Nuclear reactivity indices in the context of spin polarized density functional theory

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Abstract

In this work, the nuclear reactivity indices of density functional theory have been generalized to the spin polarized case and their relationship to electron spin polarized indices has been established. In particular, the spin polarized version of the nuclear Fukui function has been proposed and a finite difference approximation has been used to evaluate it. Applications to a series of triatomic molecules demonstrate the ability of the new functions to predict the geometrical changes due to a change in the spin multiplicity. The main equations in the different ensembles have also been presented.

1. Introduction

Density functional theory (DFT) has become a useful mathematical framework for the development of a chemical reactivity theory [1]. Based upon the Hohenberg–Kohn theorems [2], it uses the electron density $\rho(\vec{r})$ as the basic variable instead of the wave function. In this context, a number of response functions measuring the change of some system property due to a perturbation in some variable have been defined. One of the advantage of this mathematical model is its thermodynamics like structure, which permits to identify the different ensembles characterized by different independent variables and which are related through Legendre transformations [3].

Global electronic response quantities, such as the electronic chemical potential μ [4], the chemical hardness η [5], and the chemical softness S, represent global responses of the system to global perturbations:

$$
\begin{aligned}
\mu &= \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})}, \\
\eta &= \left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})}, \\
S &= \left(\frac{\partial N}{\partial \mu}\right)_{v(\vec{r})},
\end{aligned}
\tag{1}
$$

where N is the number of electrons and the derivatives are done at constant external potential $v(\vec{r})$. These indices have been found to be useful tools in the thermodynamic description of global electronic chemical reactivity [6]. Local electronic descriptors, such as the electron density $\rho(\vec{r})$, the local softness $s(\vec{r})$ [7], and the Fukui function $f(\vec{r})$ [8,9], represent local responses to global perturbations on the system:

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$$\rho(\vec{r}) = \left(\frac{\partial E}{\partial v(\vec{r})}\right)_N,$$

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_N = Sf(\vec{r}), \qquad (2)$$

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\partial \mu}{\partial v(\vec{r})}\right)_N.$$

The Fukui function, introduced by Parr and Yang [8], translates into DFT the frontier molecular orbital theory concepts of Fukui et al. [10] representing the system sensitivity to a perturbation in $v(\vec{r})$. Due to the discontinuity of the electron density with respect to N, left hand Fukui function $f^-(\vec{r})$, measuring reactivity to an electrophilic reagent, and right hand Fukui function $f^+(\vec{r})$, measuring reactivity to a nucleophilic reagent, are defined. The application and generalization of those concepts to a great variety of systems have been recently reviewed [11]. However, to complete the picture of a chemical reaction it is necessary to know what are the changes in the nuclei movement. The change of the external potential in free molecules is mapped to changes in nuclear configuration, the principal variable in a chemical reaction [12]. Although the electronic density determines all ground state properties of a molecular system, the response of the nuclei to a perturbation in N remains unknown, and a response kernel is needed to translate electron density changes in external potential changes. Cohen et al. [13] introduced an alternative to this problem defining the nuclear Fukui function (NFF) as the change of the Helmann–Feynman [14] force on the nucleus α due to a perturbation in the number of electrons at a constant external potential [15–17]

$$\vec{\phi}_\alpha = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_{v(\vec{r})}. \qquad (3)$$

Note that $\vec{\phi}_\alpha$ is a vectorial function, which does not measure the magnitude of the perturbation in the external potential $\delta v(\vec{r})$, but measures the magnitude of the early state of this perturbation. Using Maxwell relations, Baekelandt showed that the nuclear Fukui function can be interpreted as the configurational contribution to the change in the chemical potential [18]

$$\vec{\phi}_\alpha = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_{v(\vec{r})} = -\left(\frac{\delta \mu}{\delta \vec{R}_\alpha}\right)_N, \qquad (4)$$

