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# Reactivity indices and fluctuation formulas in density functional theory: Isomorphic ensembles and a new measure of local hardness

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Fluctuation formulas for the external potential  $v(\mathbf{r})$  are introduced in a modified Legendre-transformed representation of the density functional theory of electronic structure (isomorphic ensemble). A new (nuclear/geometric) reactivity index  $h(\mathbf{r})$ , having the same status as the electronic Fukui function in the canonical ensemble, is thereby identified,  $h(\mathbf{r}) = (1/N)[\delta\mu/\delta\sigma(\mathbf{r})]_{N,T} = (1/kT)[\langle\mu \cdot v(\mathbf{r})\rangle - \langle\mu\rangle\langle v(\mathbf{r})\rangle]$ , where  $\mu$  is the electronic chemical potential,  $\sigma$  is the shape factor of the electron density distribution,  $N$  is the number of electrons,  $\langle\cdots\rangle$  denotes the ensemble average of a quantity, and  $\langle v(\mathbf{r})\rangle$  is the ensemble averaged external potential. This new local quantity is shown to be an inverse of the local softness, and to provide a useful definition of a local hardness. © 1995 American Institute of Physics.

## I. INTRODUCTION

### A. Electronic versus nuclear reactivity indices

Density functional theory (dft) provides a firm theoretical basis for many intuitive concepts in chemistry, by providing a lucid description of electrons in atoms and molecules. Its basic descriptor is the electron density distribution function  $\rho(\mathbf{r})$ , which contains all information on the system in its ground state. Through the Hohenberg–Kohn<sup>1</sup> theorems,  $\rho(\mathbf{r})$  is uniquely related to the underlying external potential  $v(\mathbf{r})$ , and vice versa. The external potential determines the location of all atomic nuclei.

Since  $\rho(\mathbf{r})$  contains all information, chemical reactivity should be reflected in its sensitivity to perturbations. Various electronic reactivity indices related to  $\rho(\mathbf{r})$  have therefore been identified: the Fukui function  $f(\mathbf{r})$ ,<sup>2</sup> the local softness  $s(\mathbf{r})$ ,<sup>3</sup> the softness kernel  $s(\mathbf{r},\mathbf{r}')$ ,<sup>4</sup> and response kernel  $p(\mathbf{r},\mathbf{r}')$ .<sup>5</sup> All of these probe system responses in terms of  $d\rho(\mathbf{r})$ , thereby providing a complete description of chemical change.

In spite of this completeness, not all response information one may be interested in comes out immediately. The Fukui function, for example, is defined as the initial response in  $\rho(\mathbf{r})$  due to an infinitesimal perturbation in the total number of electrons  $N$ , at constant external potential  $v$ ,<sup>2</sup>

$$f(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v. \quad (1)$$

In a next step, this response in  $\rho(\mathbf{r})$  can be followed by a change in the external potential, but the Fukui function does not provide that information. Obtaining the  $v$ -response from  $d\rho(\mathbf{r})$  would require a “translator” of the form  $[\delta v(r)/\delta \rho(\mathbf{r})]$ , searching for the geometric (nuclear position) changes associated with the density response. Several at-

tempts in this direction have been made, but these mainly model the  $v$ -response of the system through the  $\rho$ -response (electronic reactivity) indirectly.

Very recently, a nuclear Fukui function has, e.g., been defined,<sup>6</sup> measuring the electronic force  $\mathbf{F}$  acting on the nuclei, due to a  $dN$ -perturbation at constant  $v$ ,

$$f_\alpha^n = \left( \frac{\partial \mathbf{F}_\alpha}{\partial N} \right)_v. \quad (2)$$

The force is calculated as the Coulomb force exerted by an electron on nucleus  $\alpha$  screened by the Kohn–Sham potential response function. Notice the constraint of constant external potential and the modeling of forces on nuclei through the electrons.

Also very recently,<sup>7</sup> in the atom-in-molecule (AIM) resolution, a “translator matrix” was developed to translate charge displacements ( $dq$ ) into bond length variations ( $dR^b$ ), in the local and normal representation (mapping relations), viz.,

$$\mathbf{T} = \left( \frac{d\mathbf{R}^b}{dq} \right)_N. \quad (3)$$

This approach allows one to “map” local (or normal) charge displacements (polarization and charge transfer channels) into the conjugated local (or normal) bond stretches (vibrations). It is found that the shapes of the system responses match in both the electron population and nuclear position space, and also that the corresponding force constants correlate.<sup>8</sup> The principal hardnesses of normal charge displacement modes increase with increasing force constants of the conjugated bond stretch normal modes, thus demonstrating a relation between the difficulty with which electrons and nuclei move (“chemical” and “physical” hardness).

Difficulties are encountered in these various approaches, so one may hope to profit from directly having access to  $dv(dR)$ -responses. These responses are pertinent in many chemical processes involving bond breaking and formation. We therefore are prompted to look for a language for  $v$ -reactivity indices, which we do in the present paper.

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## B. Fluctuations

Finite-temperature ensemble descriptions in density functional theory are useful for the understanding of concepts such as hardness and softness.<sup>9–11</sup> They have even served as a tool to prove the HSAB and maximum hardness principles.<sup>12,13</sup> A physical picture of global and local softness and softness kernels is nicely embodied in ensemble descriptions, through electron fluctuations. A molecular electronic ground state may be regarded as an equilibrium state at some very low temperature. Note also that a piece of a molecule, for example an atom or a functional group, is describable as an open system embedded in a bath that might indeed be appropriately modeled as possessing a finite temperature.

Since density functional theory focuses on the electron density distribution function, the canonical ensemble and grand canonical ensemble provide the most obvious ensemble descriptions.<sup>10,14</sup> They both allow  $\rho$  to fluctuate, and most well-known dft reactivity indices are situated in these ensembles. These have indeed been very useful in explaining reactivity and selectivity in chemical processes that in one way or another involve charge transfer or redistribution of electron density: acid/base, redox, electrophilic, and nucleophilic substitution, etc.

However, it has long been anticipated that “it is convenient to define new state functions (of the natural variables) that will be particularly appropriate for use when other variables are more pertinent for a particular problem at hand.”<sup>15,16</sup> In the just mentioned reactions, the main “problem at hand” is the electron (re)distribution in the system, so that low-energy electron fluctuations reflect the reactivity.<sup>9,17</sup> The Fukui function, e.g., probes the initial response in  $\rho$  to an infinitesimal perturbation in  $N$ , at constant external potential.<sup>2</sup> The  $v$ -response, accompanying the initial density response, is not discussed.

