General Relations between Molecular Sensitivities and Their Physical Content *

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The molecular Legendre transformed representations are reexamined. They correspond to alternative sets of parameters defining the constraints imposed on the system. In the *global description* the molecular (equilibrium) states are defined by the global state parameter $G = (N$ or $\mu)$ and the state function $f(\mathbf{r}) = [v(\mathbf{r})$ or $n(\mathbf{r})]$; N is the system number of electrons, μ its chemical potential, v stands for the external potential due to the nuclei, and n is the electron density. In the *local description*, capable of defining non-equilibrium molecular density distributions, the state is defined by two state functions, $g(\mathbf{r}) = [n(\mathbf{r})$ or $\mu(\mathbf{r})]$ and $f(\mathbf{r})$; here $\mu(\mathbf{r})$ is the local chemical potential of the electron distribution in small volume element around $\mathbf{r}$. The Maxwell cross differentiation identities in both approaches, relating various molecular sensitivities, are physically interpreted. A qualitative discussion of general relations between molecular sensitivities is given and their physical content and possible applications are commented upon.

1. Introduction

One of the central problems of quantum chemistry has been to determine and relate various atomic and molecular responses to small displacements in the state-parameters (generalized "coordinates", defining the system constraints). Such a sensitivity analysis provides information about various mutual interactions between such coordinates when constraints imposed on the system are slightly changed and can help to clarify bonding concepts. An example of formal relations between such sensitivities, under different constraints, is provided by the familiar Maxwell identities, which can be derived for various Legendre transformed representations (LTR's), corresponding to different sets of the state-parameters.

In recent papers [1–5] the LTR's of atomic and molecular states, within the framework of the density functional theory (DFT) [6], have been examined and the corresponding Maxwell identities explored. Also, the reduction of molecular and atomic sensitivities to an identity in terms of a small set of basic derivatives has been presented [3–5]. The discussion of the reduced atomic sensitivities [5] leads to a better understanding of various atomic responses to hypothetical or real displacements (changes in the atom environment), which is of great importance for the atoms-in-a-molecule (AIM), thermodynamic-like modeling of the chemical bond [5, 7–14]. Such semiquantitative models provide useful interpretative tools in chemistry and complement more rigorous [15] and exact [16, 17] quantum mechanical AIM treatments.

The purpose of this work is to qualitatively examine the physical content of various molecular sensitivities appearing within the LTR's of molecular states, and to explore general qualitative relations between them. The present analysis represents a local extension of the previous analysis [5] for atoms and AIM's, for which only global parameters enter the list of variables defining the equilibrium states. There are two possible approaches to the molecular states [9]. The *global description* deals only with the equilibrium molecular states and uses, besides the external potential (or its conjugate, the electronic density), a global parameter (the number of electrons or its conjugate, the *global chemical potential*) to define the equilibrium state of a molecule. The *local description* replaces this global parameter by the electron density or the *local chemical potential*, thus offering the most detailed treatment of the displacement/response changes at each local volume element, capable of defining the non-equilibrium states of a molecule [4] when there is

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no equalization of the local chemical potential throughout the system. Sections 2 and 3 summarize the relations and interpretations of molecular sensitivities for the global approach while Sect. 4 briefly examines the relations between sensitivities in the local approach.

2. Molecular LTR's, Maxwell Identities, and Sensitivities

The coulombic molecular, electronic Hamiltonian is defined by the number of electrons, N, and the external potential due to the nuclei, v. The equilibrium state energy $E(N, v)$ is given by the Schroedinger, $E(N, v) = \langle \psi(N, v) | \hat{H}(N, v) | \psi(N, v) \rangle$, or the Hohenberg-Kohn [6], $E(N, v) = \tilde{E}[n(N, v), v] = \int \mathrm{d}\boldsymbol{r}\, n\, v + \tilde{F}[n]$, functionals, with the universal functional $\tilde{F}[n]$ generating the sum of the electronic kinetic and repulsion energies. Here $\psi(N, v)$ is the ground-state wavefunction, and the equilibrium electronic density n (normalized to N, $\int \mathrm{d}\boldsymbol{r}\, n(N, v) = N$) satisfies the Euler equation [10],

$$\begin{aligned} \mu(N, v) &= \partial E(N, v)/\partial N \\ &= \delta \tilde{E}[n, v]/\delta n(\boldsymbol{r}) = v(\boldsymbol{r}) + \delta \tilde{F}/\delta n(\boldsymbol{r}), \end{aligned} \tag{1}$$

with the corresponding value of the chemical potential (global, the negative of the system electronegativity) $\mu(N, v)$.

By the Hellmann-Feynmann theorem the partial derivative

$$\delta E(N, v)/\delta v = \delta \tilde{E}[n, v]/\delta v = n(N, v), \tag{2}$$

so that the energy differential is

$$\mathrm{d}E(N, v) = \mu(N, v)\, \mathrm{d}N + \int \mathrm{d}\boldsymbol{r}\, n(N, v)\, \delta v. \tag{3}$$

The Legendre transforms of $E(N, v)$, corresponding to the alternative sets of constraints imposed upon the system, are [1]

$$\begin{aligned} Q(\mu, v) = E - \mu N,\ F(N, n) &= E - \int \mathrm{d}\boldsymbol{r}\, n\, v \\ &= \tilde{F}[n], \text{ and } R(\mu, n) = F - \mu N, \end{aligned}$$

with the respective differentials

$$\begin{aligned} \mathrm{d}Q(\mu, v) &= -N(\mu, v)\, \mathrm{d}\mu + \int \mathrm{d}\boldsymbol{r}\, n(\mu, v)\, \delta v \\ &= \int \mathrm{d}\boldsymbol{r}\, n(\mu, v)\, \delta(v - \mu), \end{aligned} \tag{4}$$

$$\begin{aligned} \mathrm{d}F(N, n) &= \mu(N, n)\, \mathrm{d}N - \int \mathrm{d}\boldsymbol{r}\, v(N, n)\, \delta n \\ &= \int \mathrm{d}\boldsymbol{r}\, [\mu(N, n) - v(N, n)]\, \delta n, \end{aligned} \tag{5}$$

$$\mathrm{d}R(\mu, n) = -N(\mu, n)\, \mathrm{d}\mu - \int \mathrm{d}\boldsymbol{r}\, v(\mu, n)\, \delta n. \tag{6}$$