where $\vec{R}_\alpha$ designates the position of the nucleus α. In addition to nuclear Fukui function (NFF), Cohen et al. [13,15] defined the nuclear softness $\vec{S}_\alpha$ as the product of the NFF with the global electronic softness and defined the nuclear softness kernel $\vec{S}_\alpha^N$ in analogy with the electronic counterpart. Similarly, De Proft et al. [19] introduced the nuclear hardness kernel and established important relations among electronic and nuclear reactivity index in the four ensembles of the DFT:

$$\vec{S}_\alpha^N = S\vec{\phi}_\alpha,$$

$$\vec{S}_\alpha^N(\vec{r}) = \left(\frac{\delta \vec{F}_\alpha}{\delta u(\vec{r})}\right),$$

$$\eta_\alpha^N(\vec{r}) = \left(\frac{\delta u(\vec{r})}{\delta \vec{F}_\alpha}\right), \qquad (5)$$

$$u(\vec{r}) = v(\vec{r}) - \mu.$$

Further relationships among electronic and nuclear indexes [18,20–22] have been developed.

The goal of this work is to generalize the nuclear reactivity index to the spin polarized case and to establish the corresponding relations among nuclear and electronic spin polarized quantities. The spin polarized version of the electronic descriptors has been developed by Galván et al. [23] where they derived expressions for the spin generalized electronic Fukui functions:

$$f_{NN} = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{N_s,v(\vec{r}),B(\vec{r})},$$

$$f_{SN} = \left(\frac{\partial \rho_s(\vec{r})}{\partial N}\right)_{N_s,v(\vec{r}),B(\vec{r})},$$

$$f_{NS} = \left(\frac{\partial \rho(\vec{r})}{\partial N_s}\right)_{N,v(\vec{r}),B(\vec{r})}, \qquad (6)$$

$$f_{SS} = \left(\frac{\partial \rho_s(\vec{r})}{\partial N_s}\right)_{N,v(\vec{r}),B(\vec{r})},$$

where $N_S = N_\alpha - N_\beta$ and $B(\vec{r})$ is an homogeneous magnetic field in the z direction. They are the electronic reactivity descriptors for chemical processes where the spin polarization plays an important role, and they have been applied to a variety of situations [24].

2. Spin polarized nuclear reactivity indices

When a molecular system is in the presence of a homogeneous magnetic field in the z-direction, $B(\vec{r})$, the energy functional adopts the following form:

$$E[N, N_s, v(\vec{r}), B(\vec{r})] = F[\rho, \rho_s] + \int \rho(\vec{r})v(\vec{r})\,\mathrm{d}\vec{r}$$
$$- \mu_B \int \rho_s(\vec{r})B(\vec{r})\,\mathrm{d}\vec{r}. \qquad (7)$$

Hence, the logical definitions of the spin polarized nuclear Fukui functions are

$$\vec{\phi}_\alpha^N = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_{N_s,v(\vec{r}),B(\vec{r})} \qquad (8)$$

and

$$\vec{\phi}_\alpha^s = \left(\frac{\partial \vec{F}_\alpha}{\partial N_s}\right)_{N,v(\vec{r}),B(\vec{r})}, \qquad (9)$$

where $\vec{F}_\alpha$ is the force on the atom α which can be calculated by applying the Helmann–Feynman theorem

$$\vec{F}_\alpha = -Z_\alpha \frac{\delta}{\delta \vec{R}_\alpha} \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_\alpha|} \, d\vec{r} + Z_\alpha \frac{\delta}{\delta \vec{R}_\alpha} \sum_\beta \frac{Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|}. \quad (10)$$

Therefore, $\vec{\phi}_\alpha^N$ is a measure of the changes in the forces acting on atom α when the number of electrons changes at constant spin polarization, external potential and magnetic field. $\vec{\phi}_\alpha^s$ is a measure of the changes in the forces acting on atom α when the spin polarization change at constant total number of electrons, external potential and magnetic field.

