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Research paper

An explicit approach to conceptual density functional theory descriptors of arbitrary order

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ABSTRACT

We present explicit formulas for arbitrary-order derivatives of the energy, grand potential, electron density, and higher-order response functions with respect to the number of electrons, and the chemical potential for any smooth and differentiable model of the energy versus the number of electrons. The resulting expressions for global reactivity descriptors (hyperhardnesses and hypersoftnesses), local reactivity descriptors (hyperFukui functions and local hypersoftnesses), and nonlocal response functions are easy to evaluate computationally. Specifically, the explicit formulas for global/local/nonlocal hypersoftnesses of arbitrary order are derived using Bell polynomials. Explicit expressions for global and local hypersoftness indicators up to fifth order are presented.

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1. Motivation

In the density functional theory (DFT) perspective to chemical reactivity, often called conceptual DFT, reactivity indicators are identified as derivatives of the ground-state energy, $E[v;N]$, or the grand potential, $\Omega[v;\mu] = E - \mu N$, with respect to the number of electrons, N, electronic chemical potential, μ, and/or the external potential, $v(\mathbf{r})$ [1–5]. The interpretation of these derivatives is that they measure the sensitivity of a molecule to electron transfer (represented as a perturbation in the number of electrons or chemical potential) and electrostatic interactions (represented as a perturbation of the external potential) with an approaching reagent, and thereby reflect the molecule's susceptibility to chemical reactions.

While traditionally only first- and second-order derivatives have been used, there has been a recent surge of interest in higher-order derivatives [6–14]. The goal of this work is to systematically present general and explicit formulas for the higher-order derivatives that arise in conceptual DFT. We achieve this by developing a recursive formulation, in terms of Bell polynomials, that gives working equations for the high-order descriptors in terms of simpler derivatives. In this way, we derive explicit expressions for global, local and non-local reactivity descriptors up to arbitrary order, many of which are reported here for the first time. The framework can be extended to spin-resolved reactivity indicators [15–17] in the standard way, but this extension will not be discussed here [18,19].

2. Explicit treatment of higher-order response functions

2.1. Energy models

In order for higher-order reactivity models to be meaningful, it is important for the energy to be a smooth function of the number of electrons. While such models are less rigorously justified than

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straight-line interpolations between the ground-state energies for systems with an integer number of electrons [20–22], they are justifiable because a fragment of a reacting system can have fractional charge, and the dependence of the energy on the amount of fractional charge is, based on both computational evidence and theoretical arguments, expected to be smooth [23–27]. Smooth $E(N)$ functions are usually constructed using either the finite-temperature grand canonical ensemble [28–30] or by interpolating the ground-state energies of integer-charged systems with a specified functional form [31–35].

In general, we are given the ground-state energies, $\{E_m\}_{m=1}^{n}$, for a molecule of interest corresponding to different values for the number of electrons, $\{N_m\}_{m=1}^{n}$. These states are then used to construct an ensemble or used as data points for an interpolating function, giving an energy model that depends on some parameters $\{a_m\}_{m=1}^{n}$. The parameters could enter directly into an interpolating function or be weights in an ensemble description, but we will focus mainly on interpolation models in this work. For example, a generalized polynomial interpolation model is [35]

$$E_{\text{model}}[v;N|a_1,a_2,\ldots,a_n] = a_1 + a_2 g(N) + a_3 g(N)^2 + \cdots + a_n g(N)^{n-1} \tag{1}$$

or, more explicitly,

$$E_{\text{model}}[v;N] = \sum_{m=1}^{n} E_m \left(\prod_{l\neq m} \frac{g(N)-g(N_l)}{g(N_m)-g(N_l)} \right) \tag{2}$$

Even in this simplest of all interpolation models, it is clear that the model parameters, $\{a_m\}_{m=1}^{n}$, are highly nonlinear functions of the reference energies. In general, determining the values of the model parameters requires solving a system of nonlinear equations, though sometimes explicit formulas can be derived. In this paper, we will assume that the $E(N)$ model is differentiable at least up to the order of the reactivity descriptors we are interested in. (This implies, for example, that the $g(N)$ function appearing in Eq. (2) must be differentiable up to that same order.)