But the problem at hand in many other reactions has to do with the geometric changes (responses) of the system, due to some perturbation or other. Reactivity indices should then primarily probe the  $v$ -sensitivity (considering the  $\rho$ -response as secondary). Such indices should be relevant in all bond breaking/forming reactions (e.g., cracking), and are most probably related to reactivity models based on vibrational effects (RRKM,...). This is to say,  $v$ -fluctuations are pertinent in those particular cases. It has indeed been suggested<sup>10</sup> that “other fluctuation formulas, in other ensembles, will exist, and some of these may ultimately prove quite valuable.”

The above reasoning embodies the general point of view of catalysis of Mortier, who has emphasized that  $\rho$  contains all information, through its dependence on  $v(\mathbf{r})$  and  $N$ : “Perturbing a molecule ultimately means interfering with the number of electrons or with the external potential.”<sup>18</sup> Whereas the *perturbations* in  $v(\mathbf{r})$  and  $N$  (i.e., in  $\rho$ ) are independent, the *responses* in the system  $\rho$  can be described in terms of  $v(\mathbf{r})$  and  $N$  as well, and these are linked.<sup>19</sup>

In the present work a theoretical framework is laid down for treating  $v$ -responses. Two new ensembles, the isomorphic ensemble and grand isomorphic ensemble, are defined. Fluctuations, interpretations, implementations, and illustrations are described and discussed. Most importantly, a new measure of local hardness is found and elaborated.

## II. CANONICAL AND ISOMORPHIC ENSEMBLES

Four “natural” Legendre transformed ensembles in dft are given in Table I, together with their defining bath parameters and state functions. The first two are the familiar canonical and grand canonical ensembles.<sup>15</sup> The next two are the isomorphic and grand isomorphic ensembles.

The two new “isomorphic” ensembles refine the  $\mathcal{F}$  and  $\mathcal{R}$  ensembles of Ref. 15. The latter had the same state functions as our new ensembles, but now the bath parameter  $\rho$  is decomposed into two variables,  $N$  and  $\sigma$ , with  $\sigma$  the “shape” factor of the electron density distribution,<sup>20,21</sup>

$$\rho(\mathbf{r}) = \sigma(\mathbf{r})N, \quad (4)$$

where  $N$  is the total number of electrons in the system. The use of  $\rho$  alone carries difficulties because derivatives with respect to  $N$  at constant  $\rho$  then appear. The shape factor  $\sigma(\mathbf{r})$  carries relative information on the electron distribution within a system of  $N$  electrons [compare with  $s(\mathbf{r}) = Sf(\mathbf{r})$ ].  $\rho(\mathbf{r})$ , on the other hand, is comparable from molecule to molecule. Notice that  $\sigma$  is everywhere non-negative and normalized to unity,

$$\int \sigma(\mathbf{r})d\mathbf{r} = \frac{1}{N} \int \rho(\mathbf{r})d\mathbf{r} = 1. \quad (5)$$

For a one-electron system,  $\sigma$  would just be the density itself.

$N$  and  $\sigma(\mathbf{r})$  are independent variables. However, because of Eq. (5) there is a linear dependence among the variable  $\sigma(\mathbf{r})$ . This problem is discussed in the Appendix.

The choice of two variables  $N$  and  $\sigma$ , replacing the variable  $\rho$ , allows one to write

$$d\rho(\mathbf{r}) = \sigma(\mathbf{r})dN + Nd\sigma(\mathbf{r}). \quad (6)$$

This enables us to resolve a change of  $\rho$  into two pieces, one at constant  $N$  and one at constant  $\sigma$ .  $\sigma$  being a shape factor, constant  $\sigma$  changes may be called isomorphic.

As a consequence of the introduction of the new variables, all quantities in Ref. 15 associated with  $\mathcal{F}$  and  $\mathcal{R}$  can be replaced, as they have been in Table I. General procedures for handling the variables  $N$  and  $\sigma$  are developed in Ref. 21.

In the isomorphic ensemble, the bath fixes  $N$ ,  $\sigma$ , and  $T$ ; that is,  $\rho$  and  $T$  will not change. At 0 K, the equilibrium system is determined from the Hohenberg–Kohn theorem ( $\rho$  determines the external potential,  $v_0$ ). The states with  $v \neq v_0$  are nonequilibrium states and they will be accessible at finite temperature. Then, in this ensemble, there will be systems with different external potentials (and also different chemical potentials) and the average of the external potentials over the ensemble will be  $\langle v(\mathbf{r}) \rangle$ ; in a similar way, its fluctuation over the ensemble can appear. In Table I, the fluctuating variables and their derivatives with respect to bath parameters, under appropriate constraints, are also listed. When the external potential is restricted only to the nuclear attraction, the isomorphic ensemble can be visualized as a collection of systems, all of them with the same electronic density, with the nuclei in different geometries, including the equilibrium state at 0 K, which corresponds to the correct nuclear conformation. Note that at finite temperature the density in the isomorphic ensemble may or may not be  $v$ -representable.

TABLE I. Fluctuations in the statistical ensembles corresponding to the four natural Legendre-transformed representations of the density functional theory.<sup>a,b</sup>

