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REGULAR ARTICLE

Computing the Fukui function from ab initio quantum chemistry: approaches based on the extended Koopmans' theorem

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Abstract The extended Koopmans' theorem is related to Fukui function, which measures the change in electron density that accompanies electron attachment and removal. Two approaches are used, one based on the extended Koopmans' theorem differential equation and the other based directly on the expression of the ionized wave function from the extended Koopmans' theorem. It is observed that the Fukui function for electron removal can be modeled as the square of the first Dyson orbital, plus corrections. The possibility of useful generalizations to the extended Koopmans' theorem is considered; some of these extensions give approximations, or even exact expressions, for the Fukui function for electron attachment.

Keywords Fukui function · Dyson orbital · Extended Koopmans' theorem · Conceptual density-functional theory

1 Introduction and background

Over the last two decades, density-functional theory (DFT) has emerged as the method of choice for routine calculations in quantum chemistry, especially for larger systems. The primary reason for this emergence is indubitably the fact that more rigorous wave-function based techniques cannot compete with DFT if one measures average accuracy per unit computational cost. Another reason, however, is that the language of DFT lends itself to chemical interpretation [1–3]. The science of interpreting chemical results with DFT, usually called conceptual density-functional theory, supersedes conventional approaches based on molecular orbitals or resonance because it makes contact with density-functional theory, which is in principle exact. The reactivity indicators of conceptual DFT, then, fully accommodate the effects of orbital relaxation and electron correlation. Studies suggest that these effects are sometimes very important [4–6].

However, the reactivity indicators associated with conceptual DFT are usually computed at a relatively low level of theory, typically Kohn–Sham DFT with approximate exchange-correlation functionals. It is well known that these methods give poor predictions of reaction barriers and thus, while they are generally adequate for conceptual purposes, they are not robust [7,8]. There is no reason, however, not to use more accurate, wave-function based, methods to compute the reactivity indicators of Kohn–Sham DFT. Most of the key reactivity indicators are readily computed if the energies and electron densities of the system, its cation, and its anion are known. Specifically, this is enough information to compute the chemical potential, μ [9], and the chemical hardness, η [10], using the quadratic model for the energy [10]

$$\mu = -\frac{I+A}{2} = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \tag{1}$$

$$\eta = I - A = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \tag{2}$$

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Alternatively, the chemical potential and chemical hardness can be computed using the zero-temperature grand canonical ensemble ansatz, wherein the derivative discontinuity of the energy produces discontinuities in the chemical potential [11–15],

$$\mu^{-} = -I = \left(\frac{\partial E}{\partial N}\right)^{-}_{v(\mathbf{r})} \tag{3}$$

$$\mu^{+} = -A = \left(\frac{\partial E}{\partial N}\right)^{+}_{v(\mathbf{r})} \tag{4}$$

and the chemical hardness

$$\eta(M) = (I - A)\delta(M - N) \quad (N - 1 < M < N + 1). \tag{5}$$

In Eqs. (1)–(5), I denotes the vertical ionization potential,

$$I = E\big[v(\mathbf{r}); N - 1\big] - E[v(\mathbf{r}); N], \tag{6}$$

and A denotes the vertical electron affinity,

$$A = E[v(\mathbf{r}); N] - E\big[v(\mathbf{r}); N + 1\big], \tag{7}$$

of the N-electron system at the equilibrium geometry of the N-electron system. In density-functional theory parlance, we say that the external potential, $v(\mathbf{r})$, is held constant as we change the number of electrons. From the chemical potential and the chemical hardness, one can compute other quantities like the electrophilicity [16], nucleofugality [3,17], and electrofugality [3,17].

The chemical potential and chemical hardness are global reactivity indicators and describe the overall reactivity of the molecule. In order to determine the most reactive places in a molecule, one needs local indicators. The key local indicators in density-functional theory are the electrostatic potential [18,19]

$$\Phi(\mathbf{r}) = -v(\mathbf{r}) - \int \frac{\rho_N(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{8}$$

and the Fukui functions [20–22],

$$f^{-}(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^{-}_{v(\mathbf{r})} \tag{9}$$

$$f^{+}(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^{+}_{v(\mathbf{r})}. \tag{10}$$

Here, $\rho_M(\mathbf{r})$ represents the electron density of the M-electron system evaluated, as before, at the geometry of the N-electron system.

In addition to the preceding indices, there is growing interest in the spin-dependent indices, where the number of α-spin and β-spin electrons is allowed to vary independently [23]. An alternative approach to spin-dependent DFT reactivity indicators, is to consider not only the total number of electrons as an independent variable, but also the number of unpaired electrons($N_S = N_\alpha - N_\beta$) [24,28]. However, the latter scheme addresses changes in the multiplicity of the system (that is, changes in N_S) while maintaining the same total number of electrons, N. Such changes are related to molecular excitation, rather than electrophilic/nucleophilic reactions, and although they can be computed from the indicators based on N_α and N_β [29], they will not be considered here. For this reason, we choose the former approach, where N_α and N_β are allowed to vary independently. In this paper we adopt the convention that β-spin is the minority spin channel, so removing a β-spin electron corresponds to increasing the spin-multiplicity of the systems, while removing an α-spin electron corresponds to reducing the spin-multiplicity. Spin-dependent chemical potentials can then be defined as

$$\mu_\alpha^{-} = -I_\alpha = \left(\frac{\partial E}{\partial N_\alpha}\right)^{-}_{v(\mathbf{r})} = E\big[v; N_\alpha - 1, N_\beta\big] - E\big[v; N_\alpha, N_\beta\big] \tag{11}$$

$$\mu_\alpha^{+} = -A_\alpha = \left(\frac{\partial E}{\partial N_\alpha}\right)^{+}_{v(\mathbf{r})} = E\big[v; N_\alpha, N_\beta\big] - E\big[v; N_\alpha + 1, N_\beta\big] \tag{12}$$

with similar formulae for the β-spin indicators. [There are also formulae corresponding to the quadratic model, Eqs. (1) and (2).] In Eqs. (11) and (12), $E\big[v; M_\alpha, M_\beta\big]$ denotes the energy of the system with M_α α-spin electrons and M_β β-spin electrons, evaluated with the external potential $v(\mathbf{r})$. There are also spin-dependent Fukui functions. Allowing $\mathbf{z} = (\mathbf{r}, s)$ to denote both the spin and spatial coordinates of the electrons, one has