If one wishes to consider a molecular system perturbed by an extra external electric field $\varphi(\boldsymbol{r})$ due to the system environment, e.g., a reaction partner, a surface of a catalyst, environment of an AIM, etc., the density and the chemical potential are those describing the equilibrium state for the resultant external potential $u = v + \varphi$, $n = n(N, u)$ and $\mu = \mu(N, u)$.

The second partial derivatives of the energy and its transforms represent various molecular sensitivities, corresponding to different constraints. The energy derivatives represent natural *molecular stiffness moduli*, relating "forces" $\mathrm{d}\mu$ and $\delta n(\boldsymbol{r})$ to the "displacements" $\mathrm{d}N$ and $\delta v(\boldsymbol{r}')$:

$$\begin{aligned} &[\mathrm{d}\mu, \delta n(\boldsymbol{r})]^{\mathrm{T}} \\ &= \begin{bmatrix} \partial\mu/\partial N & \int \mathrm{d}\boldsymbol{r}'\, \delta\mu/\delta v(\boldsymbol{r}') \\ \partial n(\boldsymbol{r})/\partial \mathrm{N} & \int \mathrm{d}\boldsymbol{r}'\, \delta n(\boldsymbol{r})/\delta v(\boldsymbol{r}') \end{bmatrix} \begin{bmatrix} \mathrm{d}N \\ \delta v(\boldsymbol{r}') \end{bmatrix}. \end{aligned} \tag{7}$$

By the same analogy, to the equations of elasticity, the fully inverted stiffness matrix operator of (7) can be regarded as the *molecular compliance matrix operator* with the compliance coefficients given by the second partial derivatives of $R(\mu, n)$. The $Q(\mu, v)$ and $F(N, n)$ potentials similarly generate the partially inverted relations between forces and displacements.

Molecular sensitivities measure the responses of a system per unit displacement in some externally controlled parameters. The derivative $\partial^2 E/\partial N^2 = (\partial\mu/\partial N)_v$ in (7) is the *molecular* (*global*) *hardness* of Parr and Pearson [13], while the mixed derivative $\partial[\delta E/\delta v(\boldsymbol{r})]/\partial N = (\partial n(\boldsymbol{r})/\partial N)_v$ is the *Fukui function*, used by Parr et al. [18] to formally relate the DFT to the principal ideas of the frontier MO theory [19].

The Maxwell identity between the mixed second partial derivatives of $E(N, v)$ is

$$(\partial n(\boldsymbol{r})/\partial N)_v = (\delta\mu/\delta v(\boldsymbol{r}))_N. \tag{8}$$

The physical picture behind this identity is the following: Any local lowering of the external potential, $\delta v(\boldsymbol{r}) < 0$, should attract more particles to the system, $\delta N > 0$, from the particle reservoir (R) coupled to the system, since it lowers the system chemical potential. Therefore, in order to keep N constant, the chemical potential of the reservoir, μ_{R} must simultaneously be lowered, $\delta\mu_{\mathrm{R}} = \delta\mu < 0$, as required by the equilibrium criterion. Therefore $(\delta\mu/\delta v(\boldsymbol{r}))_N > 0$ and, by the Maxwell relation (8), the Fukui function should also be positive.

Another identity relates the sensitivities represented by the second partial derivatives of $Q(\mu, v)$:

$$-(\delta N/\delta v(\boldsymbol{r}))_\mu = (\partial n(\boldsymbol{r})/\partial\mu)_v. \tag{9}$$

A given displacement $d\mu_R > 0$ must result in $dN > 0$ (an inflow of electrons to the system), which in turn, by the positive character of the Fukuin function, generates $\delta n(\mathbf{r}) > 0$. Notice that $dN > 0$ will also give rise to $d\mu > 0$, thus bringing the system back to the equilibrium, $\mu = \mu_R$, with the displaced state of the reservoir, in accordance with the Le Châtelier stability criterion [2, 4, 8, 9]

$$(\partial \mu / \partial N)_v > 0 . \tag{10}$$

Therefore $(\partial n(\mathbf{r})/\partial \mu)_v > 0$ and hence $(\delta N/\delta v(\mathbf{r}))_\mu < 0$. The second inequality has a similar interpretation. Namely, since a given $\delta v(\mathbf{r}) < 0$ implies $d\mu < 0$ for constant N, to fulfill the $\mu =$ const. constraint the system must absorb $dN > 0$ particles from the reservoir to rise μ to its initial level, before the primary displacement in external potential.

The Maxwell relation for the $R(\mu, n)$ potential reads

$$(\delta N/\delta n(\mathbf{r}))_\mu = (\partial v(\mathbf{r})/\delta \mu)_n = 1 , \tag{11}$$

where the second equality immediately follows from the Euler equation (1) and the known functional $N = \int d\mathbf{r}\, n(\mathbf{r})$. Thus, for a constant density the equilibrium condition requires a uniform change of the external potential everywhere, equal to a displacement in the chemical potential of a reservoir.