	State function	Bath parameters	Fluctuating variables	Response functions			
				Global	Local	Local	Kernel
Canonical ensemble	$E$	$N, v, T$	$E, \mu, \rho$	$\eta^v$	$f(\mathbf{r})$	$f(\mathbf{r})$	$p(\mathbf{r}, \mathbf{r}')$
				$\left(\frac{\partial \mu}{\partial N}\right)_v$	$\left[\frac{\delta \mu}{\delta v(\mathbf{r})}\right]_N$	$\left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_v$	$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_N$
				$-\langle\langle \mu \cdot \mu \rangle\rangle$	$-\langle\langle \mu \cdot \rho(\mathbf{r}) \rangle\rangle$	$-\langle\langle \rho(\mathbf{r}) \cdot \mu \rangle\rangle$	$-\langle\langle \rho(\mathbf{r}) \cdot \rho(\mathbf{r}') \rangle\rangle$
				$S^v$	$s(\mathbf{r})$	$s(\mathbf{r})$	$s(\mathbf{r}, \mathbf{r}')$
Grand canonical ensemble	$E - \mu N$	$\mu, v, T$	$E, N, \rho$	$\left(\frac{\partial N}{\partial \mu}\right)_v$	$-\left[\frac{\delta N}{\delta v(\mathbf{r})}\right]_\mu$	$\left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_v$	$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_\mu$
				$\langle\langle N \cdot N \rangle\rangle$	$\langle\langle N \cdot \rho(\mathbf{r}) \rangle\rangle$	$\langle\langle \rho(\mathbf{r}) \cdot N \rangle\rangle$	$-\langle\langle \rho(\mathbf{r}) \cdot \rho(\mathbf{r}') \rangle\rangle$
				$\eta^\sigma$	$h(\mathbf{r})$	$g(\mathbf{r})$	$q(\mathbf{r}, \mathbf{r}')$
Isomorphic ensemble	$F$	$N, \sigma, T$	$E, \mu, v$	$\left(\frac{\delta \mu}{\delta N}\right)_\sigma$	$\frac{1}{N} \left[\frac{\delta \mu}{\delta \sigma(\mathbf{r})}\right]_N$	$\left[\frac{\partial v(\mathbf{r})}{\partial N}\right]_\sigma$	$\frac{1}{N} \left[\frac{\delta v(\mathbf{r})}{\delta \sigma(\mathbf{r}')} \right]_N$
				$-\langle\langle \mu \cdot \mu' \rangle\rangle$	$\langle\langle \mu \cdot v(\mathbf{r}) \rangle\rangle$	$-\langle\langle v(\mathbf{r}) \cdot \mu' \rangle\rangle$	$\langle\langle v(\mathbf{r}) \cdot v(\mathbf{r}') \rangle\rangle$
				$S^\sigma$	$t(\mathbf{r})$	$r(\mathbf{r})$	$t(\mathbf{r}, \mathbf{r}')$
Grand isomorphic ensemble	$F - \mu N$	$\mu, \sigma, T$	$E, N, v$	$\left(\frac{\partial N}{\partial \mu}\right)_\sigma$	$\frac{1}{N} \left[\frac{\delta N}{\delta \sigma(\mathbf{r})}\right]_\mu$	$\left[\frac{\partial v(\mathbf{r})}{\partial \mu}\right]_\sigma$	$\frac{1}{N} \left[\frac{\delta v(\mathbf{r})}{\delta \sigma(\mathbf{r}')} \right]_\mu$
				$\langle\langle N \cdot N \rangle\rangle$	$\langle\langle N \cdot v(\mathbf{r}) \rangle\rangle$	$\langle\langle v(\mathbf{r}) \cdot N \rangle\rangle$	$\langle\langle v(\mathbf{r}) \cdot v(\mathbf{r}') \rangle\rangle$

<sup>a</sup>For each response function is given its symbol, its definition as a derivative or functional derivative, and its fluctuation formula. [See Eq. (17) of text for notation.]  
<sup>b</sup>See Eq. (4) of text for definition of  $\sigma$  and Eq. (9) for definition of  $\mu'$ .

One may note in passing that while thermal equilibrium is present in all four of the ensembles of Table I, in the isomorphic ensembles a mechanical equilibrium is present as well; energy can flow between systems and bath both as heat and as work.

III. EULER EQUATIONS AND THE QUANTITY  $h(\mathbf{r})$

The Euler equation in the canonical and grand canonical ensembles is well known,

$$\mu = \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \frac{\delta G[\rho]}{\delta \rho(\mathbf{r})} + v^*(\mathbf{r}), \tag{7}$$

where  $\mu$  is the electronic chemical potential,  $F$  and  $G$  are universal functionals of the electron density  $\rho$ , and  $v$  and  $v^*$  are the external and total electrostatic potential.

The corresponding Euler equation in the isomorphic ensemble results from the general procedure for the reduction of derivatives,

$$\begin{aligned} \left[\frac{\delta F}{\delta \sigma(\mathbf{r})}\right]_N &= \int \left[\frac{\delta F}{\delta \rho(\mathbf{r}')} \right]_N \left[\frac{\delta \rho(\mathbf{r}')}{\delta \sigma(\mathbf{r})}\right]_N d\mathbf{r}' \\ &= -N \int v(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = -N v(\mathbf{r}). \end{aligned} \tag{8}$$

Another equation in the isomorphic ensemble results from

$$\begin{aligned} \left(\frac{\partial F}{\partial N}\right)_\sigma &= \left(\frac{\partial F}{\partial N}\right)_\rho + \int \left[\frac{\delta F}{\delta \rho(\mathbf{r})}\right]_N \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_\sigma d\mathbf{r} \\ &= \mu - \int v(\mathbf{r}) \sigma(\mathbf{r}) d\mathbf{r}. \end{aligned} \tag{9}$$

The last equality follows from Ref. 15 and the definition of  $\sigma$ ,

$$\left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_\sigma = \left[\frac{\partial N \sigma(\mathbf{r})}{\partial N}\right]_\sigma = \sigma(\mathbf{r}) \left(\frac{\partial N}{\partial N}\right)_\sigma = \sigma(\mathbf{r}). \tag{10}$$

Note that in Eqs. (8) and (9), both  $(\partial F/\partial N)_\rho$  and  $(\partial F/\partial \rho)_N$  are themselves ambiguous because of the dependence that exists between  $\rho$  and  $N$ .

In the two ensembles, the differential equations for  $\mu$  are

$$\begin{aligned}\mu[N, v]: d\mu &= \left( \frac{\partial \mu}{\partial N} \right)_v dN + \int \left[ \frac{\delta \mu}{\delta v(\mathbf{r})} \right]_N dv(\mathbf{r}) d\mathbf{r} \\ &= \eta^v dN + \int \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v dv(\mathbf{r}) d\mathbf{r},\end{aligned}\quad (11)$$

where  $\eta^v$  is the absolute hardness,<sup>22</sup> and

$$\mu[N, \sigma]: d\mu = \left( \frac{\partial \mu}{\partial N} \right)_\sigma dN + \int \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N d\sigma(\mathbf{r}) d\mathbf{r}. \quad (12)$$

The last equality in Eq. (11) is the result of a Maxwell relation<sup>15</sup> for the Fukui function  $f(\mathbf{r})$ . The local derivative in Eq. (12) will be denoted by  $Nh(\mathbf{r})$  or

$$h(\mathbf{r}) = \frac{1}{N} \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N. \quad (13)$$

As we shall see, this is a very important local quantity. The factor  $N$  is included for convenience.