$$f_\alpha^{-}(\mathbf{z}) = \rho_{N_\alpha, N_\beta}(\mathbf{z}) - \rho_{N_\alpha - 1, N_\beta}(\mathbf{z}) = \left(\frac{\partial \rho(\mathbf{z})}{\partial N_\alpha}\right)^{-}_{v(\mathbf{r})} \tag{13}$$

$$f_\alpha^{+}(\mathbf{z}) = \rho_{N_\alpha + 1, N_\beta}(\mathbf{z}) - \rho_{N_\alpha, N_\beta}(\mathbf{z}) = \left(\frac{\partial \rho(\mathbf{z})}{\partial N_\alpha}\right)^{+}_{v(\mathbf{r})}. \tag{14}$$

where $\rho_{M_\alpha, M_\beta}(\mathbf{z})$ denotes the electron spin-density of the system with M_α α-spin electrons and M_β β-spin electrons. It is important to note that there are *eight* spin-dependent Fukui functions. Corresponding to Eq. (13), there are $f_\alpha^{-}(\mathbf{r}, \alpha)$ and $f_\alpha^{-}(\mathbf{r}, \beta)$, which measure how the spatial distribution of the α-spin and β-spin electrons, respectively, changes, when an α-spin electron is removed from the system. Similarly, there are two Fukui functions corresponding to Eq. (14), plus four more functions arising from the analogues of Eqs. (13) and (14) for describing changes in the number of β-spin electrons.

Most commonly, all of these reactivity indicators are computed by first performing a Kohn–Sham DFT geometry optimization on the N-electron system, followed by subsequent single-point calculations on the $N \pm 1$ electron systems. Since single point calculations are much faster than geometry optimizations, the most expensive step in this calculation is the initial geometry determination.

The situation could be different if we were using conventional, wave-function based, quantum chemistry to compute the reactivity indicators. Especially for larger systems, we would probably start by performing a geometry optimization at a low level of theory (perhaps, again, Kohn–Sham DFT). Then we would need to perform single-point calculations for the N, $N+1$, and $N-1$ electron systems. Due to the surpassing computational cost of conventional ab initio quantum chemistry, the three single-point calculations would dominate the computational cost. We could, however, cut the cost by a factor of three if we could extract the reactivity indicators from one single-point calculation. Recently, we have shown how this can be done using electron propagator theory [30]. While propagator calculations have the same scaling as their analogues in conventional ab initio theory, they tend to be a little more costly. (E.g., computing the second-order propagator is a little more expensive than a conventional MP2 calculation.)

Electron propagator theory gives very convenient expressions for the electrostatic potential, chemical hardness, and chemical potential, but less convenient forms for the Fukui functions. Here we investigate whether the extended Koopmans' theorem[31–36] might give more reasonable expressions for the Fukui functions.

The extended Koopmans' theorem (EKT) approximates the $N-1$-electron wave function of a system by removing an optimized orbital, $\phi_k^{\mathrm{EKT}}(\mathbf{z}_N)$, from the N-electron system [32,33],

$$\Psi_{k,N-1}^{\mathrm{EKT}}(\mathbf{z}_1,\ldots\mathbf{z}_{N-1}) = \int \phi_k^{\mathrm{EKT}}(\mathbf{z}_N)\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_N \tag{15}$$

Here $\mathbf{z}_i$ denotes both the space and spin coordinates of electron i, $\Psi_{k,M}$ denotes the wave function of the kth excited state of the M-electron system, and integration with respect to $\mathbf{z}$ is a useful shorthand for integration over the spatial coordinates of the electron and summing over electron spin. $\phi_k^{\mathrm{EKT}}(\mathbf{z})$ is defined so that the $N-1$-electron wave functions on the left-hand-side (LHS) of Eq. (15) are orthonormal.

The approximate ionization potential associated with the EKT can then be written as

$$I_k^{\mathrm{EKT}} = \frac{\left\langle \int \phi_k^{\mathrm{EKT}}(\mathbf{z}_N)\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_N \middle| \int \phi_k^{\mathrm{EKT}}(\mathbf{z}_N)\left(\hat{H}_{N-1}-\hat{H}_N\right)\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_N \right\rangle_{1\ldots N-1}}{\left\langle \int \phi_k^{\mathrm{EKT}}(\mathbf{z}_N)\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_N \middle| \int \phi_k^{\mathrm{EKT}}(\mathbf{z}_N)\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_N \right\rangle_{1\ldots N-1}} \tag{16}$$

where $\hat{H}_M$ denotes the Hamiltonian of the M-electron system, and thus

$$\hat{H}_{N-1} - \hat{H}_N = \frac{\nabla_N^2}{2} - v(\mathbf{z}_N) - \sum_{j=1}^{N-1}\frac{1}{\left|\mathbf{r}_j - \mathbf{r}_N\right|}. \tag{17}$$

It is important to note that, using Eq. (16), we can express the ionization potential in terms of the first ($k=1$) and second ($k=2$) order density matrices of the N-electron system

$$\Gamma_k\left(\mathbf{z}_1,\ldots,\mathbf{z}_k;\mathbf{z}'_1,\ldots\mathbf{z}'_k\right) = \left(\frac{N_\alpha!N_\beta!}{(N_\alpha-m_\alpha)!\left(N_\beta-m_\beta\right)!}\right)$$
$$\times \iint \Psi_{0,N}^*\left(\mathbf{z}'_1,\ldots,\mathbf{z}'_k,\mathbf{z}_{k+1},\ldots\mathbf{z}_N\right)\Psi_{0,N}$$
$$\times(\mathbf{z}_1,\ldots\mathbf{z}_N)\mathrm{d}\mathbf{z}_{k+1}\ldots\mathrm{d}\mathbf{z}_N, \tag{18}$$

where m_α and m_β are the number of α-spin and β-spin indices,

$$m_\sigma \equiv \sum_{i=1}^{k}\delta_{\sigma\sigma_i} = \sum_{i=1}^{k}\delta_{\sigma\sigma'_i} \tag{19}$$