Before discussing the derivatives within the $F(N, n)$ representation we shall briefly comment on the meaning of the $(\delta/\delta n(\mathbf{r}))_N$ and $(\partial/\partial N)_n$ differentiation. The first-order infinitesimal change of density, $\delta n(\mathbf{r})$, of the local infinitesimal subsystem of volume $\delta\tau$ around $\mathbf{r}$, $\delta\tau(\mathbf{r})$, affects the number of particles of the system only in the second-order: $dN \sim \delta n(\mathbf{r})\, \delta\tau(\mathbf{r})$. Similarly, because of the assumed initial equilibrium (equalization of the chemical potentials of local subsystems throughout the entire system) each local infinitesimal subsystem has the first-order share in dN (also infinitesimal) proportional to $\delta\tau(\mathbf{r})$. Therefore dN changes the local density only in the second order: $\delta n(\mathbf{r}) \sim dN/V$, where V is the total volume of the system.

We thus conclude that the constraints of constant n or N are preserved within the $F(N, n)$ representation only approximately: the first-order displacement in one of the parameters preserves the value of the other parameter constant to the first-order [20].

This situation has an analogy in statistical thermodynamics [21]. In the usual formulation an ensemble is identified with a collection of independent replicas of the system under study. In a more physical approach individual members of the ensemble are parts (subsystems) of the system under study, in contact with their surroundings (rather than abstract reservoirs), interacting throughout their mutual interfaces. In the first formulation only one of a pair of conjugate thermodynamic variables can fluctuate, while the second formulation allows fluctuations in both such parameters since the statistical independence of the individual members is then only approximately valid.

The Maxwell identity for the mixed sensitivities generated by the $F(N, n)$ potential is

$$(\delta \mu/\delta n(\mathbf{r}))_N = -\,(\partial v(\mathbf{r})/\partial N)_n . \tag{12}$$

A displacement in local density, $\delta n(\mathbf{r}) > 0$, is due to the inflow of $\delta\tau(\mathbf{r})\, \delta n(\mathbf{r})$ electrons to the local system at the expense of the system remainder acting as a reservoir. Such a change can only be effected when $\delta v(\mathbf{r}) < 0$, which implies $d\mu < 0$. Therefore $(\delta\mu/\delta n(\mathbf{r}))_N < 0$ and hence $(\partial v(\mathbf{r})/\partial N)_n > 0$. The latter inequality has a simple rationalization: an inflow of particles to the system, $dN > 0$ must rise μ, but this can be realized under the $n =$ const. constraint only by locally increasing the external potential.

3. Qualitative Discussion of Relations between Molecular Sensitivities

We now qualitatively compare the interaction between n and v under different constraints. First let us examine the diagonal elements of the symmetric density polarization kernel, $\delta^2 E/\delta v(\mathbf{r})\, \delta v(\mathbf{r}') = (\delta n(\mathbf{r})/\delta v(\mathbf{r}'))_N$. Obviously, since $\delta v(\mathbf{r}) < 0$ attracts more electrons to $\delta\tau(\mathbf{r})$, $(\delta n(\mathbf{r})/\delta v(\mathbf{r}))_N < 0$. Examine now the $\delta n(\mathbf{r})/\delta v(\mathbf{r}))_\mu$ sensitivity appearing within the $Q(\mu, v)$ representation. The primary local displacement $\delta v(\mathbf{r}) < 0$ creates, besides the direct local response $\delta n(\delta v) > 0$, an extra inflow of electrons from the reservoir, $\delta n(d\mu) > 0$, due to a nonzero indirectly induced force $d\mu(\delta v) < 0$. Hence

$$(\delta n(\mathbf{r})/\delta v(\mathbf{r}))_\mu < (\delta n(\mathbf{r})/\delta v(\mathbf{r}))_N < 0 . \tag{13}$$

A similar relation holds for atoms [5]. It should be noticed that such an indirectly coupled force, $d\mu(\delta v)$, will subsequently generate a moderating flow of particles to the remainder of the system, outside $\delta\tau(\mathbf{r})$, thus reducing the net outflow of particles from the surroundings of $\delta\tau(\mathbf{r})$, $dN \sim -\,\delta n(\mathbf{r})\, \delta\tau(\mathbf{r})$, generated by the primary displacement $\delta v(\mathbf{r})$. This is in accordance with the familiar Le Châtelier-Braun principle. Clearly, the resultant changes in the density will rise the displaced μ back to μ_R, to regain the equilibrium state with the reservoir.

For the offdiagonal elements of the density response kernel both signs are possible [22]:

$$(\delta n(\mathbf{r}'')/\delta v(\mathbf{r}))_N > 0, \quad \mathbf{r}'' \neq \mathbf{r}, \quad \text{or} \tag{14a}$$

$$(\delta n(\mathbf{r}')/\delta v(\mathbf{r}))_N < 0, \quad \mathbf{r}' \neq \mathbf{r}. \tag{14b}$$

The positive sign is in the region of $\mathbf{r}''$ where $\delta v(\mathbf{r}) > 0$ attracts electrons, and the negative sign is for $\mathbf{r}'$ where such a displacement in v repels electrons. Taking into account the additional, moderating, indirectly induced flows of particles from the reservoir, possible for the $\mu =$ const. constraint, we have the two respective inequalities for the offdiagonal sensitivities

$$0 < (\delta n(\mathbf{r}'')/\delta v(\mathbf{r}))_\mu < (\delta n(\mathbf{r}'')/\delta v(\mathbf{r}))_N, \quad \mathbf{r}'' \neq \mathbf{r}; \tag{15a}$$

$$(\delta n(\mathbf{r}')/\delta v(\mathbf{r}))_\mu < (\delta n(\mathbf{r}')/\delta v(\mathbf{r}))_N < 0, \quad \mathbf{r}' \neq \mathbf{r}. \tag{15b}$$