#### IV. FLUCTUATIONS IN THE CANONICAL AND ISOMORPHIC ENSEMBLES

Very generally, the probability distribution function in a closed system is given by<sup>23</sup>

$$P_i^0 = \frac{\exp[-\beta(\mathcal{L}_i)]}{Q}, \quad (14)$$

where  $\mathcal{L}$  is the state function in the closed system ( $N = \text{constant}$ ), for both the canonical and isomorphic ensembles there is an appropriate state function (see Table I);  $i$  represents the energy state and  $\beta = 1/kT$  ( $T$  is the absolute temperature and  $k$  the Boltzmann constant). The partition function is given by

$$Q = \sum_i \exp[-\beta(\mathcal{L}_i)] \quad (15)$$

and is used to calculate ensemble averages of quantities  $y$ , viz.,

$$\langle y \rangle = \sum_i y_i P_i^0. \quad (16)$$

The corresponding finite-temperature fluctuations are

$$\langle \langle a \cdot b \rangle \rangle \equiv \beta [\langle a \cdot b \rangle - \langle a \rangle \langle b \rangle]. \quad (17)$$

Here  $a$  refers to the response under consideration (fluctuation) and  $b$  originates from differentiating the state function with respect to the bath parameters at the proper constraints. Similarly, in an open system the probability distribution function and partition function are given by

$$P_{N,i}^0 = \frac{\exp[-\beta(\mathcal{L}_{N,i} - \mu N)]}{\Xi}$$

and

$$\Xi = \sum_{N,i} \exp[-\beta(\mathcal{L}_{N,i} - \mu N)], \quad (18)$$

and the ensemble averages and fluctuations are defined in the same way.

In the canonical and grand canonical ensembles the state function is given by  $\mathcal{L}_i = E_i$ . One then finds by elementary calculation<sup>9,10</sup>

$$\begin{aligned}s(\mathbf{r}) &= \left[ \frac{\partial \langle \rho(\mathbf{r}) \rangle}{\partial \mu} \right]_{v,T} = \frac{\partial}{\partial \mu} \left[ \sum_{N,i} \rho_{N,i}(\mathbf{r}) P_{N,i}^0 \right] \\ &= \frac{1}{kT} [\langle \rho(\mathbf{r}) \cdot N \rangle - \langle \rho(\mathbf{r}) \rangle \langle N \rangle],\end{aligned}\quad (19a)$$

$$\begin{aligned}f(\mathbf{r}) &= \left[ \frac{\partial \langle \rho(\mathbf{r}) \rangle}{\partial N} \right]_{v,T} = \frac{\partial}{\partial N} \left[ \sum_i \rho_i(\mathbf{r}) P_i^0 \right] \\ &= \frac{1}{kT} [\langle \rho(\mathbf{r}) \rangle \langle \mu \rangle - \langle \rho(\mathbf{r}) \cdot \mu \rangle].\end{aligned}\quad (19b)$$

The other fluctuation formulas reported in Table I are obtained similarly.

In the isomorphic ensemble the state function is given by

$$\mathcal{L}_i = E_i - N \int \sigma(\mathbf{r}) v_i(\mathbf{r}) d\mathbf{r} = F_i. \quad (20)$$

The fluctuation formula for  $h(\mathbf{r})$  then becomes

$$\begin{aligned}h(\mathbf{r}) &= \frac{1}{N} \left[ \frac{\partial \langle \mu \rangle}{\delta \sigma(\mathbf{r})} \right]_{N,T} = \frac{1}{N} \frac{\delta}{\delta \sigma(\mathbf{r})} \left[ \sum_i \mu_i P_i^0 \right] \\ &= \frac{1}{kT} [\langle \mu \cdot v(\mathbf{r}) \rangle - \langle \mu \rangle \langle v(\mathbf{r}) \rangle]\end{aligned}\quad (21)$$

with other results as given in Table I. Note that  $h(\mathbf{r})$  is a functional derivative.

#### V. PHYSICAL IMPLICATIONS

" $|d\mu|$  big is good!" is a postulate that generates the frontier electron theory<sup>2,16</sup> and identifies the Fukui function as a reactivity index, providing information on the relative reactivity of different sites within a molecule [Eq. (11)],

$$\left[ \frac{\delta \mu}{\delta v(\mathbf{r})} \right]_N = f(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v. \quad (22)$$

The local derivative in Eq. (12) has equivalent status and can be identified as a nuclear/geometric reactivity index,

$$\frac{1}{N} \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N = h(\mathbf{r}). \quad (23)$$

Large values either of  $f(\mathbf{r})$  or of  $h(\mathbf{r})$  produce large responses in  $\mu$ . Because of Eq. (21) above, this constitutes an argument in favor of the importance of  $v$ -fluctuations.

Two other related quantities in the isomorphic ensemble will prove to be useful,

$$g(\mathbf{r}) = \left[ \frac{\partial v(\mathbf{r})}{\partial N} \right]_\sigma \quad \text{and} \quad q(\mathbf{r}, \mathbf{r}') = \frac{1}{N} \left[ \frac{\delta v(\mathbf{r})}{\delta \sigma(\mathbf{r}')} \right]_N. \quad (24)$$

These are connected by

$$\left[ \frac{\partial v(\mathbf{r})}{\partial N} \right]_\rho = 0 = \left[ \frac{\partial v(\mathbf{r})}{\partial N} \right]_\sigma + \int \left[ \frac{\delta v(\mathbf{r})}{\delta \sigma(\mathbf{r}')} \right]_N \left[ \frac{\partial \sigma(\mathbf{r}')}{\partial N} \right]_\rho d\mathbf{r}'$$

or

$$g(\mathbf{r}) = \int q(\mathbf{r}, \mathbf{r}') \sigma(\mathbf{r}') d\mathbf{r}'. \quad (25)$$

Upon introducing  $v(\mathbf{r})$  explicitly one finds

$$g(\mathbf{r}) = \left[ \frac{\partial v(\mathbf{r})}{\partial N} \right]_{\sigma} = \sum_{\beta} \frac{-Z_{\beta}}{|\mathbf{r} - \mathbf{r}_{\beta}|^2} \left( \frac{\partial |\mathbf{r} - \mathbf{r}_{\beta}|}{\partial N} \right)_{\sigma} \quad (26)$$

and it is seen that the functions  $g(\mathbf{r})$  and  $q(\mathbf{r}, \mathbf{r}')$  “probe” how much a point  $\mathbf{r}$  will be connected to/disconnected from the system, in other words, how much a point will be “included in” or “isolated from” the system when  $N$  changes. With atoms in mind one may write [in the atom-in-molecule (AIM) resolution]

$$g_{\alpha} = \left( \frac{\partial v_{\alpha}}{\partial N} \right)_{\sigma} = \sum_{\beta \neq \alpha} \frac{-Z_{\beta}}{R_{\alpha\beta}^2} \left( \frac{\partial R_{\alpha\beta}}{\partial N} \right)_{\sigma}, \quad (27)$$

where  $g_{\alpha}$  measures how the bond distances, connecting the atom  $\alpha$  to the system, will be affected (by the  $dN$  perturbation in this case). Atom  $\alpha$  will be disconnected (“pulled out”) if  $g_{\alpha}$  is negative, i.e., if  $R_{\alpha\beta}$  increases upon increasing  $N$ . Notice that the single number  $g_{\alpha}$  for atom  $\alpha$  can originate from one or more distances, depending on their changes; bonds (or nonbonded distances) which are most sensitive to the perturbation contribute most!