Specifically, we have

$$I_k^{\mathrm{EKT}} = \frac{\left(\frac{2}{(N-1)}\right)\iint\iint \phi_k^*(\mathbf{z}'_1)\phi_k(\mathbf{z}_1)\left(\frac{\nabla_1^2}{2} - v(\mathbf{z}_1) - \frac{N-1}{|\mathbf{r}_2-\mathbf{r}_1|}\right)\Gamma_2\left(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}_2\right)\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1\mathrm{d}\mathbf{z}_2}{\iint \phi_k^*(\mathbf{z}'_1)\phi_k(\mathbf{z}_1)\Gamma_1(\mathbf{z}_1;\mathbf{z}'_1)\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1}. \tag{20}$$

Determining the orbitals, $\phi_k^{\mathrm{EKT}}(\mathbf{z})$, for which Eq. (20) is stationary gives approximations to the stationary state wave functions of the $N-1$-electron system and the ionization potentials pertaining thereto. These stationary values and orbitals are usually determined using the equations

$$\int \phi_k^{\mathrm{EKT}}(\mathbf{z}'_1)\left(\frac{-\nabla_1^2}{2}+v(\mathbf{z}_1)\right)\Gamma_1(\mathbf{z}_1,\mathbf{z}'_1)\mathrm{d}\mathbf{z}'_1 \\ +2\iint \phi_k^{\mathrm{EKT}}(\mathbf{z}'_1)\frac{\Gamma_2(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{z}'_1\mathrm{d}\mathbf{z}_2 \\ =(-I_k)\int \phi_k^{\mathrm{EKT}}(\mathbf{z}'_1)\Gamma_1(\mathbf{z}_1,\mathbf{z}'_1)\mathrm{d}\mathbf{z}'_1. \qquad (21)$$

Since the density matrices are commonly available at the conclusion of a single-point calculation, the EKT ionization potentials and orbitals are readily computed at the end of the computational procedure. Because the EKT equations are single-particle equations, the cost of finding the EKT orbitals is negligible compared to the cost of the underlying ab initio method [37,38].

The remarkable feature of the extended Koopmans' theorem is that, for a Coulombic system, the lowest ionization potential is exact and the extended-Koopmans' theorem orbital is simply related to the Dyson orbital [33,36,39–44],

$$g_0(\mathbf{z}_N)=\sqrt{N}\iiint \Psi^*_{0,N-1}(\mathbf{z}_1,\ldots,\mathbf{z}_{N-1}) \\ \times\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N)\mathrm{d}\mathbf{z}_1\ldots\mathrm{d}\mathbf{z}_{N-1}, \qquad (22)$$

according to

$$g_0(\mathbf{z})=\frac{\delta_{\sigma\sigma'}}{\sqrt{m_0N_\sigma}}\int \Gamma_1(\mathbf{z},\mathbf{z}')\phi_0^{\mathrm{EKT}}(\mathbf{z}')\mathrm{d}\mathbf{z}'. \qquad (23)$$

The number $0\leqslant m_0\leqslant 1$ is the pole strength, and is chosen so that the Dyson orbitals are normalized. N_σ is the number of electrons with the same spin as the EKT-orbital and the Dyson spin-orbital. (The two orbitals always have the same spin.)

It seems that many of the higher ionization potentials and Dyson orbitals from the EKT are also exact [40,45,46], but there is no general proof. When the N-electron state is not a singlet, the proof of exactness can be generalized to the lowest multiplicity-raising and multiplicity-lowering ionizations. More generally, Pernal and Cioslowski have shown that every state obtained from the extended Koopmans' theorem is exact if the $N-1$st order reduced density matrix has no zero eigenvalues (i.e., Γ_{N-1} is strictly positive definite) [41]. Based on this result, one might expect that for systems with no symmetry and relatively long-range interparticle forces (so that the motion of electrons is significantly correlated), Γ_{N-1} will be positive definite and all the stationary values of Eq. (20) correspond to exact ionization potentials and Dyson orbitals [41].

2 Extended Koopmans' theorem approach to the Fukui function for electron removal

The Fukui function from below (also called the nucleophilic Fukui function) can be determined directly from the extended Koopmans' theorem: using the definition of the Fukui function and the EKT wave function [Eq. (15)] one has

$$f_\alpha^-(\mathbf{r}_1,\alpha)=\rho_{N_\alpha,N_\beta}(\mathbf{r}_1,\alpha)-\rho_{N_\alpha-1,N_\beta}(\mathbf{r}_1,\alpha) \\ =N_\alpha\iiint \Psi^*_{0,N}(\mathbf{r}_1,\alpha,\mathbf{z}_2\ldots\mathbf{z}_N)\Psi_{0,N}(\mathbf{r}_1,\alpha,\mathbf{z}_2\ldots\mathbf{z}_N)\mathrm{d}\mathbf{z}_2\ldots\mathrm{d}\mathbf{z}_N \\ -(N_\alpha-1)\iiint \Psi^*_{0,N-1}(\mathbf{r}_1,\alpha,\ldots,\mathbf{z}_{N-1})\Psi_{0,N-1}(\mathbf{r}_1,\alpha,\ldots\mathbf{z}_{N-1})\mathrm{d}\mathbf{z}_2\ldots\mathrm{d}\mathbf{z}_{N-1} \\ =\frac{2N_\alpha}{N_\alpha(N_\alpha-1)}\int \Gamma_2(\mathbf{r}_1,\alpha,\mathbf{z}_N;\mathbf{r}_1,\alpha,\mathbf{z}'_N)\delta_{\sigma_N\alpha}\delta(\mathbf{r}_N-\mathbf{r}'_N)\mathrm{d}\mathbf{z}_N\mathrm{d}\mathbf{z}'_N \\ -\frac{2(N_\alpha-1)}{N_\alpha(N_\alpha-1)}\iint \left(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_N,\alpha)\right)^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_N,\alpha)\Gamma_2(\mathbf{r}_1,\alpha,\mathbf{z}_N;\mathbf{r}_1,\alpha,\mathbf{z}'_N)\mathrm{d}\mathbf{z}_N\mathrm{d}\mathbf{z}'_N \\ =\iint \Gamma_2(\mathbf{r}_1,\alpha,\mathbf{z}_2;\mathbf{r}_1,\alpha,\mathbf{z}'_2)\begin{bmatrix}\dfrac{2\delta_{\sigma_2\alpha}\delta_{\sigma'_2\alpha}\delta(\mathbf{r}_2-\mathbf{r}'_2)}{N_\alpha-1} \\ -\dfrac{2(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_2,\alpha))^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)}{N_\alpha}\end{bmatrix}\mathrm{d}\mathbf{z}_2\mathrm{d}\mathbf{z}'_2 \qquad (24)$$