The second inequality, relating the interactions between the directly coupled variables, compares the hardness sensitivities under the two alternative constraints

$$(\partial\mu/\partial N)_n > (\partial\mu/\partial N)_v > 0. \tag{16}$$

Thus, a system is harder when the density is "frozen" and softer for the fixed external potential. The justification for this relation is similar to that given for atoms [5]. Namely, any $\mathrm{d}N > 0$ leads to both $\mathrm{d}\mu(\mathrm{d}N) > 0$ (Le Châtelier rule) and $\delta n(\mathrm{d}N) > 0$ (positive character of the Fukui function). Therefore, in the first derivative of (16) there has to be an accompanying change in v, $\delta v > 0$, leading to $\delta n(\delta v) < 0$ [see (13)] and thus keeping $n =$ const. However, this change in the external potential creates an extra increase in the chemical potential, $\mathrm{d}\mu(\delta v) > 0$. Therefore the resultant response in μ is larger when n remains constrained, in comparison with the "frozen" v case.

We now examine analogous relations comparing the interactions between nondirectly coupled variables. First, let us consider the Fukui function -type derivatives, $\partial n(\mathbf{r})/\partial N$, for the system in equilibrium with a particle reservoir ($\mu =$ const.) and a system with the constrained external potential. A given primary displacement $\mathrm{d}N > 0$ must lead, by the stability criterion, to $\mathrm{d}\mu(\mathrm{d}N) > 0$. Therefore the $\mu =$ const. condition calls for a change in v such that $\mathrm{d}\mu(\delta v) < 0$, in order to offset $\mathrm{d}\mu(\mathrm{d}N)$. Now, since $(\delta\mu/\delta v(\mathbf{r}))_N > 0$ [see the discussion of (8)] this can be achieved by lowering the external potentional at some location $\mathbf{r}'$: $\delta v(\mathbf{r}') < 0$. The resulting extra change in density at $\mathbf{r}$ (in addition to that generated by $\mathrm{d}N$) will depend on the sign of the density response sensitivity $(\delta n(\mathbf{r})/\delta v(\mathbf{r}'))_N$ [see (14)]. For the positive sign the primary response $\delta n(\mathrm{d}N) > 0$ is moderated by $\delta n(\delta v) < 0$,

$$(\partial n(\mathbf{r})/\partial N)_v > (\partial n(\mathbf{r})/\partial N)_\mu > 0, \tag{17a}$$

while for the negative sign the secondary increase in local density enhances the primary response,

$$(\partial n(\mathbf{r})/\partial N)_\mu > (\partial n(\mathbf{r})/\partial N)_v > 0. \tag{17b}$$

The final interactions we wish to relate here are those between μ and v. For the "frozen" n, when no internal density readjustments within the system are allowed, $(\delta\mu/\delta v(\mathbf{r}))_n = 1$, for all locations [see (11))]. This sensitivity implies a uniform shift of v *everywhere* by a constant $\mathrm{d}\mu$, since only then the constrained density is still in equilibrium [see (1)] with the displaced v. The other derivative, $(\delta\mu/\delta v(\mathbf{r}))_N > 0$ [see the discussion of (8)] implies a *local* change of the external potential at $\delta\tau(\mathbf{r})$; such a displacement will subsequently trigger the internal flow of particles to $\delta\tau(\mathbf{r})$ from the system remainder, $\delta n(\mathbf{r}) > 0$. Such spontaneous, moderating flows will again equalize the chemical potential at a new level, with the resultant smaller magnitude of the response, $|\mathrm{d}\mu(\delta v)_N| < |\mathrm{d}\mu(\delta v)_n|$. Hence the final relation:

$$1 = (\delta\mu/\delta v(\mathbf{r}))_n > (\delta\mu/\delta v(\mathbf{r}))_N > 0. \tag{18}$$

4. Sensitivities in the Local Approach

In the local description [9] the electronic energy for a given density n and an external potential v is [4]

$$\mathscr{E}[n,v] = \min_{\psi_n} \langle\psi_n|\hat{H}(v)|\psi_n\rangle = \int \mathrm{d}\mathbf{r}\, v_n + \langle\psi[n]|\hat{F}|\psi[n]\rangle = \int \mathrm{d}\mathbf{r}\, v_n + \tilde{\mathscr{F}}[n], \tag{19}$$

where ψ_n is a wavefunction giving rise to the density n [23], and $\psi[n]$ stands for ψ_n for which the expectation value of the sum of the electronic kinetic and repulsion energies ($\hat{F} = \hat{T}_e + \hat{V}_{ee}$) reaches the minimum value. In the case of equilibrium n the Levy [24] functional $\tilde{\mathscr{F}}[n]$ yields the same $T_e + V_{ee}$ energy as does the Hohenberg-Kohn functional $\tilde{F}[n]$. The energy differential is

$$\mathrm{d}\mathscr{E} = \int \mathrm{d}\mathbf{r}\left\{\left(\frac{\delta\mathscr{E}}{\delta n(\mathbf{r})}\right)_v \delta n(\mathbf{r}) + \left(\frac{\delta\mathscr{E}}{\delta v(\mathbf{r})}\right)_n \delta v(\mathbf{r})\right\} = \int \mathrm{d}\mathbf{r}\,[\mu(\mathbf{r})\,\delta n(\mathbf{r}) + n(\mathbf{r})\,\delta v(\mathbf{r})]. \tag{20}$$

The local chemical potential,

$$\mu(\mathbf{r}) = v(\mathbf{r}) + \delta\tilde{\mathcal{F}}/\delta n(\mathbf{r}), \tag{21}$$

becomes equal throughout the whole molecular charge distribution for an equilibrium density [identical with the Lagrangian multiplier $\mu(N, v)$ of (1)].