Since V_{NN} is independent of N and N_s

$$\vec{\phi}_\alpha^N = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_{N_s, v(\vec{r}), B(\vec{r})} = -\left(\frac{\partial \mu_N}{\partial \vec{R}_\alpha}\right)_{N_s, v(\vec{r}), B(\vec{r})}, \quad (11)$$

$$\vec{\phi}_\alpha^s = \left(\frac{\partial \vec{F}_\alpha}{\partial N_s}\right)_{N, v(\vec{r}), B(\vec{r})} = -\left(\frac{\partial \mu_s}{\partial \vec{R}_\alpha}\right)_{N, v(\vec{r}), B(\vec{r})}, \quad (12)$$

where μ_N and μ_s are the electronic and spin potential, respectively [23].

Using Eq. (10) for the force, the new nuclear Fukui functions can be written as

$$\left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_{N_s, v(\vec{r}), B(\vec{r})} = -Z_\alpha \frac{\delta}{\delta \vec{R}_\alpha} \int \frac{\left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{N_s, v(\vec{r}), B(\vec{r})}}{|\vec{r} - \vec{R}_\alpha|} \, d\vec{r},$$

$$\vec{\phi}_\alpha^N = -Z_\alpha \int \frac{f_{NN}(\vec{r})(\vec{r} - R_\alpha)}{|\vec{r} - \vec{R}_\alpha|^3} \, d\vec{r}, \quad (13)$$

similarly

$$\left(\frac{\partial \vec{F}_\alpha}{\partial N_s}\right)_{N, v(\vec{r}), B(\vec{r})} = -Z_\alpha \frac{\delta}{\delta \vec{R}_\alpha} \int \frac{\left(\frac{\partial \rho(\vec{r})}{\partial N_s}\right)_{N, v(\vec{r}), B(\vec{r})}}{|\vec{r} - \vec{R}_\alpha|} \, d\vec{r},$$

$$\vec{\phi}_\alpha^S = -Z_\alpha \int \frac{f_{NS}(\vec{r})(\vec{r} - R_\alpha)}{|\vec{r} - \vec{R}_\alpha|^3} \, d\vec{r}, \quad (14)$$

where $f_{i,j}$ ($i, j = N, S$) are the generalized Fukui functions of Eq. (6). Eqs. (13) and (14) show the direct relation between electronic and nuclear indices in the spin polarized context, namely, the $\vec{\phi}_\alpha^N$ and $\vec{\phi}_\alpha^S$ are the electrostatic forces on the atom α induced by charge distributions equal to $f_{NN}(\vec{r})$ and $f_{NS}(\vec{r})$, respectively.

Additionally, it can be shown that the nuclear Fukui functions are the configurational components of the changes in electronic and spin potentials (see Appendix A). Thus

$$d\mu_N = \eta_{NN} \, dN + \eta_{NS} \, dN_s - \sum_\alpha \vec{\phi}_\alpha^N \delta \vec{R}_\alpha - \mu_B \int f_{NS} \delta B(\vec{r}), \quad (15)$$

$$d\mu_S = \eta_{SN} \, dN + \eta_{SS} \, dN_s - \sum_\alpha \vec{\phi}_\alpha^S \delta \vec{R}_\alpha - \mu_B \int f_{SS} \delta B(\vec{r}). \quad (16)$$

In Appendix A, further relationships between electronic and nuclear reactivity indices will be explored.

3. Spin nuclear Fukui function

In order to elucidate the physical significance of the spin nuclear Fukui function (SNFF), the function was calculated for a series of triatomic molecules in their singlet and triplet spin states. The set has been chosen trying to cover all the possible cases including drastic changes from linear to angular geometry due to a change in the spin multiplicity. All calculations were performed using the B3LYP density functional method combined with a 6-31++G(d,p) basis set. In the case of molecules containing iodine atom, a pseudopotential with its corresponding basis set (LANL2DZ) [25] has been used. This basis set has been augmented with a set of d polarization functions (LANL2DZ*) with an exponent of 0.29.