with a similar form for the β-spin component, $f_\alpha^-(\mathbf{r},\beta)$,

$$\begin{aligned}
f_\alpha^-(\mathbf{r}_1,\beta) &= \rho_{N_\alpha,N_\beta}(\mathbf{r}_1,\beta) - \rho_{N_\alpha-1,N_\beta}(\mathbf{r}_1,\beta) \\
&= N_\beta \iiint \Psi^*_{0,N}(\mathbf{r}_1,\beta,\mathbf{z}_2\ldots\mathbf{z}_N)\Psi_{0,N}(\mathbf{r}_1,\beta,\mathbf{z}_2\ldots\mathbf{z}_N)\mathrm{d}\mathbf{z}_2\ldots\mathrm{d}\mathbf{z}_N \\
&\quad -N_\beta\iiint \Psi^*_{0,N-1}(\mathbf{r}_1,\beta,\ldots\mathbf{z}_{N-1})\Psi_{0,N-1}(\mathbf{r}_1,\beta,\ldots\mathbf{z}_{N-1})\mathrm{d}\mathbf{z}_2\ldots\mathrm{d}\mathbf{z}_{N-1} \\
&= \frac{2N_\beta}{N_\alpha N_\beta}\int \Gamma_2(\mathbf{r}_1,\beta,\mathbf{z}_N;\mathbf{r}_1,\beta,\mathbf{z}'_N)\delta_{\sigma_N\alpha}\delta(\mathbf{r}_N-\mathbf{r}'_N)\mathrm{d}\mathbf{z}_N\mathrm{d}\mathbf{z}'_N \\
&\quad -\frac{2N_\beta}{N_\alpha N_\beta}\iint \left(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_N,\alpha)\right)^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_N,\alpha)\Gamma_2(\mathbf{r}_1,\beta,\mathbf{z}_N;\mathbf{r}_1,\beta,\mathbf{z}'_N)\mathrm{d}\mathbf{z}_N\mathrm{d}\mathbf{z}'_N \\
&= \frac{2}{N_\alpha}\iint \Gamma_2(\mathbf{r}_1,\beta,\mathbf{z}_2;\mathbf{r}_1,\beta,\mathbf{z}'_2)\begin{bmatrix}\delta_{\sigma_2\alpha}\delta_{\sigma'_2\alpha}\delta(\mathbf{r}_2-\mathbf{r}'_2) \\ -\left(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_2,\alpha)\right)^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)\end{bmatrix}\mathrm{d}\mathbf{z}_2\mathrm{d}\mathbf{z}'_2
\end{aligned} \tag{25}$$

There are similar formulae for $f_\beta^-(\mathbf{z})$.

Next, we perform a cumulant decomposition of the second-order reduced density matrix [47],

$$\begin{aligned}
2\Gamma_2(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}'_2) &= \Gamma_1(\mathbf{z}_1,\mathbf{z}'_1)\Gamma_1(\mathbf{z}_2,\mathbf{z}'_2) \\
&\quad -\Gamma_1(\mathbf{z}_1,\mathbf{z}'_2)\Gamma_1(\mathbf{z}_2,\mathbf{z}'_1) + \Delta^{(2)}(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}'_2).
\end{aligned} \tag{26}$$

Inserting these relations into Eq. (24), we have

$$\begin{aligned}
f_\alpha^-(\mathbf{r}_1,\alpha) &= \rho_{N_\alpha,N_\beta}(\mathbf{r}_1,\alpha)\left(\frac{N_\alpha}{N_\alpha-1}-\frac{N_\alpha}{N_\alpha}\right) \\
&\quad -\frac{\int\Gamma_1(\mathbf{r}_1,\alpha;\mathbf{r}_2,\alpha)\Gamma_1(\mathbf{r}_2,\alpha;\mathbf{r}_1,\alpha)\mathrm{d}\mathbf{r}_2}{N_\alpha-1} \\
&\quad +\frac{1}{N_\alpha}\left|\int\Gamma_1(\mathbf{r}_1,\alpha;\mathbf{r}_2,\alpha)\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)\mathrm{d}\mathbf{r}_2\right|^2 \\
&\quad +\iint\Delta^{(2)}(\mathbf{r}_1,\alpha,\mathbf{z}_2;\mathbf{r}_1,\alpha,\mathbf{z}'_2) \\
&\quad \times\begin{bmatrix}\dfrac{2\delta_{\sigma_2\alpha}\delta_{\sigma'_2\alpha}\delta(\mathbf{r}_2-\mathbf{r}'_2)}{N_\alpha-1} \\ -\dfrac{2(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_2,\alpha))^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)}{N_\alpha}\end{bmatrix}\mathrm{d}\mathbf{z}_2\mathrm{d}\mathbf{z}'_2
\end{aligned} \tag{27}$$

and so

$$\begin{aligned}
f_\alpha^-(\mathbf{r}_1,\alpha) &= m_0|g_0(\mathbf{r}_1,\alpha)|^2 \\
&\quad +\frac{\rho_{N_\alpha,N_\beta}(\mathbf{r}_1,\alpha)-\int\Gamma_1(\mathbf{r}_1,\alpha;\mathbf{r}_2,\alpha)\Gamma_1(\mathbf{r}_2,\alpha;\mathbf{r}_1,\alpha)\mathrm{d}\mathbf{r}_2}{N_\alpha-1} \\
&\quad +\iint\Delta^{(2)}(\mathbf{r}_1,\alpha,\mathbf{z}_2;\mathbf{r}_1,\alpha,\mathbf{z}'_2) \\
&\quad \times\begin{bmatrix}\dfrac{2\delta_{\sigma_2\alpha}\delta_{\sigma'_2\alpha}\delta(\mathbf{r}_2-\mathbf{r}'_2)}{N_\alpha-1} \\ -\dfrac{2(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_2,\alpha))^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)}{N_\alpha}\end{bmatrix}\mathrm{d}\mathbf{z}_2\mathrm{d}\mathbf{z}'_2
\end{aligned} \tag{28}$$