The *equilibrium* state corresponds to the case of no constraints on the flow of electrons between local volume elements; in the case of an open system, the molecule is additionally coupled to the reservoir R of electrons. The non-equilibrium case, in which no flows between local volume elements are allowed, represents a state of equilibrium within each local subsystem; we call it the *constrained-equilibrium* state. For open systems the constrained-equilibrium can be visualized as being realized by coupling each local subsystem $\delta\tau(\mathbf{r})$ (an infinitesimal local volume element) to its own reservoir, $R(\mathbf{r})$, characterized by the chemical potential $\mu[R(\mathbf{r})] = \mu(\mathbf{r})$ with no coupling between the reservoirs. The equilibrium and constrained-equilibrium states of an open system are schematically shown in Figure 1.

The Legendre transforms of $\mathscr{E}[n, v]$ are the functionals $\mathscr{Q}[\mu, v] = \mathscr{E} - \int d\mathbf{r}\, \mu(\mathbf{r}) n(\mathbf{r})$, $\mathscr{F}[n, n] = \mathscr{E} - \int d\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) = \tilde{\mathscr{F}}[n]$, $\mathscr{R}[\mu, n] = \mathscr{F} - \int d\mathbf{r}\, \mu(\mathbf{r}) n(\mathbf{r})$ with the corresponding differentials

$$\begin{aligned} d\mathscr{Q} &= \int d\mathbf{r}\,[-n(\mathbf{r})\,\delta\mu(\mathbf{r}) + n(\mathbf{r})\,\delta v(\mathbf{r})] \\ &= \int d\mathbf{r}\, n(\mathbf{r})\,\delta w(\mathbf{r}), \end{aligned} \tag{22}$$

$$\begin{aligned} d\mathscr{F} &= \int d\mathbf{r}\,[\mu(\mathbf{r})\,\delta n(\mathbf{r}) - v(\mathbf{r})\,\delta n(\mathbf{r})] \\ &= -\int d\mathbf{r}\; w(\mathbf{r})\,\delta n(\mathbf{r}), \end{aligned} \tag{23}$$

$$d\mathscr{R} = -\int d\mathbf{r}\,[n(\mathbf{r})\,\delta\mu(\mathbf{r}) + v(\mathbf{r})\,\delta n(\mathbf{r})], \tag{24}$$

where $w = v - \mu$ represents an effective external potential [the conjugate of $n(\mathbf{r})$].

The second-order derivatives of $\mathscr{E}$ are

$$\begin{aligned} \frac{\delta^2\mathscr{E}}{\delta n(\mathbf{r}')\,\delta n(\mathbf{r})} &= \left(\frac{\delta\mu(\mathbf{r})}{\delta n(\mathbf{r}')}\right)_v = \left(\frac{\delta\mu(\mathbf{r}')}{\delta n(\mathbf{r})}\right)_v \\ &= \frac{\delta^2\tilde{\mathscr{F}}}{\delta n(\mathbf{r}')\,\delta n(\mathbf{r})} = \eta(\mathbf{r}, \mathbf{r}'), \end{aligned} \tag{25}$$

$$\frac{\delta^2\mathscr{E}}{\delta n(\mathbf{r})\,\delta v(\mathbf{r}')} = \left(\frac{\delta n(\mathbf{r}')}{\delta n(\mathbf{r})}\right)_v = \delta(\mathbf{r} - \mathbf{r}') = \left(\frac{\delta\mu(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_n, \tag{26}$$

and, for the constrained-equilibrium case (Figure 1 b), $\delta^2\mathscr{E}/\delta v(\mathbf{r})\,\delta v(\mathbf{r}') = [\delta n(\mathbf{r}')/\delta v(\mathbf{r})]_n = 0$ [25]. Equation (25) exhibits the symmetric form of the *local hardness* kernel $\eta(\mathbf{r}, \mathbf{r}')$ [9], while (26) represents the local analogue of (8).

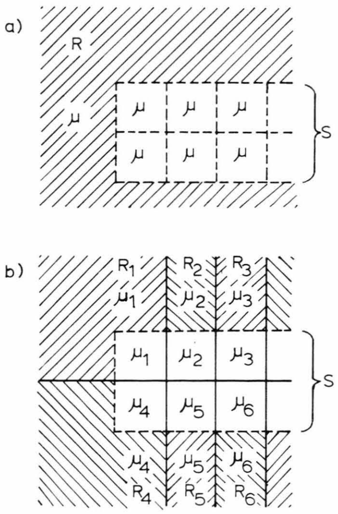

Fig. 1. The equilibrium (a) and constrained equilibrium (b) states of an open system S.

The local stability criterion is $\eta(\mathbf{r}, \mathbf{r}) > 0$. The off-diagonal local hardnesses should also be positive, $\eta(\mathbf{r}, \mathbf{r}') > 0$, since, for constant v, an inflow of electrons to $\delta\tau(\mathbf{r}')$ from its own reservoir (with the "frozen" density in the remainder of the system) should increase the chemical potential at $\delta\tau(\mathbf{r})$, due to an extra repulsive potential at $\mathbf{r}$, due to the presence of extra electronic charge in $\delta\tau(\mathbf{r}')$. The same positive structure of the AIM hardness matrix has been reported in our previous analysis [5], with the model off-diagonal AIM hardness, η_{XY}, being positive and inversely proportional to the internuclear distance R_{XY}.

