average Density Approximation for NO: The Fukui Matrix.** Having obtained the above algebraic insight into the structure of the Fukui matrix (see Table 1), it is possible to shed more light on the shortcomings of the average density[44−48] approach. Taking the average of the density matrix (which then leads to the average density) neglects the transition density matrices and thus is not in line with eq 8. It also introduces some artificial degenerate eigenpairs in the Fukui matrix. Indeed, the spectrum has no longer one large positive eigenvalue for $f_+^-$ $(\mathbf{r}, \mathbf{r}'; \mathbf{R}_0)$ but has the highest positive eigenvalues 0.4744 (doubly degenerate), 0.1393 and 0.1350 (doubly degenerate). An average density (matrix) is thus a rather different and flawed approach because it does not take into account the undefined nature of the electron density[43] and thus the existence of different roots for eq 8.[49] As a logical consequence the average density approach does not result in different Fukui matrices for a positive or negative point charge.

Using the average density approach, the Fukui orbitals are the same irrespective of $\mathbf{R}_0$ or $q_0$. This is illustrated in Figure 8. Figure 8 does not only differ in magnitude from Figure 6 but has an artificial extra symmetry.

Note that all symmetries are automatically respected in the correct degenerate perturbation theory approach without the need for any special symmetry corrections. This means that all symmetries from the Hamiltonians and wave functions are automatically present and that no artificial extra symmetry is introduced nor that some symmetries remain disregarded. The perturbation matrix and its elements automatically take into account the correct symmetry provided the initial geometries and wave function calculations reflect these symmetries properly, as is the case for the all valence CAS calculations in this work. For highly symmetrical molecules and in the case of exact degeneracies, the weighted average approach means that one considers all possible symmetry equivalent positions of the perturbation, computes the eigenvectors, and then takes the average. Taking a random value for the zenith angle and the full 360° span for the azimuthal angle, the average weight of the first ($c_{11}^2$ in eq 10) and second state ($c_{12}^2$ in eq 10) equals 0.5 with the products of the coefficients of both states ($c_{11}c_{12}$ in eq 10) averaging to exactly zero, independent of the sign of the unit point charge. In this sense, the average ensemble at no point corresponds to the solution of the perturbation matrix, although it equals the average over all values for the azimuthal angle for a given zenith angle.
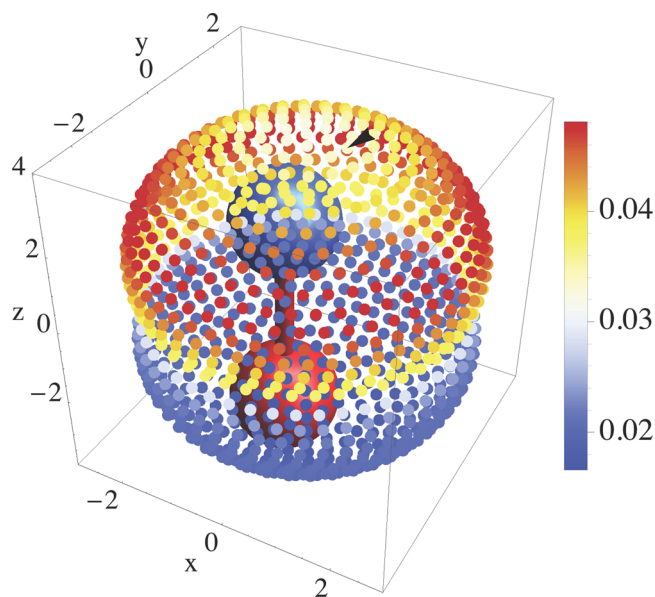
**Figure 8.** Fukui function $f_+^-$ $(\mathbf{r};\mathbf{R}_0)$ originating from a positive unit point charge located at the point indicated (arrow) but using an average density over the degenerate states.