We will now study how to obtain the explicit expressions for the reactivity descriptors, given an energy model like Eqs. (1) or (2). As such, whenever we take the derivatives of energy or grand potential we will be implicitly referring to a given E versus N model, however, for the sake of simplicity, the sub-index "model" is dropped in the following expressions.

2.2. Global reactivity indicators

The first and second derivatives of the energy with respect to the number of electrons define the electronic chemical potential [36],

$$\mu = \left(\frac{\partial E[v;N]}{\partial N} \right)_{v(\mathbf{r})} \tag{3}$$

and chemical hardness [26],

$$\eta = \left(\frac{\partial^2 E[v;N]}{\partial N^2} \right)_{v(\mathbf{r})} = \left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})} \tag{4}$$

These expressions are readily evaluated for any explicit form of the energy model. Subsequent derivatives with respect to N define the hyperhardnesses [6],

$$\eta^{(k)} = \left(\frac{\partial^{k+1} E[v;N]}{\partial N^{k+1}} \right)_{v(\mathbf{r})} = \left(\frac{\partial^k \mu}{\partial N^k} \right)_{v(\mathbf{r})} \qquad k = 0,1,2,\ldots \tag{5}$$

The "ordinary" hardness is defined as $k = 1$ and the chemical potential can be viewed as the zeroth-order hyperhardness, $k = 0$.

A second family of fundamental global reactivity indicators is defined by differentiating the grand potential with respect to the chemical potential. The negative of the first derivative gives the number of electrons

$$N = -\left(\frac{\partial \Omega[v;\mu]}{\partial \mu} \right)_{v(\mathbf{r})} \tag{6}$$

and the negative of the second derivative is called the global chemical softness because of its relationship to the chemical hardness from Eq. (4) [37],

$$S = -\left(\frac{\partial^2 \Omega[v;\mu]}{\partial \mu^2} \right)_{v(\mathbf{r})} = \left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} = \frac{1}{\eta} \tag{7}$$

The global hypersoftnesses are defined by subsequent derivatives of the grand potential [10],

$$S^{(k)} = -\left(\frac{\partial^{k+1} \Omega[v;\mu]}{\partial \mu^{k+1}} \right)_{v(\mathbf{r})} = \left(\frac{\partial^k N}{\partial \mu^k} \right)_{v(\mathbf{r})} \qquad k = 0,1,2,\ldots \tag{8}$$

The "ordinary" softness is defined as $k = 1$ and the number of electrons can be viewed as the zeroth-order hypersoftness, $k = 0$. The global hypersoftnesses are not easy to evaluate in this form because they are not written as derivatives of the energy with respect to N.

The inverse relationship between the global softness and the chemical hardness is a consequence of the inverse function theorem for derivatives,

$$\left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} = \left[\left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})} \right]^{-1} \tag{9}$$

Expressing $S^{(2)}$ as an energy derivative requires the inverse function theorem for second derivatives,

$$\left(\frac{\partial^2 N}{\partial \mu^2} \right)_{v(\mathbf{r})} = -\frac{\left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} \left(\frac{\partial^2 \mu}{\partial N^2} \right)_{v(\mathbf{r})}}{\left(\left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})} \right)^2} = -\left[\left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} \right]^3 \left(\frac{\partial^2 \mu}{\partial N^2} \right)_{v(\mathbf{r})} \tag{10}$$

Higher-order hypersoftnesses can also be rewritten in terms of the hyperhardnesses using the inverse function theorem for higher-order derivatives, which is a corollary of the Faà di Bruno formula.

The Faà di Bruno formula is the higher-order generalization of the chain rule for derivatives. Given any sufficiently differentiable function $g(\mu)$, we can rewrite its kth derivative with respect to N in terms of its lower-order derivatives with respect to μ and the derivatives of μ with respect to N. Specifically, for $k \geqslant 1$,

$$\begin{aligned} \left(\frac{\partial^k g(\mu)}{\partial N^k} \right)_{v(\mathbf{r})} &= \sum_{j=1}^{k} \left(\frac{\partial^j g}{\partial \mu^j} \right)_{v(\mathbf{r})} \\ &\quad \cdot B_{k,j}\left(\left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})}, \left(\frac{\partial^2 \mu}{\partial N^2} \right)_{v(\mathbf{r})}, \ldots, \left(\frac{\partial^{k-j+1} \mu}{\partial N^{k-j+1}} \right)_{v(\mathbf{r})} \right) \\ &= \sum_{j=1}^{k} \left(\frac{\partial^j g}{\partial \mu^j} \right)_{v(\mathbf{r})} \cdot B_{k,j}(\eta^{(1)}, \eta^{(2)}, \ldots, \eta^{(k-j+1)}) \end{aligned} \tag{11}$$