The second-order derivatives of $\mathscr{Q}$ lead to the general symmetry relation

$$\delta^2\mathscr{Q}/\delta w(\mathbf{r})\,\delta w(\mathbf{r}') = \delta n(\mathbf{r})/\delta w(\mathbf{r}') = \delta n(\mathbf{r}')/\delta w(\mathbf{r}). \tag{27}$$

Its particular cases are

$$\left(\frac{\delta^2\mathscr{Q}}{\delta\mu(\mathbf{r})\,\delta\mu(\mathbf{r}')}\right)_v = \left(\frac{\delta n(\mathbf{r})}{\delta\mu(\mathbf{r}')}\right)_v = \left(\frac{\delta n(\mathbf{r}')}{\delta\mu(\mathbf{r})}\right)_v = \tilde{\eta}^{-1}(\mathbf{r}', \mathbf{r}), \tag{28}$$

$$\frac{\delta^2\mathscr{Q}}{\delta v(\mathbf{r}')\,\delta\mu(\mathbf{r})} = -\left(\frac{\delta n(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_\mu = \left(\frac{\delta n(\mathbf{r}')}{\delta\mu(\mathbf{r})}\right)_v, \tag{29}$$

$$\left(\frac{\delta^2\mathscr{Q}}{\delta v(\mathbf{r})\,\delta v(\mathbf{r}')}\right)_\mu = \left(\frac{\delta n(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_\mu = \left(\frac{\delta n(\mathbf{r}')}{\delta v(\mathbf{r})}\right)_\mu = \tilde{\beta}(\mathbf{r}', \mathbf{r}). \tag{30}$$

Equation (29), $-\tilde{\beta}(\mathbf{r},\mathbf{r}') = \tilde{\eta}^{-1}(\mathbf{r}',\mathbf{r})$, constitutes the local analogue of (9) and provides a valuable relation between the density relaxation and the system stability [22]. We call the inverse hardness kernel, the *softness kernel* [26, 27]. The qualitative interpretation of (29) is similar to that of (9). Consider first the diagonal case, $\mathbf{r}' = \mathbf{r}$. A given $\delta v(\mathbf{r}) < 0$ displacement must result in an inflow of electrons from the reservoir $R(\mathbf{r})$ to $\delta\tau(\mathbf{r})$: $\tilde{\beta}(\mathbf{r},\mathbf{r}) < 0$. Similarly, an increase of $\mu[R(\mathbf{r})]$ causes an inflow of electrons to $\delta\tau(\mathbf{r})$: $\tilde{\eta}^{-1}(\mathbf{r},\mathbf{r}) > 0$. The off-diagonal "softness" sensitivity, $\tilde{\eta}^{-1}(\mathbf{r},\mathbf{r}')$, measures a response in density at $\mathbf{r}$ to a unit displacement of $\mu[R(\mathbf{r}')]$. Now, $\delta\mu[R(\mathbf{r}')] > 0$ produces $\delta n(\mathbf{r}') > 0$, and by the positive value of $\eta(\mathbf{r},\mathbf{r}')$ this in turn generates the secondary change $\delta\mu(\mathbf{r}) > 0$, leading to an outflow of electrons from $\delta\tau(\mathbf{r})$ to $R(\mathbf{r})$: $\tilde{\eta}^{-1}(\mathbf{r},\mathbf{r}') < 0$. From the Maxwell relation (29) we therefore have $\tilde{\beta}(\mathbf{r}',\mathbf{r}) > 0$. The qualitative reason for the last inequality is the following: $\delta v(\mathbf{r}) < 0$ implies $\delta n(\mathbf{r}) > 0$, and this induces a change $\delta\mu(\mathbf{r}') > 0$, triggering an outflow of electrons from $\delta\tau(\mathbf{r}')$ to $R(\mathbf{r}')$. Equations (28) and (30), respectively, demonstrate the symmetric character of the local softness and the density response kernels.

The general symmetry relation between sensitivities generated by the functional $\mathscr{F}$ is

$$\frac{\delta^2\mathscr{F}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')} = \frac{\delta w(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta w(\mathbf{r}')}{\delta n(\mathbf{r})}. \tag{31}$$

Its particular case, for the fixed v, recovers the symmetry relation (25) for the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$. Assuming the fixed μ one obtains from (31) the symmetry relation for the $\tilde{\beta}^{-1}$ kernel, the negative of the hardness kernel $\tilde{\eta}$ in the $\mathscr{Q}$ representation [see (29)]. Hence, $[\delta v(\mathbf{r})/\delta n(\mathbf{r}')]_\mu < 0$; the displacement $\delta n(\mathbf{r}) > 0$ changes the local chemical potential $\delta\mu(\mathbf{r}) > 0$ and $\delta\mu(\mathbf{r}') > 0$ [since $\eta(\mathbf{r},\mathbf{r}') > 0$], and thus, in order to satisfy the fixed μ constraint one has to lower the external potential at both locations.

Finally, within the $\mathscr{R}[\mu, n]$ representation one again obtains the symmetry relation of the $\tilde{\beta}^{-1}(\mathbf{r},\mathbf{r}') = -\tilde{\eta}(\mathbf{r}',\mathbf{r})$ kernel, and the inverted equation (26):

$$\frac{\delta^2\mathscr{R}}{\delta\mu(\mathbf{r})\,\delta n(\mathbf{r}')} = \left(\frac{\delta v(\mathbf{r}')}{\delta\mu(\mathbf{r})}\right)_n = \left(\frac{\delta n(\mathbf{r})}{\delta n(\mathbf{r}')}\right)_\mu = \delta(\mathbf{r}-\mathbf{r}').$$

Again, in the constrained equilibrium state, $\delta^2\mathscr{R}/\delta\mu(\mathbf{r})\,\delta\mu(\mathbf{r}') = [\delta n(\mathbf{r})/\delta\mu(\mathbf{r}')]_n = 0$ [25].