Similarly, for the β-spin component,

$$\begin{aligned}
f_\alpha^-(\mathbf{r}_1,\beta) &= \frac{1}{N_\alpha}\iint\Delta^{(2)}(\mathbf{r}_1,\beta,\mathbf{z}_2;\mathbf{r}_1,\beta,\mathbf{z}'_2) \\
&\quad \times\begin{bmatrix}\delta_{\sigma_2\alpha}\delta_{\sigma'_2\alpha}\delta(\mathbf{r}_2-\mathbf{r}'_2) \\ -\left(\phi_0^{\mathrm{EKT}}(\mathbf{r}'_2,\alpha)\right)^*\phi_0^{\mathrm{EKT}}(\mathbf{r}_2,\alpha)\end{bmatrix}\mathrm{d}\mathbf{z}_2\mathrm{d}\mathbf{z}'_2.
\end{aligned} \tag{29}$$

In the preceding two derivations, we have used the fact that

$$N_\sigma\delta_{\sigma\sigma'} = \int\left(\phi_0^{\mathrm{EKT}}(\mathbf{z}')\right)^*\Gamma_1(\mathbf{z},\mathbf{z}')\phi_0^{\mathrm{EKT}}(\mathbf{z})\mathrm{d}\mathbf{z}, \tag{30}$$

where σ denotes the spin of the EKT orbitals. This equation, which just says that EKT orbitals with different spin are orthogonal with respect to the metric defined by the first-order density matrix, directly follows from the normalization condition for the $N-1$-electron wave function. The final expression, Eq. (28), expresses the Fukui function as the square of the Dyson orbital, plus a correction. A result of the same form arises in electron propagator theory [30].

The natural orbitals are orthogonal and are related to the first-order reduced density matrix by the formula

$$\begin{aligned}
\Gamma_1(\mathbf{z},\mathbf{z}') &= \sum_{i=0}^{\infty} n_i\chi_i^*(\mathbf{z}')\chi_i(\mathbf{z}) \\
&= \sum_{i=0}^{\infty} n_i\left|\sigma_i\right\rangle\chi_i^*(\mathbf{r}')\chi_i(\mathbf{r})\left\langle\sigma_i\right|.
\end{aligned} \tag{31}$$

It follows from Eq. (31) that the spin-components of the first-order density matrix are

$$\begin{aligned}
\Gamma_1\left(\mathbf{r},\alpha,\mathbf{r}',\alpha\right) &\equiv \sum_{i=0}^{\infty} n_i\delta_{\sigma_i\alpha}\chi_i^*\left(\mathbf{r}'\right)\chi_i(\mathbf{r}) \\
\Gamma_1\left(\mathbf{r},\beta,\mathbf{r}',\beta\right) &\equiv \sum_{i=0}^{\infty} n_i\delta_{\sigma_i\beta}\chi_i^*\left(\mathbf{r}'\right)\chi_i(\mathbf{r}) \\
\Gamma_1\left(\mathbf{r},\alpha,\mathbf{r}',\beta\right) &\equiv 0 \\
\Gamma_1\left(\mathbf{r},\beta,\mathbf{r}',\alpha\right) &\equiv 0 \qquad (32)
\end{aligned}$$

Using the definition of the natural spin orbitals and the fact that the natural orbital occupation numbers are always between zero and one, one sees that the second term in the last equality of Eq. (28) is never negative:

$$\begin{aligned}
&\int \Gamma_1\left(\mathbf{z},\mathbf{z}'\right)\Gamma_1\left(\mathbf{z}',\mathbf{z}\right)\mathrm{d}\mathbf{z}' \\
&\quad = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} n_i n_j \chi_i(\mathbf{z})\chi_j(\mathbf{z})\int \chi_i\left(\mathbf{z}'\right)\chi_j\left(\mathbf{z}'\right)\mathrm{d}\mathbf{z}' \\
&\quad = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} n_i n_j \chi_i(\mathbf{z})\chi_j(\mathbf{z})\delta_{ij} = \sum_{i=0}^{\infty} n_i^2\left|\chi_i(\mathbf{z})\right|^2 \\
&\quad \leqslant \Gamma_1(\mathbf{z},\mathbf{z}) = \rho_{N_\alpha,N_\beta}(\mathbf{r},\sigma) \qquad (33)
\end{aligned}$$

(Moreover, the second term is only zero when the wave function is a Slater determinant, in which all the natural orbital occupation numbers are either zero or one.) There is decisive numerical evidence that the Fukui function is sometimes negative [48], and clearly this behavior cannot be described without including the term that depends on the density-matrix cumulant, $\Delta^{(2)}$. The reader may wish to verify that both Eqs. (28) and (29) are exact for noninteracting electrons, where $\Delta^{(2)} = 0, m_0 = 1$, and $g_0(\mathbf{z})$ is equal to the HOMO orbital.

An alternative expression for the Fukui function can be derived directly from the equations for the extended Koopmans' theorem orbitals, Eq. (21). Multiplying both sides of Eq. (21) by $\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*$ and integrating, we obtain

$$\begin{aligned}
-\delta_{\sigma_1\sigma_1'}N_{\sigma_1}I_k &= \iint \phi_k^{\mathrm{EKT}}\left(\mathbf{z}'_1\right)\left(\frac{-\nabla_1^2}{2}+v(\mathbf{z}_1)\right) \\
&\qquad \times\Gamma_1\left(\mathbf{z}_1,\mathbf{z}'_1\right)\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1 \\
&\quad +2\iiint \phi_k^{\mathrm{EKT}}\left(\mathbf{z}'_1\right)\frac{\Gamma_2\left(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}_2\right)}{\left|\mathbf{r}_1-\mathbf{r}_2\right|} \\
&\qquad \times\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1\mathrm{d}\mathbf{z}_2 \qquad (34)
\end{aligned}$$