Given the discontinuity of the Fukui functions with respect to the number of electrons, in analogy with the electronic Fukui function, three SNFFs can be introduced, namely, $\vec{\phi}_\alpha^{s+}$, $\vec{\phi}_\alpha^{s-}$ and $\vec{\phi}_\alpha^{s0}$. A finite difference approximation was adopted, which gives for the perturbation from singlet to triplet state

$$\vec{\phi}_\alpha^{s+} = \left(\frac{\partial \vec{F}_\alpha}{dN_s}\right)_{v, B, N} = \frac{\vec{F}_\alpha(\text{triplet}) - \vec{F}_\alpha(\text{singlet})}{2} \quad (17)$$

and for the perturbation from triplet to singlet state

$$\vec{\phi}_\alpha^{s-} = \left(\frac{\partial \vec{F}_\alpha}{dN_s}\right)_{v, B, N} = \frac{\vec{F}_\alpha(\text{singlet}) - \vec{F}_\alpha(\text{triplet})}{2}. \quad (18)$$

In the first case, the forces are calculated in the equilibrium geometry of the singlet state, and in the second one in the equilibrium geometry of the triplet state. It is convenient to transform the SNFF from Cartesian coordinates ϵ to internal ones $\mathbf{R}$ through the transformation $\mathbf{R} = \mathbf{W}\epsilon$, where $\mathbf{W}$ is the non-square matrix of transformation from cartesian to internal coordinates [26]. For triatomic molecules (ACB) there are three internal coordinates: AC bond, CB bond and θ molecular angle, which yield three SNFFs

$$\vec{\phi}_{AC}^s = \left(\frac{\partial \vec{F}_{AC}}{dN_s}\right)_{v, B, N}, \quad (19)$$

$$\vec{\phi}_{CB}^s = \left(\frac{\partial \vec{F}_{CB}}{dN_s}\right)_{v, B, N}, \quad (20)$$

$$\vec{\phi}_\theta^s = \left(\frac{\partial \vec{F}_\theta}{dN_s}\right)_{v, B, N}. \quad (21)$$

Tables 1 and 2 display the results obtained for $\vec{\phi}^{s+}$ and $\vec{\phi}^{s-}$. In the tables, the changes in bond length and molecular angle have also been presented. With the exception of molecules containing fluorine atom and asymmetric molecules, all the studied systems present a bond shortening and angle opening when its spin moment is raised from singlet to triplet. This may be interpreted in terms of the Berlin's division of molecular space in binding and antibinding regions [27]. The density rearrangement due to spin polarization implies a charge transfer from anti-binding regions to binding ones, which increases the charge density in the molecular bonds and may be traduced in a bond length shortening. The factor which should be responsible for the opening

Table 1
Spin nuclear Fukui function Φ^{s+} (in a.u.) and bond (in Å) and bent angle changes from singlet to triplet spin configuration

ABC	Φ_{AC}^{+}	Φ_{CB}^{+}	Φ_{θ}^{+}	ΔAC	ΔCB	$\Delta\theta$
BrCBr	−0.00461	−0.00461	0.03255	−0.030	−0.030	19.24
BrCl	−0.00444	−0.00813	0.03158	−0.067	−0.068	21.32
ClCBr	−0.00363	−0.00506	0.03462	−0.043	−0.069	18.80
ClCCl	−0.00401	−0.00401	0.03769	−0.049	−0.049	18.31
FCF	0.01395	0.01395	0.04715	0.013	0.013	14.76
FCCl	0.01085	−0.00404	0.03862	0.017	−0.066	16.69
HCCl	−0.00564	−0.00042	0.03138	−0.027	−0.041	24.71
HCF	−0.00642	0.00920	0.03220	−0.034	0.001	19.69
HCCl	−0.00542	−0.00359	0.02998	−0.028	−0.057	27.21
ICl	−0.00660	−0.00660	0.03117	−0.112	−0.112	60.08
HCH	−0.00542	−0.00542	0.03405	−0.033	−0.033	33.80
BeCBe	0.01398	0.01398	0.00005	0.110	0.110	−137.40