Analogously, the kernel  $q(\mathbf{r}, \mathbf{r}') = [\partial v(\mathbf{r}) / \partial \sigma(\mathbf{r}')]_N$ , which is a nonlocal linear potential response function, measures the (dis)connection of point  $\mathbf{r}$  to the system, due to a  $\delta\sigma(\mathbf{r}')$  perturbation at constant  $N$ .

In the ensemble interpretation, a large  $h(\mathbf{r})$  value reflects large  $v$ -fluctuations; i.e., large local variations in the distances. Large deviations from mean bond lengths reflect an increased probability for bonds to break; bond length variations can ultimately lead to cleavage. Low-energy  $v$ -fluctuations should then favor bond breaking (or formation).

## VI. THE QUANTITY $h(\mathbf{r})$ AS A NEW LOCAL HARDNESS INDEX

It is interesting to examine the mutual relations between the several quantities in the different ensembles. In particular, relations involving the different constraints ( $v$ ,  $\rho$ , and  $\sigma$ ) allow one to link the electronic and nuclear reactivity indices.

Following Ref. 21, one may write

$$\left( \frac{\partial \mu}{\partial N} \right)_{\rho} = \left( \frac{\partial \mu}{\partial N} \right)_{\sigma} + \int \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N \left[ \frac{\partial \sigma(\mathbf{r})}{\partial N} \right]_{\rho} d\mathbf{r} = 0. \quad (28)$$

Similarly one has

$$\left( \frac{\partial \mu}{\partial N} \right)_{\nu} = \left( \frac{\partial \mu}{\partial N} \right)_{\sigma} + \int \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N \left[ \frac{\partial \sigma(\mathbf{r})}{\partial N} \right]_{\nu} d\mathbf{r}. \quad (29)$$

Now define the global hardnesses in both the canonical and isomorphous ensemble,

$$\left( \frac{\partial \mu}{\partial N} \right)_{\nu} = \eta^{\nu} \quad (30a)$$

and

$$\left( \frac{\partial \mu}{\partial N} \right)_{\sigma} = \eta^{\sigma}. \quad (30b)$$

These are two different, almost equal numbers; the first,  $\eta^{\nu}$ , is the absolute hardness as defined by Parr and Pearson;<sup>22</sup> the second,  $\eta^{\sigma}$ , is a new quantity—a hardness under different conditions. Reciprocals are denoted respectively as  $S^{\nu}$  and  $S^{\sigma}$ .

Since

$$\left[ \frac{\partial \sigma(\mathbf{r})}{\partial N} \right]_{\nu} = \frac{1}{N} \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{\nu} - \frac{\rho(\mathbf{r})}{N^2} = \frac{f(\mathbf{r}) - \sigma(\mathbf{r})}{N}, \quad (31)$$

one has, via Eq. (29),

$$\begin{aligned} \eta^{\nu} &= \eta^{\sigma} + \int h(\mathbf{r}) [f(\mathbf{r}) - \sigma(\mathbf{r})] d\mathbf{r} \\ &= \eta^{\sigma} + \int h(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} - \int h(\mathbf{r}) \sigma(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (32)$$

and one then finds the interesting result, that both

$$\eta^{\nu} = \int h(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} \quad (33a)$$

and

$$\eta^{\sigma} = \int h(\mathbf{r}) \sigma(\mathbf{r}) d\mathbf{r}. \quad (33b)$$

Notice that the global hardness at constant external potential and the global hardness at constant  $\sigma$  each contain a “nuclear response” part ( $h$ ) and an “electronic response” part, since  $f$  and  $\sigma$  can be considered to be the electronic responses in the respective ensembles,

$$\left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{\nu} = f(\mathbf{r}) \quad \text{and} \quad \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{\sigma} = \sigma(\mathbf{r}). \quad (34)$$

The new quantity  $h$  appears in both  $\eta^{\nu}$  and  $\eta^{\sigma}$ . In  $\eta^{\nu}$ , it is combined with the original Fukui function; also in subsequent equations it is combined with original softness quantities (local softness and softness kernel) and with the original hardness kernel. There is no need to introduce a new softness hierarchy in the new ensemble. We do not further elaborate on the various quantities for the grand isomorphous ensemble.

One can now write two basic equations for the change in the electronic chemical potential, one describing electronic response effects, the other describing nuclear/geometric response effects,

$$d\mu = \eta^{\nu} dN + \int f(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r} \quad (35)$$

and

$$d\mu = \eta^{\sigma} dN + \int h(\mathbf{r}) d\sigma(\mathbf{r}) d\mathbf{r}. \quad (36)$$

Equation (33a) is to be compared with the local hardness equation,<sup>25,10</sup>

$$\eta^{\nu} = \int \eta(\mathbf{r}) f(\mathbf{r}) d\mathbf{r}$$

with

$$\eta(\mathbf{r}) = \int \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}'. \quad (37)$$

This is to say that both  $\eta(\mathbf{r})$  and  $h(\mathbf{r})$  are inverses of local softness [ $s(\mathbf{r}) = f(\mathbf{r})/\eta^v$ ] in the sense that

$$\int h(\mathbf{r}) s(\mathbf{r}) d\mathbf{r} = \int \eta(\mathbf{r}) s(\mathbf{r}) d\mathbf{r} = 1. \quad (38)$$

Notice that local hardness as defined in Eq. (37) is equalized;  $h$  is not.  $s(\mathbf{r})$  integrates to  $S^v$ , the original Parr–Pearson global softness.