where $B_{k,j}(x_1, x_2, \ldots, x_{k-j+1})$ denotes the Bell polynomial. To evaluate the global hypersoftnesses in terms of lower-order hypersoftnesses and hyperhardnesses, consider the special case of Eq. (11) defined by $g(\mu) = N$. Then, because

$$\left(\frac{\partial^k N}{\partial N^k} \right)_{v(\mathbf{r})} = \begin{cases} 1 & k = 1 \\ 0 & k \geqslant 2 \end{cases} \tag{12}$$

Eq. (11) implies that for $k \geqslant 2$,

$$\begin{aligned}0 &= \sum_{j=1}^{k}\left(\frac{d^{j}N}{d\mu^{j}}\right)_{v(\mathbf{r})}\cdot B_{k,j}(\eta,\eta^{(2)},\ldots,\eta^{(k-j+1)})\\ &= \sum_{j=1}^{k} S^{(j)}\cdot B_{k,j}(\eta,\eta^{(2)},\ldots,\eta^{(k-j+1)}) \qquad (13)\end{aligned}$$

This can be rearranged into an explicit formula for the hypersoftnesses of orders $k \geqslant 2$,

$$S^{(k)} = -\frac{\sum_{j=1}^{k-1} S^{(j)}\cdot B_{k,j}(\eta,\eta^{(2)},\ldots,\eta^{(k-j+1)})}{B_{k,k}(\eta)} \qquad (14)$$

As it is straightforward to evaluate the hyperhardnesses (cf. Eq. (5)) by differentiating an interpolated energy model, $E_{\text{model}}[v;N]$, it is likewise straightforward to evaluate the global hypersoftnesses using Eq. (14). Equations for global hypersoftnesses up to fifth order are presented in Table 1.

2.3. Local reactivity indicators

The most fundamental local reactivity indicator is the electron density corresponding to the energy model,

$$\rho(\mathbf{r}) = \left(\frac{\delta E}{\delta v(\mathbf{r})}\right)_{N} = \left(\frac{\delta \Omega}{\delta v(\mathbf{r})}\right)_{N} \qquad (15)$$

In Eq. (15) we assume that none of the reference states used to parameterize the model has spatially degenerate ground states [38,39]. Derivatives of the density with respect to N and μ define the local reactivity indicators of conceptual DFT. The first derivative with respect to N is the Fukui function [40–42],

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}, \qquad (16)$$

the second derivative is the dual descriptor [12,14,43],

$$f^{(2)}(\mathbf{r}) = \left(\frac{\partial^{2} \rho(\mathbf{r})}{\partial N^{2}}\right)_{v(\mathbf{r})} \qquad (17)$$

and the subsequent derivatives are usually simply called hyperFukui functions,

$$f^{(k)}(\mathbf{r}) = \left(\frac{\partial^{k} \rho(\mathbf{r})}{\partial N^{k}}\right)_{v(\mathbf{r})} \qquad k = 0,1,2,\ldots \qquad (18)$$

The zeroth-order Fukui function corresponds to the ground state electron density of the N-electron system. Similarly, the derivative of the density with respect to the chemical potential is called the local softness [37],

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_{v(\mathbf{r})} \qquad (19)$$

and its subsequent derivatives are the local hypersoftnesses [10,44],

$$s^{(k)}(\mathbf{r}) = \left(\frac{\partial^{k} \rho(\mathbf{r})}{\partial \mu^{k}}\right)_{v(\mathbf{r})} \qquad k = 0,1,2,\ldots \qquad (20)$$