and so

$$\begin{aligned}
f^-\left(\mathbf{z}''\right) &= \frac{1}{N_{\sigma_1}}\iint \phi_k^{\mathrm{EKT}}\left(\mathbf{z}'_1\right)\left(\delta\left(\mathbf{z}_1-\mathbf{z}''\right)\right)\Gamma_1\left(\mathbf{z}_1,\mathbf{z}'_1\right) \\
&\qquad \times\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1 \\
&\quad +\frac{2}{N_{\sigma_1}}\iiint \frac{\phi_k^{\mathrm{EKT}}\left(\mathbf{z}'_1\right)\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*}{\left|\mathbf{r}_1-\mathbf{r}_2\right|} \\
&\qquad \times\frac{\delta\Gamma_2\left(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}_2\right)}{\delta v(\mathbf{z}'')}\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1\mathrm{d}\mathbf{z}_2 \\
&= \sqrt{\frac{m_0}{N_{\sigma''}}}\left(\phi_k^{\mathrm{EKT}}\left(\mathbf{z}''\right)\right)^* g_0\left(\mathbf{z}''\right) \\
&\quad +\frac{2}{N_{\sigma_1}}\iiint \frac{\phi_k^{\mathrm{EKT}}\left(\mathbf{z}'_1\right)\left(\phi_k^{\mathrm{EKT}}(\mathbf{z}_1)\right)^*}{\left|\mathbf{r}_1-\mathbf{r}_2\right|} \\
&\qquad \times\frac{\delta\Gamma_2\left(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}_2\right)}{\delta v(\mathbf{z}'')}\mathrm{d}\mathbf{z}_1\mathrm{d}\mathbf{z}'_1\mathrm{d}\mathbf{z}_2 \qquad (35)
\end{aligned}$$

Insofar as this formula depends on difficult to compute perturbations of the second-order reduced density matrix, it is probably not very useful. However, the first term in Eq. (35) is probably more closely normalized than the first term in Eq. (28). That is, we suspect that neglecting the higher-order terms in Eq. (35) may be more justified than it is for Eq. (28).

3 Generalized extended Koopmans' theorem approach to the Fukui function for electron addition

In the previous section, we showed how the change in the electron density associated with electron removal can be computed from ab initio wave function theory using the extended Koopmans' theorem. Owing to the exactness of the extended Koopmans' theorem, our results were exact. The situation is not so favorable when we are examining electron addition. If we make an approximation to the $N+1$ electron wave function that is analogous to (15), i.e. we add an orbital to the N-electron wave function and then antisymmetrize the result,

$$\begin{aligned}
\Psi_{k,N+1}^{\mathrm{EKT}}\left(\mathbf{z}_1,\ldots\mathbf{z}_{N-1}\right) = \mathcal{A}\Big(&\Psi_{0,N}(\mathbf{z}_1,\ldots,\mathbf{z}_N) \\
&\times\varphi_k^{\mathrm{EKT}}\left(\mathbf{z}_{N+1}\right)\Big) \qquad (36)
\end{aligned}$$

then correlations between the additional electron and the original electrons have been neglected. This ansatz was already present in the original paper of Smith and Day [32], but owing to the expected inaccuracies, it has not been thoroughly tested.

Equations like Eq. (36) are most readily stated in second quantization. If we write the orbital as a linear combination of basis functions,

$$\varphi_k^{\mathrm{EKT}}(\mathbf{z}) = \sum_i c_{k,i}^{\mathrm{EKT}} \chi_i(\mathbf{z}) \tag{37}$$

then Eq. (36) can be written in terms of the creation operators for these orbitals,

$$\left|\Psi_{k,N+1}^{\mathrm{EKT}}\right\rangle = \sum_i c_{k,i}^{\mathrm{EKT}} a_i^{+} \left|\Psi_{0,N}\right\rangle. \tag{38}$$

Insofar as the main shortcoming of this expression is the fact that the additional electron is not correlated with the original electrons, one might imagine constructing a $N+1$ electron wave function by first annihilating an electron, and then adding two electrons. In this way, the additional electrons are partially correlated. The resulting expression for the $N+1$ electron wave function is

$$\left|\Psi_{k,N+1}^{\mathrm{EKT}}\right\rangle = \sum_{i_1 i_2} \sum_{j} c_{k,j i_1 i_2}^{\mathrm{EKT}} a_{i_2}^{+} a_{i_1}^{+} a_j \left|\Psi_{0,N}\right\rangle, \tag{39}$$

which is reminiscent of the particle–particle–hole terms that contribute to the electron affinity in electron propagator theory [49,50].

This general ansatz provides the basis for an entire family of extended-Koopmans' theorems. One starts with a fundamental expression for the wave function of the $N+P-Q$ electron system,

$$\left|\Psi_{k,N+P-Q}^{\mathrm{EKT}}\right\rangle = \sum_{i_1 i_2 \ldots i_P} \sum_{j_1 j_2 \cdots j_Q} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} a_{i_P}^{+} \cdots a_{i_2}^{+} a_{i_1}^{+} a_{j_Q} \cdots a_{j_2} a_{j_1} \left|\Psi_{0,N}\right\rangle, \tag{40}$$

and then seeks to minimize the energy. The "generalized extended Koopmans' theorem" is then derived in the usual way, starting with the energy of the $N+P-Q$ electron system

$$E_{k,N+P-Q} = \underbrace{\min}_{c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}}} \frac{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} \mathcal{H} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]}{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]} \tag{41}$$

where $\mathcal{H}$ denotes the second-quantized Hamiltonian. Next one subtracts off the energy of the N electron system,

$$\begin{aligned} I_{k,N+P-Q} &= \underbrace{\min}_{c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}}} \left(\frac{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} \mathcal{H} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]}{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]} - E_{0,N} \right) \\ &= \underbrace{\min}_{c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}}} \left(\begin{array}{l} \dfrac{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} \mathcal{H} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]}{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]} \\ - \dfrac{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \mathcal{H} \middle| \Psi_{0,N} \right\rangle \end{array}\right]}{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}^{\mathrm{EKT}} c_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P}^{\mathrm{EKT}} \\ \times\left\langle \Psi_{0,N} \middle| a_{j'_1}^{+} \cdots a_{j'_Q}^{+} a_{i'_1} \cdots a_{i'_P} a_{i_P}^{+} \cdots a_{i_1}^{+} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array}\right]} \end{array} \right) \end{aligned} \tag{42}$$