Table 2
Spin nuclear Fukui function Φ^{s-} (in a.u.) and bond (in Å) and bent angle changes from triplet to singlet spin configuration

ABC	Φ_{AC}^{-}	Φ_{CB}^{-}	Φ_{θ}^{-}	ΔAC	ΔCB	$\Delta\theta$
BrCBr	−0.00724	−0.00724	0.03908	0.030	0.030	−19.24
BrCl	−0.00406	−0.00755	0.03637	0.067	0.068	−21.32
ClCBr	−0.00535	−0.00775	0.04161	0.043	0.069	−18.80
ClCCl	−0.00576	−0.00575	0.04486	0.049	0.049	−18.31
FCF	0.00901	0.00901	0.05497	−0.013	−0.013	−14.76
FCCl	0.00708	0.00708	0.04896	−0.017	0.066	−16.69
HCCl	−0.00409	−0.00409	0.02801	0.027	0.041	−24.71
HCF	−0.00850	−0.00850	0.04308	0.034	−0.001	−19.69
HCl	−0.00422	−0.00049	0.03038	0.028	0.057	−27.21
ICl	−0.01873	−0.01873	0.00002	0.112	0.112	−60.08
HCH	−0.00264	−0.00264	0.00272	0.033	0.033	−33.80
BeCBe	−	−	−	−	−	−

of the angle is the spin density distribution. In fact, in the case of CBr$_2$ and CCl$_2$ molecules, the spin density is more concentrated on the halogen atoms than on the carbon ones which implies a repulsive interaction of the atoms at both sides. This behavior is predicted by the nuclear spin Fukui function $\vec{\phi}^{s+}$ and $\vec{\phi}^{s-}$. Negative values of the $\vec{\phi}^{s+}$ function associated to bonds, i.e., $\vec{\phi}_{AC}^{s+}$ and $\vec{\phi}_{CB}^{s+}$, imply that the bond length should decrease when the spin moment change from singlet to triplet. At the same time a negative value of $\vec{\phi}^{s-}$ predicts the bond lengthening when the spin moment is changed from triplet to singlet. This interpretation agrees very well with the structural changes observed in the compounds under consideration when the spin moment is changed. It is worth noting that the bent angle opening is in agreement with the positive values observed for $\vec{\phi}_{\theta}^{s+}$ and $\vec{\phi}_{\theta}^{s-}$. In the case of asymmetric molecules as ClCBr, HCCl, BrCl and HCl, the same conclusions can be deduced.

On the contrary, for CF$_2$ the change of spin moment implies a charge transfer from binding to anti-binding regions which in this case are situated in the halogen atoms. Thus, we observe a lengthening of the bonds. The opening of the bent angle is weak in comparison with the other molecules because the spin density is more concentrated in the carbon atom than in the fluorine one. Here, also the predictions of the spin nuclear functions are in agreement with the structural changes. Indeed, the observation of a positive value of $\vec{\phi}^{s+}$ means a lengthening of the bonds when the spin is changed from singlet to triplet, while the same sign of $\vec{\phi}^{s-}$ predicts a shortening of the bonds from triplet to singlet state.

In the case of asymmetric molecules containing a fluorine atom, as HCF and FCCl, the structural perturbations are different in both sides of the system, a shortening of the C–Cl and C–H bonds and a lengthening of the C–F bond when the spin moment is changed from singlet to triplet. The prediction of the spin nuclear Fukui function is in agreement with these findings.

The case of CBe$_2$ should be considered as a special one. In fact, in the singlet ground state the molecule is linear, but when spin multiplicity is increased, the molecule tends to break the bonds. This fact can be explained by the spin nuclear Fukui function. In the singlet state of CBe$_2$, $\vec{\phi}_{CB}^{s+}$ is positive and presents a high value compared to the other studied molecules, which indicates that the change of spin multiplicity yields to a significant increase of bond length, and the very small $\vec{\phi}^{s+}$ (virtually 0) indicates that the bent angle is only slightly reduced with the change of the spin multiplicity. An increasing of bond length without reduction of the bent angle implies molecular dissociation.