In the same manner, the zeroth-order softness function corresponds to the ground state electron density of N-electron system. To obtain an easily computable expression for local hypersoftnesses, the above equation can be expressed in terms of hyperFukukui functions by applying the Faà di Bruno formula in Eq. (11) to the function $\rho(\mathbf{r})$,

$$\begin{aligned}\left(\frac{\partial^{k}\rho(\mathbf{r})}{\partial \mu^{k}}\right)_{v(\mathbf{r})} &= \sum_{j=1}^{k}\left(\frac{\partial^{j}\rho(\mathbf{r})}{\partial N^{j}}\right)_{v(\mathbf{r})}\\ &\quad\cdot B_{k,j}\left(\left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})},\left(\frac{\partial^{2} N}{\partial \mu^{2}}\right)_{v(\mathbf{r})},\ldots,\left(\frac{\partial^{k-j+1} N}{\partial \mu^{k-j+1}}\right)_{v(\mathbf{r})}\right) s^{(k)}(\mathbf{r})\\ &= \sum_{j=1}^{k} f^{(j)}(\mathbf{r})\cdot B_{k,j}(S,S^{(2)},\ldots,S^{(k-j+1)})\end{aligned} \qquad (21)$$

Explicit expressions for the local (hyper)softnesses up to fifth order are presented in Table 2.

The local hypersoftnesses integrate to the global hypersoftnesses [10],

$$\int s^{(k)}(\mathbf{r})d\mathbf{r} = B_{k,1}\left(S,S^{(2)},\ldots,S^{(k)}\right) = S^{(k)} \qquad (22)$$

because the hyperFukui functions integrate to either one (for the ordinary Fukui function) or zero (for higher orders),

$$\int f^{(k)}(\mathbf{r})d\mathbf{r} = \begin{cases} N & k = 0\\ 1 & k = 1\\ 0 & k \geqslant 2\end{cases} \qquad (23)$$

Notice that in this notation, the zeroth-order Fukui function, $f^{(0)}(\mathbf{r}) = (\partial^{0}\rho(\mathbf{r})/\partial N^{0})_{v(\mathbf{r})} = \rho(\mathbf{r})$, is the electron density of the N-electron ground state. If the electron density of the interpolation model, as defined from Eq. (24), is not normalized to the number of electrons, then Eq. (12) will not be valid for the energy model and the normalization conditions in Eqs. (22) and (23) will not hold. This, in practice, limits the types of interpolation models that are useful to consider in conceptual DFT [35].

Table 1
Expressions for the global (hyper)softnesses in terms of (hyper)hardnesses.

$$\begin{aligned}S^{(1)} &= (\eta^{(1)})^{-1} = S\\ S^{(2)} &= -\eta^{(2)}S^{3}\\ S^{(3)} &= -\eta^{(3)}S^{4} + 3(\eta^{(2)})^{2}S^{5}\\ S^{(4)} &= -\eta^{(4)}S^{5} + 10\eta^{(2)}\eta^{(3)}S^{6} - 15(\eta^{(2)})^{3}S^{7}\\ S^{(5)} &= -\eta^{(5)}S^{6} + 10(\eta^{(3)})^{2}S^{7} + 15\eta^{(2)}\eta^{(4)}S^{7} - 105(\eta^{(2)})^{2}\eta^{(3)}S^{8} + 105(\eta^{(2)})^{4}S^{9}\end{aligned}$$

Table 2
Expressions for the local (hyper)softnesses in terms of (hyper)Fukui functions.

$$\begin{aligned}s^{(1)}(\mathbf{r}) &= S\cdot f(\mathbf{r})\\ s^{(2)}(\mathbf{r}) &= S^{2}\cdot f^{(2)}(\mathbf{r}) + S^{(2)}\cdot f(\mathbf{r})\\ s^{(3)}(\mathbf{r}) &= S^{3}\cdot f^{(3)}(\mathbf{r}) + (3S)S^{(2)}\cdot f^{(2)}(\mathbf{r}) + S^{(3)}\cdot f(\mathbf{r})\\ s^{(4)}(\mathbf{r}) &= S^{4}\cdot f^{(4)}(\mathbf{r}) + (6S^{2})S^{(2)}\cdot f^{(3)}(\mathbf{r}) + [(4S)S^{(3)} + 3(S^{(2)})^{2}]\cdot f^{(2)}(\mathbf{r}) + S^{(4)}\cdot f(\mathbf{r})\\ s^{(5)}(\mathbf{r}) &= S^{5}\cdot f^{(5)}(\mathbf{r}) + (10S^{3})S^{(2)}\cdot f^{(4)}(\mathbf{r}) + [(10S^{2})S^{3} + 15S(S^{(2)})^{2}]\cdot f^{(3)}(\mathbf{r}) + [(5S)S^{(4)} + 10S^{(2)}S^{(3)}]\cdot f^{(2)}(\mathbf{r}) + S^{(5)}\cdot f(\mathbf{r})\end{aligned}$$