Wo now would like to compare the sensitivities in the local approach for different constraints imposed on the system. Since the functional differentiation $\delta/\delta x(\mathbf{r})$ implies the fixed $x(\neq\mathbf{r})$, we use the symbol $\partial/\partial x(\mathbf{r})$, when we want the freedom to change the constraints on the rest of the system, which we call the complementary subsystem.

Let us first consider the diagonal density response, $\partial n(\mathbf{r})/\partial v(\mathbf{r})$, when $n(\mathbf{r}'\neq\mathbf{r})$ and $\mu(\mathbf{r}'\neq\mathbf{r})$ are fixed, respectively. The fixed density constraint on the complementary subsystem cancels all the $\delta\tau(\mathbf{r}') - R(\mathbf{r}')$ exchanges of electrons which are allowed when the chemical potentials of $R(\mathbf{r}')$ are fixed. In both cases a given primary displacement $\delta v(\mathbf{r}) = \delta\mu(\mathbf{r}) < 0$ generates the direct response $\delta n(\mathbf{r}) > 0$ via the $R(\mathbf{r}) \to \delta\tau(\mathbf{r})$ flow, leading the the chemical potential equalization of $\tau(\mathbf{r})$ back at the $\mu[R(\mathbf{r})]$ level. This inflow of electrons to $\delta\tau(\mathbf{r})$ creates extra forces, $\delta\mu(\mathbf{r}') > 0$, in the complementary subsystem, which effect the $\delta\tau(\mathbf{r}') \to R(\mathbf{r}')$ flows in the case of the $\mu(\neq\mathbf{r})$ constraint. But this change additionally lowers the chemical potential at $\mathbf{r}$, thus enhancing the primary, directly induced inflow of electrons to $\delta\tau(\mathbf{r})$. Hence the final result is

$$[\delta n(\mathbf{r})/\partial v(\mathbf{r})]_{\mu(\neq\mathbf{r})} < [\partial n(\mathbf{r})/\partial v(\mathbf{r})]_{n(\neq\mathbf{r})} < 0, \tag{32}$$

the local equivalent of (13). One can similarly derive the local analogues of (15).

We now turn to the diagonal hardness, $\partial\mu(\mathbf{r})/\partial n(\mathbf{r})$. The flows between the complementary subsystem and the reservoirs, due to the extra forces $\delta\mu(\mathbf{r}') > 0$ generated by the primary displacement $\delta n(\mathbf{r}) > 0$, will moderate the primary force $\delta\mu(\mathbf{r}) > 0$. Hence [see (16)],

$$[\partial\mu(\mathbf{r})/\partial n(\mathbf{r})]_{n(\neq\mathbf{r})} > [\partial\mu(\mathbf{r})/\partial n(\mathbf{r})]_{\mu(\neq\mathbf{r})} > 0. \tag{33}$$

The same relation holds for the off-diagonal hardness sensitivities, $\partial\mu(\mathbf{r})/\partial n(\mathbf{r}')$, due to moderating flows $\delta\tau(\mathbf{r}'') \to R(\mathbf{r}'')$, which are allowed for the $\boldsymbol{\mu}(\neq\mathbf{r}')$ constraint and forbidden when $\mathbf{n}(\neq\mathbf{r}')$ is fixed.

5. Conclusion

As mentioned before the relations (13)–(18) and (32), (33) constitute the local analogues of the corresponding relations derived for atoms and AIM [5]. In the atomic systems the (global) state variables include N, Z (nuclear atomic number), and their respective conjugates, μ and $\zeta = V_{\text{ne}}/Z$ (the electron-nucleus attraction energy per unit charge of the nucleus). The atomic relations comparing the same displacement-response interactions under different constraints are [5]

$$(\partial\mu/\partial N)_\zeta > (\partial\mu/\partial N)_Z > 0\,, \tag{34}$$

$$(\partial\zeta/\partial Z)_\mu < (\partial\zeta/\partial Z)_N < 0\,, \tag{35}$$

$$(\partial\zeta/\partial N)_\mu < (\partial\zeta/\partial N)_Z < 0\,, \tag{36}$$

$$(\partial\mu/\partial Z)_\zeta < (\partial\mu/\partial Z)_N < 0\,. \tag{37}$$

All these relations directly follow from the exact reduced expressions for the sensitivities involved, in terms of a few basic derivatives [5] and their known signs and relative magnitudes [8].

Assuming a definite partitioning of the molecular space into the atomic (or molecular fragment) regions [16, 17] and integrating the local sensitivities over the respective atomic (or fragment) regions [22] yield the AIM (fragment) sensitivities [5]. The AIM equivalents of (32), (33) are:

$$(\partial N_X/\partial Z_X)_{\boldsymbol{\mu}(\neq X)} > (\partial N_X/\partial Z_X)_{\boldsymbol{N}(\neq X)} > 0\,, \tag{32a}$$

$$(\partial\mu_X/\partial N_X)_{\boldsymbol{N}(\neq X)} > (\partial\mu_X/\partial N_X)_{\boldsymbol{\mu}(\neq X)} > 0\,; \tag{33a}$$

here $\boldsymbol{\mu} = (\mu_1, \dots, \mu_M)$ are the AIM chemical potentials, $\mu_X = (\partial E/\partial N_X)_{\boldsymbol{N}(\neq X)}$, and $\boldsymbol{N} = (N_1, \dots, N_M)$ groups the numbers of electrons associated with each atom.

The relations (34)–(37) must also hold for diagonal AIM sensitivities, e.g.,

$$(\partial\mu_X/\partial N_X)_{\zeta_X, \boldsymbol{C}} > (\partial\mu_X/\partial N_X)_{Z_X, \boldsymbol{C}} > 0\,, \tag{34a}$$

no matter what form the constraints on the remaining atoms, $\boldsymbol{C}$, may assume.

