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Efficient evaluation of analytic Fukui functions

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An efficient method for the analytic evaluation of Fukui functions is proposed. Working equations are derived and numerical results are used to validate the method on medium size set of molecules. In addition to the obvious advantages of analytic differentiation, the proposed method is efficient enough to be considered a practical alternative to the finite difference formulation used routinely. The reliability of the approximations used here is demonstrated and discussed. Problems found in other methods for prediction of electrophilic centers are corrected automatically when using the new method. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3036926]

I. INTRODUCTION

The Fukui function[1,2] is one of the most fundamental and widespread reactivity descriptors in density functional theory (DFT).[2–5] This function is defined as the derivative of the electron density $\rho(\mathbf{r})$ with respect to the total number of electrons of the system, N, under a constant external potential $v(\mathbf{r})$,

$$f(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}. \tag{1}$$

In most applications, the Fukui function is calculated by the finite difference formula. This method involves single point calculations on the $(N\pm 1)$-electron systems.[6,7] Whereas the finite difference formula yields, in most cases, results that are sufficiently accurate to predict site selectivity, this method sometimes encounters practical problems. For example, it is common to find convergence problems with ionic systems and the calculation of anionic systems usually requires a better basis set in comparison to those that suffice for uncharged species. This requirement is due to the diffuse nature of some anionic valence orbitals. It must be emphasized that the Fukui function is a property of the system with N electrons, so that any dependence on (or practical difficulty associated with) $(N\pm 1)$-electron systems is artificial and should be removed.

The finite difference formulation is frequently used in combination with the condensed Fukui function. The condensed form of the Fukui function[8,9] is simply based on the difference of atomic populations between the N and the $(N\pm 1)$-electron systems. Obviously, the procedure for obtaining the condensed Fukui function is arbitrary as it depends on a population analysis scheme.[10] However, it is chemically more appealing to talk about nucleophilic or electrophilic centers associated with a given atom or atoms in the molecule rather than a spatial region.

Despite all the inaccuracies in evaluation of the Fukui function, it has been used with great success in many applications to chemical reactivity and site selectivity studies.[5,7] However, in some systems these inaccuracies introduce not only quantitative but also qualitative errors that lead to incorrect predictions of reactive centers.[6]

Although it is clear that the Fukui function and other reactivity descriptors can be obtained from linear response theory,[7,11–13] analytic evaluations of Fukui functions with linear response methods are not generally used. This is related to their high computation cost. Traditionally, the solution of linear response equation in DFT involves a linear equation system of the same size as in configuration interaction with single excitations.[14–21] This requirement makes the calculation of analytic Fukui functions prohibitive. Therefore, in most practical applications the finite difference method, $\Delta\rho_{\mathrm{SCF}}$, is preferred over analytical evaluations.[6,7] Nonetheless, analytical methods to compute the Fukui function have been implemented. Michalak *et al.*[11] described a practical method for the calculation of analytic Fukui functions using a localized basis. However, their method neglected the contribution of exchange-correlation response (*vide infra*). Methods including exchange[22] and exchange-correlation contributions[23] have been suggested. The mathematical theory of the Fukui functions derived from *ab initio* theories is also established[24,25] but not yet computed.

In the present work, we propose an alternative method for the evaluation of the analytic Fukui function. The new method has been developed using auxiliary density perturbation theory (ADPT). ADPT is based on a variational fitting of the Coulomb potential[26,27] and the associated approximation of the exchange-correlation energy.[28] Thus, we use the auxiliary density functional method in order to obtain the linear response of the density,[29,30] e.g., the Fukui function. This new formulation is highly efficient because of the advantages of using ADPT and would facilitate the calculation of analytic Fukui functions on much larger systems.

This paper is organized as follows. In Sec. II the new

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method for the Fukui function evaluation is described. Computational details are given in Sec. III. In Sec. IV, we discuss some results that show the accuracy of the approach and compare them with other calculations found in the literature. It is also demonstrated how it corrects not only qualitative errors in the prediction of electrophilic centers. Finally, an outlook and conclusions are presented in Sec. V.

II. METHOD

In this section we describe the formulation of the new method. First, the analytic calculation of the Fukui function is revised. Then specific details of the new approach are given. For simplicity, the derivation assumes a closed-shell system.