We agree with Flores-Moreno[48] that atom condensing may hide some of the problems described in the present paper. In this sense, they give the right answer but not for the right reasons. Taking as an example the Mulliken[34] atom or atom plus bond condensed Fukui functions,[32,60] one readily understands that through multiplication of the Fukui matrix in terms of the Gaussian basis functions with the overlap matrix in this same basis, the effect of the transition density matrices disappears. This is due to the fact that the basis functions composing the $\pi_x^*$ and $\pi_y^*$ orbitals are mutually orthogonal. This is, however, a consequence of using the Mulliken recipe, and one must also consider that Mulliken charges do quite badly at reproducing the electrostatic potential[62] and are thus of limited interest for reactivity prediction. We strongly suggest to use the correct derivation and to wisely determine whether atom condensation is advised, as this raises other issues such as the impact of choosing a specific model for the atom in the molecule, commutability of operations etc. Moreover, it has been shown before that one can now also treat the entire Fukui function as a descriptor in, for example, 3-D QSAR.[63]

All these results clearly indicate that the Fukui matrix and Fukui function *can* be extended to systems with degenerate states but that they will differ as they depend in a parametric fashion on $\mathbf{R}_0$ and the sign of $q_0$ for the case considered here. Still other cases, differing in the nature of the perturbation (such as a set of point charges, or smoother charge distributions for example[61]), will result in still other Fukui matrices and Fukui functions. Choosing a good representative perturbing potential to derive the Fukui matrix and function from for cases with degenerate states will always require thorough knowledge of the nature of the interaction (e.g., spatial arrangement). This is a fundamental consequence of the need to use degenerate perturbation theory and is inescapable. For nondegenerate states this is not so as the functional derivatives are straightforward. Nevertheless, the nondegenerate case can be expressed in exactly the same way as presently described with the understanding that the perturbation matrix has dimension 1 × 1.

In the above example, the degeneracy is a consequence of exact symmetry, which always entails some constraints. As was previously shown for the electrostatic potential,[49] quasi-degeneracies may lead to still larger effects, and it is therefore suggested to always use the degenerate theory in both cases of degeneracies and quasi-degeneracies.

## V. CONCLUSIONS

The Fukui function and, by extension, the Fukui matrix for systems containing degeneracies depend in a parametric sense on the nature of the perturbation considered for the calculation of the derivative of the energy with respect to the external potential. Using a perturbation theory approach, it is shown how the density matrix derived from the lowest eigenvalue of the perturbation matrix reflects the effects of changing the nature of the perturbation. This is illustrated using the molecule NO, which has a degenerate ground state in the neutral radical.

It is further shown that the Fukui matrix loses its special spectral properties (such as the coupling of eigenvalues as $-x$ and $+x$) even when the states are obtained using Hartree−Fock level calculations, where the Slater determinant for each state separately results in an idempotent density matrix. This is a clear manifestation of the need to always invoke all degenerate states. It is furthermore shown that the Fukui function can depend significantly on the nature of the perturbation by choosing point charge perturbations with unit charges of different sign or considering a Dirac delta operator as perturbing potential and changing the location of the perturbing charge or potential.

All this shows that for systems where degenerate states are present, one cannot use a single Fukui function for a given process of electron removal or attachment. One must model the perturbing potential and compute the corresponding Fukui function. A simple average over the states does not suffice because the Fukui function, such as other $\mathbf{r}$-dependent indicators in conceptual DFT, depends—often dramatically and even discontinuously—on the type and sign of the perturbing potential used to mimic an attacking reagent. The dependence of reactivity indicators on the nature of the reaction-partner is inconvenient but also potentially elucidating. For example, molecules with degenerate states in the $N$, $N \pm 1$ electron systems have an increased ability to adapt to their reaction partner; they should therefore be able to react more vigorously, with a larger range of reaction partners. This also stresses that the present work is not merely an academic exercise. As more and more often the reactivity of molecules containing transition metals is studied, proper treatment of degenerate or quasi-degenerate states will become more important. The same is true for radical species but even for molecules such as benzene where the requirement to keep the molecular geometry fixed introduces degeneracies in the ionized species. Moreover, it is always very important to make theories generally and widely applicable and not constrained to special cases. In this sense, the generalization of reactivity descriptors to degenerate systems is of prime interest. Our work succeeds in this and, as expected, the more common expressions for nondegenerate cases appear as special cases of the more general theory.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: cardena@macul.ciencias.uchile.cl.

## Notes

The authors declare no competing financial interest.

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