The relations comparing hardness sensitivities for different constraints [(16), (33), (34), (33a) and (34a)] are examples of the *generalized le Châtelier principle* [4, 28]

$$\begin{aligned}(\partial P_k/\partial x_k)_{\boldsymbol{x}(\neq k)} &\geq (\partial P_k/\partial x_k)_{P_1, \boldsymbol{x}[\neq(1,k)]} \geq \dots \\ &\geq (\partial P_k/\partial x_k)_{P_1, \dots, P_{k-1}, x_{k+1}, \dots, x_m} > 0\,, \\ &\qquad k = 1, 2, \dots, m,\end{aligned} \tag{38}$$

where $\boldsymbol{x} = (x_1, \dots, x_m)$ are the extensive parameters (*densities*) and $P = (P_1, \dots, P_m)$ represent their corresponding intensive conjugates (*intensities*). This relation reads [28]: "A locally stable system is displaced from its equilibrium by the displacement δx_k. The system responds by changing its conjugate intensity by δP_k. This response is largest if all the other x_i are fixed, and it decreases upon relaxation of each constraint that frees a variable x_i by coupling the system to a reservoir of intensity P_i."

The $F(\mathscr{F})$ representation, defined for the "extensive" parameters N, $n(\boldsymbol{r})$, and ζ, defines the respective conjugates: μ, $-w(\boldsymbol{r}) = \mu(\boldsymbol{r}) - v(\boldsymbol{r})$, and $-Z$. Hence, for a local description, $\delta[-w(\boldsymbol{r})]_v = \delta\mu(\boldsymbol{r})$ and (33) [or (33a)] directly follows from the generalized Le Châtelier rule (38). The same is true for (34), since Z should be interpreted as the negative "intensity" and ζ as the conjugate "density".

It follows from (35) that for atomic systems (isolated or AIM),

$$(\partial(-Z)/\partial\zeta)_N > (\partial(-Z)/\partial\zeta)_\mu > 0\,. \tag{35a}$$

This equation is also of the form of the generale rule (38).

It should also be observed that (38) immediately suggests additional relations between directly coupled variables. For example, in the local approach

$$\begin{aligned}&\left(\frac{\partial\mu(\boldsymbol{r})}{\partial n(\boldsymbol{r})}\right)_{n(\neq \boldsymbol{r})} \geq \left(\frac{\partial\mu(\boldsymbol{r})}{\partial n(\boldsymbol{r})}\right)_{n[\neq(\boldsymbol{r},\boldsymbol{r}')],\,\mu(\boldsymbol{r}')} \geq \\ &\left(\frac{\partial\mu(\boldsymbol{r})}{\partial n(\boldsymbol{r})}\right)_{n[\neq(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}'')],\,\mu(\boldsymbol{r}'),\,\mu(\boldsymbol{r}'')} \geq \dots \geq \left(\frac{\partial\mu(\boldsymbol{r})}{\partial n(\boldsymbol{r})}\right)_{\mu(\neq \boldsymbol{r})} > 0\,,\end{aligned} \tag{39}$$

and for the AIM representation,

$$\begin{aligned}&\left(\frac{\partial\mu_X}{\partial N_X}\right)_{\boldsymbol{N}(\neq X)} \geq \left(\frac{\partial\mu_X}{\partial N_X}\right)_{\boldsymbol{N}[\neq(X,Y)],\,\mu_Y} \\ &\geq \left(\frac{\partial\mu_X}{\partial N_X}\right)_{\boldsymbol{N}[\neq(X,Y,Z)],\,\mu_Y,\mu_Z} \geq \dots \geq \left(\frac{\partial\mu_X}{\partial N_X}\right)_{\boldsymbol{\mu}(\neq X)} > 0\,.\end{aligned} \tag{40}$$

Both the present and previous qualitative analyses [5, 7–9] provide a basic conceptual framework for the perturbative treatment of the chemically significant responses of molecular and atomic systems to changes in the system environment. They also provide an attractive way of approaching the states of the AIM's. All such responses can be expressed, via the corresponding Jacobian transformations [3–5], in terms of the sensitivities appearing within the LTR's, which themselves can further be reduced to an identity in terms of a set of a few basic derivatives and kernels.

The sensitivity analysis of AIM's should lead to a new, thermodynamic-like approaches to the fundamental problem in chemistry, of characterizing various types of the chemical bond and chemical reactivity. The set of sensitivities forms a flexible and at the same time a sufficiently wide collection of indexes through which one should be able to characterize and distinguish between various bonding situations. We would like to recall that the local sensitivities can be combined into those of the AIM's, and these in turn can be used to obtain the molecular fragment sensitivities [5, 29]. The use of such indexes should help in better understanding of the various factors influencing the formation of the chemical bond. Also, as we have demonstrated, such sensitivities allow a qualitative understanding of rather complicated couplings between different attributes of the chemical bond and a state of an AIM. This is of particular importance for chemistry, where such qualitative and intuitive concepts and considerations are still widely used.

The abstract reservoirs we have referred to in our analysis represent the atomic (molecular) environment (a catalyst, an electrode, the remainder of a large molecule, etc.). Our local, constrained-equilibrium discussion has implications for non-equilibrium, intermediate states of large molecules adsorbed on a surface of a catalyst, when different molecular fragments are coupled by different active centers (different, uncoupled between themselves local reservoirs), of which some may act as donors and others as acceptors of electrons. Therefore, the constrained-equilibrium approach provides a phenomenological framework for a discussion of intermediate stages of molecular rearrangements on such surfaces. Also, rather abstract displacements in the external potential related state-parameters should be interpreted as those resulting from changes in molecular environment (an approaching reagent, an extra field of the catalyst, etc).

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