The second line of this equation holds only if $\Psi_{0,N}$ is the exact eigenfunction of this second-quantized Hamiltonian. Equation (42) is then rearranged into the usual second-quantized expression of the extended Koopmans' theorem,

$$I_{k,N+P-Q} = \underbrace{\min}_{c^{\mathrm{EKT}}_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P}} \left(\frac{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c^{\mathrm{EKT}}_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P} c^{\mathrm{EKT}}_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P} \\ \times \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} \cdots a^{+}_{j'_Q} a_{i'_1} \cdots a_{i'_P} \left[\mathcal{H}, a^{+}_{i_P} \cdots a^{+}_{i_1} a_{j_Q} \cdots a_{j_1} \right] \middle| \Psi_{0,N} \right\rangle \end{array} \right]}{\displaystyle\sum_{i_1 \ldots i_P} \sum_{j_1 \ldots j_Q} \sum_{i'_1 \ldots i'_P} \sum_{j'_1 \ldots j'_Q} \left[\begin{array}{l} c^{\mathrm{EKT}}_{k,j_1 j_2 \ldots j_Q i_1 i_2 \ldots i_P} c^{\mathrm{EKT}}_{k,j'_1 j'_2 \ldots j'_Q i'_1 i'_2 \ldots i'_P} \\ \times \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} \cdots a^{+}_{j'_Q} a_{i'_1} \cdots a_{i'_P} a^{+}_{i_P} \cdots a^{+}_{i_1} a_{j_Q} \cdots a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{array} \right]} \right). \quad (43)$$

The resulting expressions are exact when $P = 0$; in that case, only electron removal is modeled, and the method is exact because, for a specific choice of coefficients, it will give the same result as sequentially applying the usual extended Koopmans' theorem for one-electron removal Q times. All of the cases with $P = 0$ were addressed in the original paper by Morrell et al. [33]. The expression is also exact when $Q = N$ (in which case the method reduces to full configuration interaction). The most interesting cases are when P and Q are both small, but Q is greater than zero (so that the additional electron is correlated). The $P = Q = 2$ case might be interesting for studying excitations. The $P = 1, Q = 0$ case was first explored by Smith and Day [32]. The $P = 2, Q = 1$ case [cf. Eq. (39)] is the case of greatest interest here. Solving this case requires that one solve the eigenvalue problem

$$\mathbf{Vc} = \mathbf{nc} \quad (44)$$

where

$$\begin{aligned} \mathbf{V} &\equiv \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a_{i'_1} a_{i'_2} \left[\mathcal{H}, a^{+}_{i_2} a^{+}_{i_1} a_{j_1} \right] \middle| \Psi_{0,N} \right\rangle \\ \mathbf{n} &\equiv \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a_{i'_1} a_{i'_2} a^{+}_{i_2} a^{+}_{i_1} a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{aligned} \quad (45)$$

replace the usual extended Koopmans' theorem matrices. Using the commutation relations for creation and annihilation operators,

$$\mathbf{V} = a^{+}_{j'_1} a_{i'_1} a_{i'_2} \begin{pmatrix} \delta_{r,i_2} \delta_{s,i_1} a^{+}_{r'} a^{+}_{s'} a_{j_1} - \delta_{s,i_2} \delta_{r,i_1} a^{+}_{r'} a^{+}_{s'} a_{j_1} \\ -\delta_{r,i_2} a^{+}_{r'} a^{+}_{s'} a^{+}_{i_1} a_s a_{j_1} + \delta_{s,i_2} a^{+}_{r'} a^{+}_{s'} a^{+}_{i_1} a_r a_{j_1} \\ -\delta_{j_1,r'} a^{+}_{i_2} a^{+}_{i_1} a^{+}_{s'} a_s a_r + \delta_{j_1,s'} a^{+}_{i_2} a^{+}_{i_1} a^{+}_{r'} a_s a_r \\ +\delta_{r,i_1} a^{+}_{r'} a^{+}_{s'} a^{+}_{i_2} a_s a_{j_1} - \delta_{s,i_1} a^{+}_{r'} a^{+}_{s'} a^{+}_{i_2} a_r a_{j_1} \end{pmatrix} \quad (46)$$

$$\begin{aligned} \mathbf{n} = {} & \delta_{i'_2,i_2} \delta_{i'_1,i_1} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & -\delta_{i'_2,i_1} \delta_{i'_1,i_2} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & -\delta_{i'_2,i_2} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a^{+}_{i_1} a_{i'_1} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & -\delta_{i'_1,i_1} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a^{+}_{i_2} a_{i'_2} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & +\delta_{i'_2,i_1} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a^{+}_{i_2} a_{i'_1} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & +\delta_{i'_1,i_2} \left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a^{+}_{i_1} a_{i'_2} a_{j_1} \middle| \Psi_{0,N} \right\rangle \\ & +\left\langle \Psi_{0,N} \middle| a^{+}_{j'_1} a^{+}_{i_2} a^{+}_{i_1} a_{i'_1} a_{i'_2} a_{j_1} \middle| \Psi_{0,N} \right\rangle \end{aligned} \quad (47)$$

and so this theory requires computing the third- and fourth-order reduced density matrices. This is better than the naïve expectation (normally modeling a three-electron process for a two-electron reduced Hamiltonian operator would require the fifth-order reduced density matrix), but it is still not a very practical approach. One could, however, derive (necessarily approximate) results for the Fukui function for electron addition based on this ansatz.

There is an alternative that requires only the third-order reduced density matrix. Instead of considering the $P = 2, Q = 1$ generalized EKT for the molecule itself, we could investigate the $P = 0, Q = 2$ generalized EKT for the $N + 1$ electron system at the optimal geometry for the N-electron system. This resulting method is more difficult that the usual extended Koopmans' theorem because the third-order reduced density matrix is needed and also because one is not looking for optimal orbitals, but optimal geminals. Since we are only interested in the $N - 1$ electron ground state, we can use a more efficient procedure. First, we determine the Fukui function from above for the N-electron system by evaluating the Fukui function from below for the $N+1$ electron system at appropriate geometry for N electrons. We then form the second-order reduced density matrix for the ground state of the N-electron from the third-order reduced density matrix of the $N+1$-electron system,

$$\Gamma_2^{(N)}(\mathbf{z}_1,\mathbf{z}_2;\mathbf{z}'_1,\mathbf{z}'_2) = \left(\frac{3}{N-2}\right)\int\cdots\int\left(\phi_{k=0}^{\mathrm{EKT}}(\mathbf{z}_3)\right)^*\phi_{k=0}^{\mathrm{EKT}}(\mathbf{z}'_3) \times\Gamma_3^{(N+1)}(\mathbf{z}_1,\mathbf{z}_2,\mathbf{z}_3;\mathbf{z}'_1,\mathbf{z}'_2,\mathbf{z}'_3)\mathrm{d}\mathbf{z}_3\mathrm{d}\mathbf{z}'_3. \qquad (48)$$

The usual extended Koopmans' theorem equations, (21), are now solved, and the Fukui functions from below are determined using the expressions in Sect. 2. Though the spin-resolved Fukui functions from below are readily obtained by this procedure, determining the spin-resolved Fukui functions from above requires information about excited states of the $N+1$-electron system.