A. Fukui function via linear response

Our interest is to compute the Fukui function defined as the limit

$$f^{\pm}(\mathbf{r}) \equiv \lim_{\Delta N \to 0^{\pm}} \frac{\rho_{N+\Delta N}(\mathbf{r}) - \rho_N(\mathbf{r})}{\Delta N}. \tag{2}$$

This expression reflects peculiarity of derivatives of $\rho(\mathbf{r})$ with respect to N at integer values of N. Left and right derivatives yield different results. Therefore, in general, we will deal with the evaluation of two functions: $f^{-}(\mathbf{r})$ useful for the prediction of nucleophilic centers and $f^{+}(\mathbf{r})$ used to locate electrophilic centers.

We restrict ourselves to the evaluation of this derivative in the Kohn–Sham DFT[2,4] framework. The electronic density is given by the fictitious, noninteracting reference system,

$$\rho(\mathbf{r}) = \sum_q n_q |\varphi_{\mathbf{q}}(\mathbf{r})|^2. \tag{3}$$

Here, the functions $\{\varphi_q(\mathbf{r})\}$ are the Kohn–Sham molecular orbitals (MOs) and $\{n_q\}$ is the corresponding set of orbital occupation numbers. In most implementations, MOs are expanded as linear combinations of atomic basis functions,

$$\varphi_q(\mathbf{r}) = \sum_\mu C_{\mu q} \mu(\mathbf{r}), \tag{4}$$

where $\mu(\mathbf{r})$ represents the atomic basis functions and $C_{\mu q}$ are the MO coefficients used to build the $\mathbf{C}$ matrix. The description of the electronic density by atomic orbitals is then given by

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

where $P_{\mu\nu}$ represents an element of the atomic orbital density matrix. This matrix is given by

$$\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^{\dagger}, \tag{6}$$

being $\mathbf{n}$ a diagonal matrix whose nonzero entries correspond to the electron occupation numbers of the canonical orbitals. Derivatives of the density matrix with respect to the total number of electrons in the system are calculated in a straightforward way,

$$\frac{\partial \mathbf{P}}{\partial N} = \mathbf{C}\frac{\partial \mathbf{n}}{\partial N}\mathbf{C}^{\dagger} + \frac{\partial \mathbf{C}}{\partial N}\mathbf{n}\mathbf{C}^{\dagger} + \mathbf{C}\mathbf{n}\frac{\partial \mathbf{C}^{\dagger}}{\partial N}. \tag{7}$$

Following Michalak *et al.*,[11] we separate the so-called frontier and relaxation contributions to the latter equation,

$$\frac{\partial \mathbf{P}}{\partial N} = \mathbf{P}^F + \mathbf{P}^R. \tag{8}$$

The frontier contribution is given by

$$\mathbf{P}^F = \mathbf{C}\frac{\partial \mathbf{n}}{\partial N}\mathbf{C}^{\dagger} = \mathbf{C}\Delta\mathbf{n}\mathbf{C}^{\dagger}, \tag{9}$$

where $\Delta\mathbf{n}$ plays the role of a perturbation and describes the change in the MO occupation numbers. This quantity is provided as an input to the calculation. One may assume that electrons are to be removed/added from/to a single valence orbital or from a set of them, depending on the information available for the system under consideration. In most cases a change of ± 1 in the occupation of a frontier orbital and a change of 0 in the rest of the orbitals will produce a good prediction of reactive centers using the resulting Fukui function. The remaining terms in Eq. (7) account for the relaxation contribution,

$$\mathbf{P}^R = \frac{\partial \mathbf{C}}{\partial N}\mathbf{n}\mathbf{C}^{\dagger} + \mathbf{C}\mathbf{n}\frac{\partial \mathbf{C}^{\dagger}}{\partial N}. \tag{10}$$

Restriction of the variation in orbital occupations to a single frontier MO has been suggested.[11] Such assumption may have a clearer interpretation, however, the restriction to a single MO is not necessary. Furthermore, in some systems the variation in the electronic density with respect to the number of electrons might not be described well because of this restriction. Therefore, we decided to implement a more general approach where more than one, possibly all, MOs may change their occupation number,

$$\frac{\partial \mathbf{n}}{\partial N} = \begin{pmatrix} \Delta n_1 & 0 & \cdots \\ 0 & \Delta n_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{11}$$

An example of a possible application of this feature is found in systems with degeneracy in the highest occupied MO where for all of them one could use an equal fractional change in the number of electrons. In general, this feature is meant to give flexibility for analysis. The nature of the distribution will depend on the purpose of the application.