Generally, one would prefer the local hardness to be obtainable from integration of the hardness kernel with a function  $x$ , viz.,

$$h(\mathbf{r}) = \int \eta(\mathbf{r}, \mathbf{r}') x(\mathbf{r}') d\mathbf{r}'. \quad (39)$$

Various functions  $x$  have been proposed in the literature;<sup>5,10</sup>  $x$  can be obtained as a function of  $h$ , by inverting Eq. (39); multiply both sides with the softness kernel and integrate:

$$x(\mathbf{r}) = \int s(\mathbf{r}, \mathbf{r}') h(\mathbf{r}') d\mathbf{r}'. \quad (40)$$

The normalization of  $x$  to unity follows from Eq. (38),

$$\int x(\mathbf{r}) d\mathbf{r} = \int \int s(\mathbf{r}, \mathbf{r}') h(\mathbf{r}') d\mathbf{r} d\mathbf{r}' = \int s(\mathbf{r}) h(\mathbf{r}) d\mathbf{r} = 1. \quad (41)$$

Imposing equalization of hardness (i.e.,  $h = \text{const} = \eta^v$ ) directly identifies  $x$  with the Fukui function<sup>5(c)</sup>

$$x(\mathbf{r}) = \eta^v \int s(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \eta^v s(\mathbf{r}) = f(\mathbf{r}). \quad (42)$$

To obtain  $x$  corresponding to the present definition of  $h$ , on the other hand, we proceed as follows:

$$\begin{aligned} x(\mathbf{r}) &= \int s(\mathbf{r}, \mathbf{r}') h(\mathbf{r}') d\mathbf{r}' \\ &= \int \frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')} \frac{1}{N} \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r}')} \right]_N d\mathbf{r}'. \end{aligned} \quad (43)$$

In the isomorphic ensemble one has

$$\begin{aligned} \frac{\delta \mu}{\delta \rho(\mathbf{r}')} &= \left( \frac{\partial \mu}{\partial N} \right)_\sigma \frac{\delta N}{\delta \rho(\mathbf{r}')} + \int \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N \frac{\delta \sigma(\mathbf{r})}{\delta \rho(\mathbf{r}')} d\mathbf{r} \\ &= \eta^\sigma + \int \frac{1}{N} \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N [\delta(\mathbf{r} - \mathbf{r}') - \sigma(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (44)$$

or

$$h(\mathbf{r}) = \frac{1}{N} \left[ \frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right]_N = \frac{\delta \mu}{\delta \rho(\mathbf{r})}. \quad (45)$$

Equation (43) then becomes [using  $s(\mathbf{r}, \mathbf{r}') = s(\mathbf{r}', \mathbf{r})$ ]

$$x(\mathbf{r}) = \int \frac{\delta \rho(\mathbf{r}')}{\delta u(\mathbf{r})} \frac{\delta \mu}{\delta \rho(\mathbf{r}')} d\mathbf{r}' = \frac{\delta \mu}{\delta u(\mathbf{r})}. \quad (46)$$

From the Euler equation  $\mu = u(\mathbf{r}) + v(\mathbf{r})$  we have

$$\frac{\delta \mu}{\delta u(\mathbf{r})} = \delta(\mathbf{r} - \mathbf{r}') + \frac{\delta v(\mathbf{r}')}{\delta u(\mathbf{r})}. \quad (47)$$

An explicit expression for  $h(\mathbf{r})$  follows

$$\begin{aligned} h(\mathbf{r}') &= \eta(\mathbf{r}'', \mathbf{r}') + \int \eta(\mathbf{r}'', \mathbf{r}) \frac{\delta v(\mathbf{r}')}{\delta u(\mathbf{r})} d\mathbf{r} \\ &= \eta(\mathbf{r}'', \mathbf{r}') + \frac{\delta v(\mathbf{r}')}{\delta \rho(\mathbf{r}'')}. \end{aligned} \quad (48)$$

Notice that  $h$  explicitly contains the “translator” information as referred to in the Introduction. From this formula we see that  $h$  involves nuclear position changes through  $\delta v$  (cf.  $v$ -fluctuations). By this very fact, and because of relation (33), the hardness in the isomorphic ensemble may be presumed to be related to Pearson’s physical hardness.<sup>26</sup> It would be interesting to examine the maximum hardness principle (MHP) in the isomorphic ensemble.

## VII. IMPLEMENTATION IN THE ATOMS IN MOLECULES RESOLUTION

A simple semiempirical implementation of the Euler equation (7) for the canonical ensemble has been developed by Mortier *et al.*<sup>27</sup> The method is called electronegativity equalization method (EEM) and is particularly suitable for the study of large systems and molecular interactions. An atom-in-molecule (AIM) resolution and a second-order expansion for the  $G$ -term are adopted, viz.,

$$\bar{\chi} = \frac{dG[q]}{dq_\alpha} + \phi_\alpha = \chi_\alpha^* + 2\eta_\alpha^* q_\alpha + k \sum_{\beta \neq \alpha} \frac{q_\beta}{R_{\alpha\beta}} \quad (49)$$

with  $q$  the atomic charge,  $\bar{\chi}$  the effective electronegativity of the molecule,  $\chi^*$  and  $\eta^*$  the expansion coefficients (the electronegativity and hardness of the AIM), and  $k$  an energy conversion factor (14.4 eV for  $R$  expressed in Å). Rigorous derivations can be found in the literature.<sup>27</sup> Equation (49) can be written for each atom in the  $n$ -atomic molecule. Together with a limiting condition fixing the total number of electrons in the system,  $\sum_\gamma^n q_\gamma = Q_m$  (where  $Q_m$  is the molecular charge), a set of  $(n+1)$  linear equations is obtained in  $(n+1)$  unknowns  $(\bar{\chi}, q_\alpha, q_\beta, \dots, q_n)$  which is exactly soluble. The expansion coefficients are calibrated against *ab initio* data.<sup>28</sup>

For a given structure  $(1/R, v)$  EEM allows one to analytically determine the equilibrium charge distribution  $q(R)$  and electronegativity  $\bar{\chi}[q(R)]$ . An extension of the method<sup>29,30</sup> enables one to analytically calculate second order properties of the canonical and grand canonical ensemble in the AIM resolution  $[\bar{\eta}, S, f_\alpha, s_\alpha, s(\alpha, \beta), \eta(\alpha, \beta), p(\alpha, \beta)]$ . In principle, all quantities can also be generated by imposing constraints and perturbations on the system (in the fixed terms) and calculating the new charge distribution and charge sensitivities in finite difference approximation (known to be quite accurate<sup>29</sup>).

In matrix notation for a two-atomic system one has

$$\begin{pmatrix} 2\eta_1^* & k/R_{12} & -1 \\ k/R_{12} & 2\eta_2^* & -1 \\ 1 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} q_1 \\ q_2 \\ \bar{\chi} \end{pmatrix} = - \begin{pmatrix} \chi_1^* \\ \chi_2^* \\ -Q_m \end{pmatrix}. \quad (50)$$

Given the potential, the corresponding equilibrium charge distribution results.