This method is a practical alternative to conventional finite difference formulae for the Fukui functions when the third-order reduced density matrix can be computed from one's computational method. Using the second-order reduced density matrix of the ground state of the anion will produce two of the four Fukui functions from above (the Fukui functions linking the ground-state spin densities of the neutral species and the anion) using the ordinary extended Koopmans theorem. Next, one uses Eq. (48) to determine the ground-state second order density matrix of the neutral system from the third-order reduced density matrix of the anion. All four Fukui functions from below are then computed. When the ground state of the neutral molecule is a closed-shell species, the spin-symmetry ensures that the two doublet states of the anion are equivalent, and so the remaining two Fukui functions from above are identical to the ones that were computed in the first step of this procedure. When the ground state of the neutral molecule has multiplicity $S \neq 1$, the two pairs of Fukui functions from above are distinct and density matrices for the ground-state anions of multiplicity $S+1$ and $S-1$ would both be needed.

4 Conclusion

Perhaps the most attractive feature of conceptual density-functional theory, as compared to alternative qualitative descriptions of chemical reactivity based on molecular orbitals or resonance structures, is its mathematical rigor. Conceptual DFT is, in principle, exact. Nonetheless, most applications of conceptual DFT employ approximate density-functionals or other similar models (e.g., Hartree–Fock) based on independent-electron descriptions. For most purposes, this is adequate. However, thorough and rigorous investigations of conceptual density-functional theory require moving to more accurate computational methods. As a first step in this direction, we recently showed how to compute chemical reactivity indicators using electron propagator theory [30]. For describing electron removal processes, however, the extended Koopmans' theorem seems to give superior accuracy to electron propagator theory. This is certainly true for extremely accurate full-CI implementations, but may also be true for approximate implementations based on conventional many-body approaches to quantum chemistry (e.g., perturbation theory) [38].[1]

Thus motivated, in this paper we have showen how the extended Koopmans' theorem can be used to compute ionization potentials and Fukui functions for electron removal (Sect. 2). Electron affinities and Fukui functions for electron attachment can also be computed, although the most efficient way to do so is to start from a calculation of the $N+1$ electron system (Sect. 3). This general approach provides access to the entire family of conceptual DFT indices that are relevant for describing electron-transfer processes. In all cases, the primary computational cost is that associated with the underlying ab initio calculation for the second-order reduced density matrix. (The third-order reduced density matrix must be computed when both electron attachment and electron removal are of interest. However, because the number of ambiphilic reagents is rather small, information about the third-order density matrix is rarely needed.) Once the second-order reduced density matrix is obtained, the extended Koopmans' theorem is solved. From the results, one can construct not only the usual Fukui functions, but all the related spin-Fukui function indicators. In light of results from electron propagator theory [30], it is unsurprising that the change in σ-spin electron density associated with removal of a electron of the same spin can be written in terms of square of the Dyson orbital for removal of a σ-spin electron, plus a correction related to orbital relaxation and electron correlation [cf. Eq. (28)]. The change in σ-spin density when an electron of opposite spin is removed depends only on the cumulant of the second-order reduced density matrix [cf. Eq. (29)]; this is unsurprising if one considers that opposite-spin electrons move independently whenever this term is set equal to zero. Though it is most

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[1] We, however, would prefer propagator theory methods to extended Koopmans' theorem methods when many-body expansion techniques are used, mostly since propagator methods have been more thoroughly tested, but also because propagator methods may be more efficient computationally.

computationally efficient to treat electron attachment to the N-electron system as electron detachment from the $N+1$-electron system, one may protest that such an approach is inelegant, and not in keeping with the spirit of the extended Koopmans' theorem. For that reason, we have derived a family of generalized extended Koopmans' theorems which can be used to model electron attachment with greater accuracy than the original approach proposed by Smith and Day [32]. Even the simplest of these approaches uses the *fourth*-order reduced density matrix, and so these results are primarily of academic interest. Nonetheless, the general construction serves to emphasize the ingenuity in the extended Koopmans' theorem construction because it allows one to treat the energy differences (relative to any eigenstate of the N-electron system) of k-electron processes (e.g., removal of one electron with addition of two electrons as a $k = 3$ approach to electron affinities) using only the $k+1$-order reduced density matrix, whereas the $k+2$-order reduced density matrix would be required to construct the energy directly. The dependence of these methods on multiple creation and annihilation operators [cf. Eqs. (40)–(43)] is reminiscent of the forms that arise in the MCEP [51] and MCSTEP [52] methods.

Future work should concentrate on the computational implementation of these ideas and comparison to the usual, more approximate, methods for computing Fukui functions, ionization potentials, and electron affinities. Such comparisons will hopefully establish the general reliability of commonly employed approximations. However, at this stage little of the methodology for computing Fukui functions, chemical potentials, and chemical hardnesses has been thoroughly tested against accurate results. What we do know is that, in general, the existing methods "work", in the sense that they give reasonable agreement with intuitive expectations and experimental findings. Despite the utility of common approaches, maybe even *because* of their utility, it is important to establish a hierarchy of methods for accurately computing chemical reactivity indicators. When common approaches—e.g., Kohn–Sham density-functional theory with approximate exchange-correlation potentials and moderate basis sets,—fail, methods like electron propagator theory and the extended Koopmans' theorem allow one to determine whether the problem is theoretical (conceptual DFT indicators do not work for a given chemical system) or computational (the method used to compute the chemical reactivity indicators is inadequate). The full-CI + extended Koopmans' theorem paradigm [37] rests at the very pinnacle of this hierarchy, and can be used to provide benchmark results for small systems. At lower levels, electron propagator theory and the extended Koopmans' theorem (but using more practical ab initio methods for computing the density matrices [38]) are practical computational approaches for many molecules of chemical interest and should give more accurate results than typical Kohn–Sham DFT calculations of conceptual DFT indicators.

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