The variation in MO coefficients with respect to the total number of electrons, as required in Eq. (10), can be obtained by standard techniques such as the solution of the coupled perturbed Hartree–Fock/Kohn–Sham equations.[14–21] An alternative approach is the density-matrix-based method of McWeeny *et al.*[31–35] Here we are proposing the use of ADPT[29,30] as an efficient, reliable alternative method for evaluation of the Fukui function.

B. Auxiliary DFT

Before the evaluation of linear response of the density matrix, it is necessary to understand the way how this matrix is calculated and its relation to other quantities found in

Kohn–Sham DFT. Our new proposal requires the use of variational fitting of the Coulomb potential[26,27] and the further evaluation of the exchange-correlation energy using the auxiliary density.[28] The auxiliary density is given as a linear combination of a second set of functions—distinct from those of Eq. (4)—namely, the auxiliary functions $k(\mathbf{r})$,

$$\tilde{\rho}(\mathbf{r}) = \sum_k x_k k(\mathbf{r}), \tag{12}$$

where the tilde is used to distinguish the auxiliary density from the actual density of Eq. (5). A number of auxiliary functions, here labeled with k or l, are introduced. The fitting coefficients x_k are calculated from an extremum condition,[26]

$$\sum_l \langle k \| l \rangle x_l = \sum_{\mu,\nu} P_{\mu\nu} \langle \mu\nu \| k \rangle. \tag{13}$$

Here $\langle k \| l \rangle$ and $\langle \mu\nu \| k \rangle$ denote, respectively, two- and three-index electron repulsion integrals.[36] For convenience we adopt the definition of the Coulomb vector,[36]

$$J_k(\mathbf{P}) \equiv \sum_{\mu,\nu} P_{\mu\nu} \langle \mu\nu \| k \rangle, \tag{14}$$

and the Coulomb charge density matrix,

$$G_{kl} \equiv \langle k \| l \rangle. \tag{15}$$

Thus, Eq. (13) is equivalent to

$$\mathbf{G}\mathbf{x} = \mathbf{J}(\mathbf{P}). \tag{16}$$

When the auxiliary density is used for the evaluation of the exchange-correlation energy functional, the Kohn–Sham matrix is given by[28]

$$K_{\mu\nu} = H_{\mu\nu} + \sum_k (x_k + z_k) \langle k \| \mu\nu \rangle, \tag{17}$$

where $H_{\mu\nu}$ contains the one-electron contributions and the z_k are exchange-correlation fitting coefficients,

$$z_k \equiv \sum_l G_{kl}^{-1} \langle l | v_{xc} \rangle. \tag{18}$$

The principal change in the self-consistent field (SCF) process originating from the use of the auxiliary density lies in the way the Kohn–Sham matrix is built.

C. ADPT

Differentiation of the variational condition for fitting the Coulomb potential, Eq. (16), yields a way to obtain the auxiliary density response when the orbital density response is known. Because the Coulomb vector is a linear function of the density matrix elements in Eq. (14),

$$\mathbf{G}\frac{\partial \mathbf{x}}{\partial N} = \mathbf{J}\left(\frac{\partial \mathbf{P}}{\partial N}\right) = \mathbf{J}(\mathbf{P}^F) + \mathbf{J}(\mathbf{P}^R). \tag{19}$$

Evaluation of $\mathbf{J}(\mathbf{P}^F)$ is easily realized by substitution of Eq. (9) into Eq. (14). In fact, the same FORTRAN 90 routine is used for evaluation of Eq. (14) in the SCF and for the evaluation of $\mathbf{J}(\mathbf{P}^F)$ in our implementation. A modified version of the DEMON2K program[37] includes now this method. Efficient, previously reported techniques[38] may be employed advantageously. For the evaluation of $\mathbf{J}(\mathbf{P}^R)$, the formula obtained by McWeeny[31] can be adapted,

$$\mathbf{P}^R = \sum_{i,a} \frac{2}{\epsilon_i - \epsilon_a} \mathbf{c}_i^\dagger \frac{\partial \mathbf{K}}{\partial N} \mathbf{c}_a (\mathbf{c}_i \mathbf{c}_a^\dagger + \mathbf{c}_a \mathbf{c}_i^\dagger), \tag{20}$$

where i and a label occupied and virtual orbitals, respectively. Orbital energies are symbolized with ϵ. Substitution of Eq. (20) into Eq. (14) yields

$$J_k(\mathbf{P}^R) = \sum_{i,a} \frac{4}{\epsilon_i - \epsilon_a} c_i^\dagger \frac{\partial \mathbf{K}}{\partial N} \mathbf{c}_a \langle ia \| k \rangle, \tag{21}$$

being $\langle ia \| k \rangle$ the MO representation of three-index electron repulsion integrals. The response of the Kohn–Sham matrix is obtained by differentiation of Eq. (17),

$$\frac{\partial K_{\mu\nu}}{\partial N} = \sum_k \left(\frac{\partial x_k}{\partial N} + \frac{\partial z_k}{\partial N} \right) \langle k \| \mu\nu \rangle. \tag{22}$$