In contrast, in the isomorphic ensemble, for a given charge distribution one has to search for the underlying external potential. Upon introducing  $N_\alpha = \sigma_\alpha N$  and  $q_\alpha = Z_\alpha - N_\alpha$  one can obtain  $h$  by differentiating Eq. (49) with respect to  $\sigma$  at constant  $N$  for atoms  $\alpha$  and  $\gamma$  respectively, viz.,

$$h_\alpha = -\frac{1}{N} \left( \frac{\delta \bar{\chi}_\alpha}{\delta \sigma_\alpha} \right)_N = 2\eta_\alpha^* + \frac{k}{N} \sum_{\beta \neq \alpha} \frac{q_\beta}{R_{\alpha\beta}^2} \left( \frac{\delta R_{\alpha\beta}}{\delta \sigma_\alpha} \right)_N, \quad (51)$$

$$h_\alpha = -\frac{1}{N} \left( \frac{\delta \bar{\chi}_\gamma}{\delta \sigma_\alpha} \right)_N = \frac{k}{R_{\gamma\alpha}} + \frac{k}{N} \sum_{\beta \neq \gamma} \frac{q_\beta}{R_{\gamma\beta}^2} \left( \frac{\delta R_{\gamma\beta}}{\delta \sigma_\alpha} \right)_N, \quad (52)$$

or, in general,

$$h_\alpha = -\frac{1}{N} \left( \frac{\delta \bar{\chi}}{\delta \sigma_\alpha} \right)_N = \eta(\alpha, \gamma) + \frac{k}{N} \sum_{\beta \neq \gamma} \frac{q_\beta}{R_{\gamma\beta}^2} \left( \frac{\delta R_{\gamma\beta}}{\delta \sigma_\alpha} \right)_N. \quad (53)$$

In matrix form, one has for a diatomic molecule and perturbation at atom 1,

$$\begin{pmatrix} kq_2/R_{12}^2 & 1 \\ kq_1/R_{12}^2 & 1 \end{pmatrix} \cdot \begin{pmatrix} [\partial R_{12}/\partial \sigma_1]_N \\ [\partial \bar{\chi}/\partial \sigma_1]_N \end{pmatrix} = - \begin{pmatrix} 2\eta_1^* \cdot N \\ k \cdot N/R_{12} \end{pmatrix}. \quad (54)$$

Differentiating Eq. (49) with respect to  $N$  at constant  $\sigma$  gives

$$\begin{aligned} \bar{\eta}^\sigma = - \left( \frac{\partial \bar{\chi}_\alpha}{\partial N} \right)_\sigma &= 2\eta_\alpha^* \sigma_\alpha + k \sum_{\beta \neq \alpha} \frac{\sigma_\beta}{R_{\alpha\beta}} \\ &+ k \sum_{\beta \neq \alpha} \frac{q_\beta}{R_{\alpha\beta}^2} \left( \frac{\partial R_{\alpha\beta}}{\partial N} \right)_\sigma \end{aligned} \quad (55)$$

or, in general,

$$\bar{\eta}^\sigma = \sum_\beta \eta(\alpha, \beta) \sigma_\beta + k \sum_{\beta \neq \alpha} \frac{q_\beta}{R_{\alpha\beta}^2} \left( \frac{\partial R_{\alpha\beta}}{\partial N} \right)_\sigma = \sum_\beta h_\beta \sigma_\beta. \quad (56)$$

In matrix form one gets

$$\begin{pmatrix} kq_2/R_{12}^2 & 1 \\ kq_1/R_{12}^2 & 1 \end{pmatrix} \cdot \begin{pmatrix} [\partial R_{12}/\partial N]_\sigma \\ [\partial \bar{\chi}/\partial N]_\sigma \end{pmatrix} = - \begin{pmatrix} 2\eta_1^* \sigma_1 + k\sigma_2/R_{12} \\ 2\eta_2^* \sigma_2 + k\sigma_1/R_{12} \end{pmatrix}. \quad (57)$$

This is to be compared with the expression for the hardness in the canonical ensemble (at constant external potential) derived earlier<sup>29</sup>

$$\bar{\eta}^v = 2\eta_\alpha^* f_\alpha + k \sum_{\beta \neq \alpha} \frac{f_\beta}{R_{\alpha\beta}} = \sum_\beta \eta(\alpha, \beta) f_\beta = \sum_\beta h_\beta f_\beta. \quad (58)$$

The last equality is Eq. (33a).

TABLE II. Model calculations for CO and CO<sub>2</sub>.

	C <sub>1</sub>	O <sub>2</sub>	O <sub>3</sub>	C <sub>1</sub>	O <sub>2</sub>
$r_\alpha$	0.000	1.171	-1.189	0.000	1.189
$\chi_\alpha^*$	5.680	8.500	8.500	5.680	8.500
$\eta_\alpha^*$	9.051	11.083	11.083	9.051	11.083
$q_\alpha$	0.180	-0.180	-0.176	0.353	-0.176
$N_\alpha$	5.820	8.180	8.176	5.647	8.176
$\bar{\chi}_\alpha$	6.725	6.725	7.794	7.794	7.794
$\bar{\eta}_\alpha^v$	15.951	15.951	13.608	13.608	13.608
$\bar{\eta}_\alpha^\sigma$	16.385	16.385	13.617	13.617	13.617
$f_\alpha$	0.630	0.370	0.375	0.250	0.375
$s_\alpha$	0.0395	0.023	0.0275	0.018	0.0275
$\sigma_\alpha$	0.4165	0.584	0.372	0.257	0.372
$h_\alpha$	15.198	17.230	13.251	14.676	13.251
$g_\alpha$	74.585	55.938	-0.813	-1.301	-0.813
$\eta(\alpha, 1)$	18.101	12.295	12.107	18.101	12.107
$\eta(\alpha, 2)$	12.295	22.166	6.054	12.107	22.166
$\eta(\alpha, 3)$	...	...	22.166	12.107	6.054
$q(\alpha, 1)$	-129.141	-96.856	-97.140	-155.424	-97.140
$q(\alpha, 2)$	219.540	164.655	-104.633	51.925	169.539
$q(\alpha, 3)$	...	...	169.539	51.925	-104.633
$[\partial R_{12}/\partial \sigma_\alpha]_N$	21.529	-36.600	-56.393	20.994	-56.393
$[\partial R_{13}/\partial \sigma_\alpha]_N$	...	...	42.365	20.994	42.365
$[\partial R_{23}/\partial \sigma_\alpha]_N$	...	...	-14.028	41.988	-14.028
$[\partial R_{12}/\partial N]_\sigma$	-0.888			0.008	
$[\partial R_{13}/\partial N]_\sigma$	...			0.008	
$[\partial R_{23}/\partial N]_\sigma$	...			0.016	

Various perturbations can push the system to a new equilibrium geometry. Solving Eqs. (53) and (56) gives the bond sensitivity coefficients, which via Eqs. (25) and (26) provide the disconnectivity index  $g$ . Notice that the set of equations is soluble for a diatomic. For larger systems Eqs. (54) and (57) are no longer applicable in their present form (underdetermined set of equations). One should impose constraints for  $v$ , linear in  $R$ ; this will be demonstrated in the examples below.