Unlike the global reactivity indicators, directly determining the Fukui function from an energy versus number of electrons model is nontrivial. One starts by determining the electron density corresponding to the energy model. If the explicit dependence of the energy model on the reference energies is known, we can evaluate the model density as a function of the electron densities of the reference states using the chain rule,

$$\begin{aligned}\rho(\mathbf{r}) &= \left(\frac{\delta E_{\text{model}}[v;N]}{\delta v(\mathbf{r})}\right)_N = \sum_{m=1}^{n}\left(\frac{\partial E_{\text{model}}[v;N]}{\partial E_m}\right)_{E_{l\neq m}}\left(\frac{\delta E_m}{\delta v(\mathbf{r})}\right)_N \\ &= \sum_{m=1}^{n}\left(\frac{\partial E_{\text{model}}[v;N]}{\partial E_m}\right)_{E_{l\neq m}}\rho_m(\mathbf{r})\end{aligned} \tag{24}$$

The (hyper)Fukui functions are then evaluated as

$$f^{(k)}(\mathbf{r}) = \sum_{m=1}^{n}\left(\frac{\partial \eta^{(k)}}{\partial E_m}\right)_{E_{l\neq m}}\rho_m(\mathbf{r}) \tag{25}$$

When $\eta^{(k)}$ can be analytically or symbolically evaluated according to Eq. (5) as an explicit function of the reference energies, the (hyper) Fukui functions in Eq. (25) can be evaluated directly. However, in some cases, it may be necessary to numerically evaluate the derivatives in Eq. (25) with finite differences. This occurs when determining the parameters of the energy model requires numerical solution of a system of nonlinear equations. In these cases, it is less efficient to numerically evaluate the derivatives with respect to the reference ground-state energy E_m in Eqs. (24) and (25) than it is to rewrite these expressions so their dependence on model parameters is explicit,

$$\rho(\mathbf{r}) = \sum_{i=1}^{n}\left(\frac{\partial E_{\text{model}}\left[v;N|\{a_i\}_{i=1}^{n}\right]}{\partial a_i}\right)_{a_{j\neq i}}\left\{\sum_{m=1}^{n}\left(\frac{\partial a_i}{\partial E_m}\right)_{E_{l\neq m}}\rho_m(\mathbf{r})\right\} \tag{26}$$

$$f^{(k)}(\mathbf{r}) = \sum_{i=1}^{n}\left(\frac{\partial \eta^{(k)}}{\partial a_i}\right)_{a_{j\neq i}}\left\{\sum_{m=1}^{n}\left(\frac{\partial a_i}{\partial E_m}\right)_{E_{l\neq m}}\rho_m(\mathbf{r})\right\} \tag{27}$$

The derivatives with respect to the model parameters in the outermost sums of Eqs. (26) and (27) can be evaluated analytically, while the derivatives of the model parameters with respect to the reference energies in the innermost sums can be evaluated numerically. Notice that Eq. (25) is just the special case of Eq. (27) where $a_m = E_m$.

2.4. Nonlocal reactivity indicators

Higher-order functional derivatives with respect to the external potential define the nonlocal reactivity indicators. For example, the linear response function [45,46] is defined as

$$\chi(\mathbf{r},\mathbf{r}') = \left(\frac{\delta^2 E}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right)_N, \tag{28}$$

the Fukui response is defined as,

$$f(\mathbf{r},\mathbf{r}') = \left(\frac{\partial \chi(\mathbf{r},\mathbf{r}')}{\partial N}\right)_{v(\mathbf{r})} \tag{29}$$

and the hyperFukui responses for $k > 1$ are defined as

$$f^{(k)}(\mathbf{r},\mathbf{r}') = \left(\frac{\partial^k \chi(\mathbf{r},\mathbf{r}')}{\partial N^k}\right)_{v(\mathbf{r})} \tag{30}$$

The linear response function can be evaluated directly by perturbation theory [47–49], and the (hyper)Fukui responses can then be evaluated using the same approach we used to compute the (hyper)Fukui functions, cf. Eqs. (24)–(27), by replacing electron density of m-electron system with linear response function of m-electron system.