Therefore,

$$J_k(\mathbf{P}^R) = \sum_l \left(\frac{\partial x_l}{\partial N} + \frac{\partial z_l}{\partial N} \right) \sum_{i,a} \langle l \| ia \rangle \frac{4}{\epsilon_i - \epsilon_a} \langle ia \| k \rangle. \tag{23}$$

This result leads us to the definition of the Coulomb coupling matrix,[30]

$$A_{kl} = \sum_{i,a} \langle l \| ia \rangle \frac{1}{\epsilon_i - \epsilon_a} \langle ia \| k \rangle. \tag{24}$$

The final formula for the evaluation of $\mathbf{J}(\mathbf{P}^R)$ is

$$\mathbf{J}(\mathbf{P}^R) = 4\mathbf{A}\left(\frac{\partial \mathbf{x}}{\partial N} + \frac{\partial \mathbf{z}}{\partial N} \right). \tag{25}$$

Derivatives of the exchange-correlation fitting coefficients are obtained after differentiation of Eq. (18),

$$\frac{\partial z_k}{\partial N} = \sum_{l,m} G_{kl}^{-1} \langle l | \Gamma(\mathbf{r}, \mathbf{r}') | m \rangle \frac{\partial x_m}{\partial N}, \tag{26}$$

where $\Gamma(\mathbf{r}, \mathbf{r}')$ is the exchange-correlation kernel. For the case of a local functional

$$\Gamma(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta^2 E_{xc}[\tilde{\rho}]}{\delta\tilde{\rho}(\mathbf{r})\, \delta\tilde{\rho}(\mathbf{r}')}. \tag{27}$$

In the generalized gradient approximation (GGA), Eq. (26) remains valid, but Eq. (27) is modified. Therefore, the evaluation of the integrals $\langle l | \Gamma(\mathbf{r}, \mathbf{r}') | m \rangle$ changes. Thus, for the local density approximation and GGA, the final equation system is

$$\left[\frac{1}{4}\mathbf{G} - \mathbf{A}(\mathbf{1} + \mathbf{G}^{-1}\boldsymbol{\Gamma}) \right] \frac{\partial \mathbf{x}}{\partial N} = \frac{1}{4}\mathbf{J}(\mathbf{P}^F). \tag{28}$$

The only difference between Eq. (28) and that required for evaluation of polarizabilities or analytic vibrational frequencies lies in the inhomogeneous term or the perturbation vector. Thus, Eq. (28) can be used for efficient evaluation of the auxiliary density response.

TABLE I. Accuracy of Fukui function calculated with the approximated density in the exchange-correlation energy functional