In the spirit of the charge sensitivity analysis (CSA), developed by Nalewajski,<sup>31,32</sup> one can then proceed along the same lines to complete the description of the system responses, by a bond sensitivity analysis (BSA). This will be useful in particular cases where nuclear displacements are the variables of interest (e.g., bond breaking/formation, vibrational models of reactivity,...).

## VIII. ILLUSTRATIVE CALCULATIONS ON CO AND CO<sub>2</sub>

Model calculations have been carried out on two small molecules CO and CO<sub>2</sub>. Using EEM, the nuclear sensitivity coefficients were calculated by using Eqs. (53) and (56). For the electronic indices we refer to the literature.<sup>27,29,30</sup> Starting configuration, parameters, and results are reported in Table II.

Notice that the calculations of the triatomic molecule CO<sub>2</sub> can be performed by imposing a constraint of linearity:  $dR_{23} = dR_{12} + dR_{13}$ ; this gives an independent equation: that makes the set exactly soluble.

Considering the global quantities, it is seen that the hardness in the isomorphic ensemble is somewhat larger than in the canonical;  $\bar{\eta}^\sigma > \bar{\eta}^v$ .



Locally, one can compare the electronic responses in both ensembles [ $f$  and  $\sigma$ ; cf. see Eq. (34)]. For  $\text{CO}_2$  these quantities are nearly identical. However, in  $\text{CO}$  the constraints reverse the electronic responses to a  $dN$  perturbation;  $f_{\text{C}} > f_{\text{O}}$  and  $\sigma_{\text{C}} < \sigma_{\text{O}}$ . Comparing the absolute quantity (local softness) it is seen that the oxygens in both molecules have comparable local softness:  $s_{\text{O}} = 0.023\,22$  in  $\text{CO}$  and  $s_{\text{O}} = 0.027\,54$  in  $\text{CO}_2$ . However the carbon in  $\text{CO}$  ( $s_{\text{C}} = 0.039\,47$ ) is much softer than in  $\text{CO}_2$  ( $s_{\text{C}} = 0.018\,40$ ). Notice that the Fukui function (or local softness) does not always follow the sequence of the AIM hardness parameters ( $\eta_{\alpha}^*$ ;  $\eta_{\text{C}}^* < \eta_{\text{O}}^*$ , but in  $\text{CO}_2$ ,  $f_{\text{C}} < f_{\text{O}}$ ). This reflects the external potential contributions.

We now analyze the external potential indices. The  $h$ -values clearly bear other information than the Fukui function; both are reactivity indices according to the  $|d\mu|$  postulate,<sup>2</sup> and show different relative preferences for the different sites within a molecule. In  $\text{CO}$ , e.g., the C atom is the softest, while the  $h$ -index is largest for O. The softest electron fluctuations are thus expected at C, while  $v$ -fluctuations are preferred at O. In a diatomic molecule these  $v$ -fluctuations can of course not be interpreted in terms of preferences in bond breaking, since only one bond contributes.

The (dis)connectivity index  $g$  shows large differences between the two molecules. The large positive value for  $\text{CO}$  is due to the considerable contraction of the molecule upon adding electrons ( $dR/dN < 0$ ). Removing electrons thus disconnects the atoms, i.e., weakens the  $\text{CO}$  bond. In  $\text{CO}_2$ , the bonds are much less sensitive to  $dN$  perturbation (which is to be expected for a larger system in which the response is spread over the whole molecule; cf. the same effect can be observed for electronic responses).

Chemically speaking, a unit displacement of  $\sigma$  is drastic. Responses to such perturbations are generally large. Notice that Maxwell relations do not translate into permutivity with respect to the indices here [ $q(1,2) \neq q(2,1)$ ].

## IX. SUMMARY

The modified  $\mathcal{F}$ -Legendre transformed representation of the density functional theory has been shown to provide the ensemble of choice when  $v$ -fluctuations are envisaged. Nuclear/geometric response parameters are thereby identified as reactivity indices (through the postulated criterion of  $d\mu$ ), having the same status as the electronic reactivity indices such as the Fukui function and local softness in the (grand) canonical ensemble. Low-energy  $v$ -fluctuations favor bond breaking or formation while low-energy  $\rho$ -fluctuations reflect an increased probability for a charge transfer process to occur. Explicit expressions demonstrate that  $v$ -fluctuations measure the (dis)connection of points or atoms to (from) the system, by changing the equilibrium distances.

A nuclear reactivity index has been defined which provides an attractive definition for local hardness. The defined sensitivity coefficients should be of primary importance in all bond breaking/forming reactions, so that the present development is complementary to the electronic description, which is especially suited for charge transfer processes. In

the atom-in-molecule resolution bond sensitivity analyses can be performed.

There remains, of course, the overriding fundamental question of why, in fact, the magnitude of the chemical potential change is so signally important for understanding chemical reactivity.

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## APPENDIX: REMARK ON CERTAIN FUNCTIONAL DERIVATIVES

For every quantity  $A$  which is a functional of  $x$ ,  $A[x]$ , with a constraint for  $x$ ,

$$\int x(\mathbf{r})d\mathbf{r} = \text{constant} \quad (\text{A1})$$

the functional derivative of  $A$  with respect to  $x$ ,

$$\frac{\delta A[x]}{\delta x(\mathbf{r})}, \quad (\text{A2})$$

is defined only up to a constant.<sup>20</sup> This kind of derivative appears in the original paper introducing Legendre transforms in dft,<sup>15</sup> and also in the present paper. For example Eq. (8) of the text may be written in the form

$$\frac{1}{N} \left[ \frac{\delta F}{\delta \sigma(\mathbf{r})} \right]_N + v(\mathbf{r}) = C, \quad (\text{A3})$$

where  $C$  is an arbitrary constant which cannot be determined without additional information. But the constant never appears if one starts with an explicit analytical formula or computational procedure for working with the quantity  $A$  (as is the case with the EEM approach). Also it does not affect the fluctuation formulas. For example,

$$\begin{aligned} & \frac{1}{kT} \{ \langle \mu \cdot [v(\mathbf{r}) + C] \rangle - \langle \mu \rangle \langle v(\mathbf{r}) + C \rangle \} \\ &= \frac{1}{kT} [ \langle \mu \cdot v(\mathbf{r}) \rangle - \langle \mu \rangle \langle v(\mathbf{r}) \rangle ], \end{aligned} \quad (\text{A4})$$

which appears in Eq. (21).

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