The quadratic,

$$\chi(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \left(\frac{\delta^3 E_{\text{model}}[v;N]}{\delta v(\mathbf{r})\delta v(\mathbf{r}')\delta v(\mathbf{r}'')}\right)_N = \left(\frac{\delta^2 \rho(\mathbf{r})}{\delta v(\mathbf{r}')\, v(\mathbf{r}'')}\right)_N \tag{31}$$

and higher-order density response functions,

$$\begin{aligned}\chi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p) &= \left(\frac{\delta^p E_{\text{model}}[v;N]}{\delta v(\mathbf{r}_1)\delta v(\mathbf{r}_2)\cdots\delta v(\mathbf{r}_p)}\right)_N \\ &= \left(\frac{\delta^{p-1}\rho(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)\delta v(\mathbf{r}_3)\cdots\delta v(\mathbf{r}_p)}\right)_N\end{aligned} \tag{32}$$

and their derivatives with respect to N can be determined by similar techniques to those used for evaluating the (hyper)Fukui functions. Specifically, analogous to Eq. (27), we have an expression for the response functions and their derivatives in terms of the response functions of the reference systems,

$$\begin{aligned}f^{(k)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p) &= \left(\frac{\partial^k \chi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p)}{\partial N^k}\right)_{v(\mathbf{r})} \\ &= \sum_{i=1}^{n}\left(\frac{\partial \eta^{(k)}}{\partial a_i}\right)_{a_{j\neq i}}\left\{\sum_{m=1}^{n}\left(\frac{\partial a_i}{\partial E_m}\right)_{E_{l\neq m}}\chi_m(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p)\right\}\end{aligned} \tag{33}$$

All the response functions at constant number of electrons are normalized to zero

$$\int f^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_p)d\mathbf{r} = 0 \qquad \begin{aligned}p &= 2,3,\ldots \\ k &= 0,1,\ldots\end{aligned} \tag{34}$$

Derivatives of the grand potential with respect to the external potential are more complicated. The analogue of the linear density response function is

$$s(\mathbf{r},\mathbf{r}') = -\left(\frac{\delta^2\Omega}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right)_\mu = -\left(\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_\mu \tag{35}$$

which can be computed from the linear-response function using the Berkowitz-Parr relation [45],

$$s(\mathbf{r},\mathbf{r}') = \frac{f(\mathbf{r})f(\mathbf{r}')}{\eta} - \chi(\mathbf{r},\mathbf{r}') \tag{36}$$

The higher-order responses of the grand potentials are defined as

$$\begin{aligned}s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p) &= (-1)^p\left(\frac{\delta^p\Omega}{\delta v(\mathbf{r}_1)\delta v(\mathbf{r}_2)\cdots\delta v(\mathbf{r}_p)}\right)_\mu \\ &= (-1)^k\left(\frac{\delta^{p-1}\rho(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)\cdots\delta v(\mathbf{r}_p)}\right)_\mu\end{aligned} \tag{37}$$

which is defined so that for $k = 1$, $s(\mathbf{r}) = \rho(\mathbf{r})$ and for $k = 2$ Eq. (37) is obtained. $s^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1})$ can be expressed in terms of derivatives with respect to the number of electrons recursively, starting from Eq. (39). Specifically, using the higher-order extension of the Berkowitz-Parr relation,

$$\begin{aligned}s(\mathbf{r}_1,\ldots,\mathbf{r}_{p+1}) &= -\left(\frac{\delta s(\mathbf{r}_1,\ldots\mathbf{r}_p)}{\delta v(\mathbf{r}_{p+1})}\right)_\mu \\ &= -\left(\frac{\partial s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\partial N}\right)_{v(\mathbf{r})}\left(\frac{\delta N}{\delta v(\mathbf{r}_{p+1})}\right)_\mu - \left(\frac{\delta s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\delta v(\mathbf{r}_{p+1})}\right)_N \\ &= s(\mathbf{r}_{p+1})\left(\frac{\partial s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\partial N}\right)_{v(\mathbf{r})} - \left(\frac{\delta s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\delta v(\mathbf{r}_{p+1})}\right)_N \\ &= \frac{f(\mathbf{r}_{p+1})}{\eta}\left(\frac{\partial s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\partial N}\right)_{v(\mathbf{r})} - \left(\frac{\delta s(\mathbf{r}_1,\ldots,\mathbf{r}_p)}{\delta v(\mathbf{r}_{p+1})}\right)_N\end{aligned} \tag{38}$$