		Condensed Fukui function					
		Numeric				Analytic	
		$E_{xc}[\rho]$		$E_{xc}[\bar{\rho}]$		$E_{xc}[\bar{\rho}]$	
Molecule	Atom	f_A^+	f_A^-	f_A^+	f_A^-	f_A^+	f_A^-
H_2O	H	0.5649	0.1372	0.5650	0.1364	0.5708	0.1505
	O	−0.1297	0.7256	−0.1301	0.7273	−0.1430	0.6990
HCN[a]	H	0.1109	0.1502	0.1114	0.1504	0.1193	0.1599
	C	0.6481	0.4440	0.6480	0.4441	0.6137	0.5378
	N	0.2409	0.4058	0.2406	0.4055	0.2670	0.3022
H_2CO	H	0.1435	0.2141	0.1425	0.2134	0.1388	0.2262
	C	0.4753	0.1731	0.4788	0.1751	0.4742	0.1659
	O	0.2377	0.3987	0.2363	0.3981	0.2488	0.3817
HCCH	H	0.0686	0.1198	0.0678	0.1186	0.0730	0.1202
	C	0.4314	0.3802	0.4322	0.3814	0.4270	0.3798
FCCF	C	0.4891	0.3069	0.4897	0.3071	0.4485	0.3292
	F	0.0107	0.1931	0.0102	0.1929	0.0515	0.1708
NH_3	H	0.4472	0.1444	0.4469	0.1441	0.4581	0.1579
	N	−0.3399	0.5667	−0.3390	0.5679	−0.3777	0.5261
$MeNH_2$	H(N)	0.3991	0.1239	0.4000	0.1235	0.4428	0.1424
	N	−0.2589	0.3518	−0.2614	0.3529	−0.3317	0.3543
	C	−0.0477	0.0326	−0.0442	0.0340	0.0579	0.0154
$EtNH_2$	$C(CH_2)$	−0.0049	−0.0076	−0.0038	−0.0066	−0.1400	−0.0283
	$C(CH_3)$	0.0232	0.0299	0.0238	0.0302	0.1199	0.0235
	N	0.3777	0.3167	0.3779	0.3170	−0.1932	0.3753
$HONH_2$	N	−0.1843	0.4000	−0.1843	0.4010	0.2840	0.4120
	O	−0.0318	0.2426	−0.0328	0.2429	−0.0205	0.2015
	H(N)	0.3753	0.1319	0.3750	0.1314	0.0992	0.1489
	H(O)	0.4657	0.0921	0.4672	0.0914	0.5380	0.0886
$MeONH_2$	C	−0.0172	−0.0105	−0.0148	−0.0093	0.1599	−0.0204
	O	−0.0121	0.1855	−0.0128	0.1853	0.0083	0.1394
	H(N)	0.1498	0.0755	0.1489	0.0750	0.1201	0.0699
	N	−0.2059	0.3508	−0.2075	0.3519	0.2806	0.3737
MeOH	C	−0.0145	0.0491	−0.0092	0.0508	0.1440	0.0054
	O	−0.1085	0.4029	−0.1103	0.4036	−0.1591	0.4505
	H(O)	0.5767	0.1035	0.5775	0.1028	0.6662	0.1238
Average $\|\Delta\|$[b]		0.0000	0.0000	0.0012	0.0008	⋯	⋯
Average $\|\Delta\|$[c]		⋯	⋯	0.1000	0.0253	0.0000	0.0000

[a]A level shift of 0.1 was used to achieve convergence for the anion of HCN.
[b]The reference is the numerical method with $E_{xc}[\rho]$.
[c]The reference is the analytical method with $E_{xc}[\bar{\rho}]$.

Recall that although this response is very similar to the Fukui function, it is not recommend interpreting it as an approximate Fukui function. Equations (20), (22), and (26) should be used to recover $\mathbf{P}^R$.

III. COMPUTATIONAL DETAILS

All calculations were done using the DEMON2K program.[37] The implementation of the analytic Fukui function was realized by extending the functionality of version 2.3 of DEMON2K. All structures used in this work correspond to optimized geometries at the VWN/DZVP/A2 (Refs. 39 and 40) level. The auxiliary density was used for the evaluation of the exchange-correlation energy functional during the structure optimizations. A medium grid with adaptive generation[41,42] was used. The principal characteristic of these grids is how the number of grid points used on each atom is adapted to the system under study and, therefore, low cost grids with high accuracy are achieved.

Unless otherwise specified, calculations of Fukui functions were realized using the DZVP basis and the GEN-A2* (Refs. 43 and 44) auxiliary function set.

IV. RESULTS AND DISCUSSION

First, we tested the effect of the auxiliary functions for the evaluation of the exchange-correlation energy on the Fukui function. For this purpose, we calculated condensed Fukui function values, $f_A^{\pm}$ with ($E_{xc}[\tilde{\rho}]$) and without ($E_{xc}[\rho]$) this approximation. The results are listed in Table I. Numerical differentiation was used to obtain these results, i.e., neutral and ionic systems were calculated and the condensed Fukui functions were obtained using the Mulliken partition scheme. As can be seen in Table I, the values of the con-

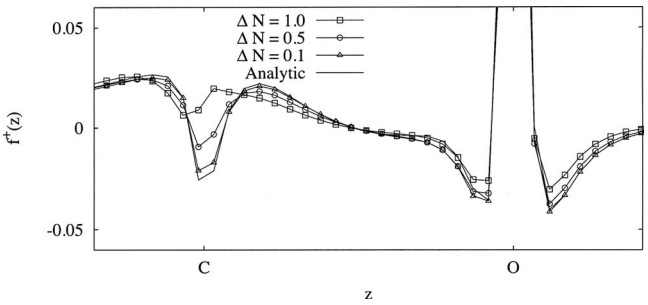

FIG. 1. Fukui function $f^+(\mathbf{r})$ of MeOH along the C–O bond axis. Comparison between numerical method with $E_{xc}[\rho]$ and the here proposed analytic method with $E_{xc}[\tilde{\rho}]$.