To simplify this expression, one uses the fact that $s^{(k-1)}(\mathbf{r}_1,\ldots,\mathbf{r}_k)$ is already known in terms of the derivatives of the energy with respect to N (at constant $v(\mathbf{r})$) and $v(\mathbf{r})$ (at constant N), and so the derivatives on the right-hand-side of Eq. (38) can be evaluated. In the same way, the derivatives of $s^{(l)}(\mathbf{r}_1,\ldots,\mathbf{r}_{l+1})$ with respect to the chemical potential can be evaluated, recursively, using the extension of Eq. (21),

$$\begin{aligned} s^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_{p+1}) &= \left(\frac{\partial^k s(\mathbf{r}_1,\ldots,\mathbf{r}_{p+1})}{\partial\mu^k}\right)_{v(\mathbf{r})} \\ &= \sum_{j=1}^{k}\left(\frac{\partial^j s(\mathbf{r}_1,\ldots,\mathbf{r}_{p+1})}{\partial N^j}\right)_{v(\mathbf{r})} \\ &\quad \cdot B_{k,j}\left(S, S^{(2)},\ldots,S^{(k-j+1)}\right) \end{aligned} \tag{39}$$

The derivatives that appear on the right-hand-side are evaluated from the expression one obtains from Eq. (38).

The higher-order responses of the grand potential satisfy a normalization relation, namely [9],

$$\int s^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_{p+1})d\mathbf{r}_{p+1} = s^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_p) \tag{40}$$

This is particularly useful for the hypersoftness kernels [10],

$$s^{(k)}(\mathbf{r},\mathbf{r}') = \left(\frac{\partial^{k-1} s(\mathbf{r},\mathbf{r}')}{\partial\mu^{k-1}}\right)_{v(\mathbf{r})} \qquad k = 1,2\ldots \tag{41}$$

which integrate to the local hypersoftnesses,

$$s^{(k)}(\mathbf{r}) = \int s^{(k)}(\mathbf{r},\mathbf{r}')d\mathbf{r}' \qquad k = 1,2\ldots \tag{42}$$

3. Discussion

The goal of this paper is to systematically establish working equations for global, local, and nonlocal response functions, of arbitrary order for a given energy versus the number of electrons model. We have implemented these equations in a development version of *ChemTools*, a post-processing module for interpreting the results of molecular quantum chemistry calculations within the HORTON program [50]. In general, we have tried to explicitly implement the analytical expressions of reactivity indicators for simple energy models, and symbolically handle any user-specified energy interpolation model, $E_{\text{model}}(N)$. In this regard, we have used SymPy for symbolic computations, which allows manipulating mathematical expressions and other mathematical objects, to solve systems of nonlinear equations, and to differentiate expressions to arbitrary-order to determine the reactivity indicators associated with complicated energy interpolation models $E_{\text{model}}(N)$. The formulas in Tables 1 and 2 were generated symbolically as well, and then checked by hand. The ease with which these formulas were automated within a unified framework dictated by the energy model, compared to the cumbersome nature of previous approaches, is a powerful argument for this approach. Another feature of this approach is the ease with which expressions for response functions of arbitrary order can be evaluated. (The explicit formulas based on the Bell polynomials, Eqs. (14), (21) and (39), are especially helpful in this regard.) To our knowledge, only one previous paper has presented a framework for evaluating response functions of arbitrary order [8].

The expressions presented here are, of course, mathematically and numerically identical to those obtained by existing approaches; we have verified this explicitly in several cases. The primary advantage of our approach is the ease with which arbitrary-order response functions are systematically and consistently implemented and evaluated for a given energy model. We anticipate that these expressions will be helpful as we, and other researchers, explore the chemical importance of higher-order response functions for the interpretation and prediction of chemical phenomena.

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