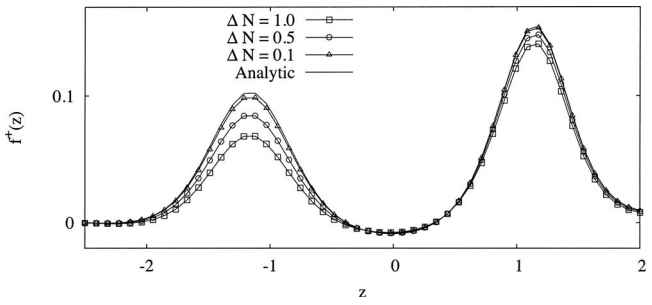

FIG. 2. Fukui function $f^+(\mathbf{r})$ of H_2CO along a line parallel to the C–O bond, 0.5 a.u. above the molecular plane. C is located at −1.147 714 and O at 1.146 803.

densed Fukui functions calculated with these two numerical methods are in very good agreement between them. Average absolute deviations is only 0.001 a.u.. Thus, the use of the auxiliary density for the calculation of exchange-correlation functionals does not present any danger to the quality of condensed Fukui functions.

Table I contains also the condensed Fukui functions $f_A^{\pm}$ calculated with the analytical method proposed here. The average absolute deviations of numerical condensed Fukui functions with respect to the analytical methods are of 0.1 for f_A^+ and 0.025 for f_A^-. Note that the error from the use of numerical differentiation is much larger the one of the approximations proposed here. Therefore, overall the accuracy improves. Notice also that the function f_A^+ has much larger deviations than those of f_A^-.

Clearly, qualitative errors found in numeric methods for the prediction of electrophilic centers with f_A^+ in $EtNH_2$ and $MeONH_2$ are corrected by the analytic method.

For the particular case of methanol a plot of the Fukui function $f^+(\mathbf{r})$ along the C–O bond axis is shown in Fig. 1. The numerical method using $E_{xc}[\rho]$ is calculated with integer and fractional charges. The use of partial charges was realized with the transition operator method[45–47] by adding electrons to the lowest unoccupied MO during the SCF. Using a recently reported strategy[48] the transition operator method was implemented in the DEMON2K program.[37] Comparison to the new analytical method with $E_{xc}[\tilde{\rho}]$ shows that the limit for $\Delta N \rightarrow 0^+$ converges to the result of the new method. Therefore, our method is more reliable than the numerical differentiation even with $E_{xc}[\rho]$.

From Table I and Fig. 1 it is possible to conclude that reactivity predictions will be improved using the analytical approach. Our experience shows that moderate-size, auxiliary function set GEN-A2 suffices to obtain reliable results for condensed Fukui function values.

To compare with previous work[11] we calculated the Fukui function $f^+(\mathbf{r})$ for H_2CO. As shown in Fig. 2, the analytic curve corresponds to the limit of the numerical results with $E_{xc}[\tilde{\rho}]$ when the step size approaches zero. Note that this Fig. 2 corresponds to Fig. 6(a) in the work Michalak *et al.*[11] The auxiliary set GEN-A2 was used for the calculations associated with this plot. It is important to remark how the inclusion of exchange-correlation terms corrects the analytic curve, making it coincide with the limit of numerical calculations.

V. CONCLUSIONS

An approach for the evaluation of Fukui functions with ADPT has been derived and implemented. In contrast to the standard response method, the implementation of this method is very simple. The resulting method has a formal N^4 arithmetic scaling. It practically removes storage demands for memory demand scales quadratically with N. Thus, evaluation of Fukui functions in analytic form is now available for much larger systems.

It has been demonstrated that the approximations used here are accurate enough for the calculation of Fukui functions and the subsequent prediction of reactive centers. Qualitative errors found in numerical method are corrected with the new method. Inclusion of the exchange-correlation response is important, as can be seen in Fig. 2. Thus, we have proposed a way to efficiently evaluate Fukui functions while minimizing human errors and eliminating artifacts of the numerical method. The present formulation has been described and coded in a widely used program for the benefit of the chemical community. The new method has been implemented in a private version of the DEMON2K program[37] and can be made available to the scientific community upon request to R.F.-M.

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