The geometry changes of the CH$_2$ and BeH$_2$ molecules can be studied to the light of the Walsh diagrams [28]. For CH$_2$, the ground state is the triplet with a configuration $(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$ and its first singlet excited state has the configuration $(2a_1)^2(1b_2)^2(3a_1)^2$. The molecular orbital of symmetry $3a_1$ is stabilized in energy when the bent angle

is diminished, while the molecular orbital of symmetry $1b_1$ remains unchanged in energy when the bent angle is changed. For that reason, and assuming that the minimization of the sum of the valence electron orbital energies should determine the geometry, when the spin multiplicity is changed from triplet to singlet in CH_2, the bent angle should be diminished. This is in accordance with the prediction of the SNFF. For BeH_2, the ground term is the singlet of the configuration $(2a_1)^2(1b_2)^2$, and its first triplet excited state has the configuration $(2a_1)^2(1b_2)^1(3a_1)^1$. The orbital energy of molecular orbital $1b_2$ rapidly increases as the molecule is bent, whereas the molecular orbital $3a_1$ is stabilized. In consequence, the BeH_2 will be bent in the triplet state, whereas it is linear in the singlet state.

4. Concluding remarks

The nuclear Fukui function has been generalized to the spin polarized version of the reactivity descriptors model of density functional theory. The thermodynamics like structure of the model has been preserved and the main equations in the different ensembles have also been exposed. A numerical approximation to calculate the spin nuclear Fukui functions has been developed and results for a series of triatomic molecules have been discussed. It has been found that the new developed functions are capable of predicting the geometrical changes due to a change in the spin multiplicity.

Acknowledgments

Appendix A. Spin polarized nuclear reactivity in four ensembles of the DFT

A.1. Canonical ensemble

In analogy with Eq. (5), we can write the spin polarized version of generalized potential, nuclear softness kernel and nuclear hardness

$$u_s(\vec{r}) = v(\vec{r}) - B(\vec{r}) - \mu_N - \mu_S, \tag{A.1}$$

$$\vec{S}_\alpha^{N,s}(\vec{r}) = \frac{\delta\vec{F}_\alpha}{\delta u_s(\vec{r})}, \tag{A.2}$$

$$\vec{\eta}_\alpha^{N,s}(\vec{r}) = \frac{\delta u_s(\vec{r})}{\delta\vec{F}_\alpha}. \tag{A.3}$$

This leads to

$$d\vec{F}_\alpha = \int \frac{\delta\vec{F}_\alpha}{\delta u_s(\vec{r})}\delta u_s(\vec{r})\,d\vec{r} = -\int \vec{S}_\alpha^{N,s}(\vec{r})\delta u_s(\vec{r})\,d\vec{r}, \tag{A.4}$$

and given that $\vec{\eta}_\alpha^{N,s}(\vec{r})$ exists

$$\delta u_s(\vec{r}) = \sum_\alpha \frac{\delta u_s(\vec{r})}{\delta\vec{F}_\alpha}\delta\vec{F}_\alpha = -\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\delta\vec{F}_\alpha. \tag{A.5}$$

In the canonical ensemble, the variation of the generalized potential in terms of the basic variables $[N, N_s, v(\vec{r}), B(\vec{r})]$ is given by

$$-\delta u_s(\vec{r}) = \eta_{NN}\,dN + \eta_{SN}\,dN + \eta_{NS}\,dN_s + \eta_{SS}\,dN_s$$
$$- \int \delta(\vec{r}-\vec{r}')\delta v(\vec{r}')\,d\vec{r}' - \int \delta(\vec{r}-\vec{r}')\delta B(\vec{r}')\,d\vec{r}'$$
$$+ \int f_{NN}(\vec{r})\delta v(\vec{r})\,d\vec{r} + \int f_{NS}(\vec{r})\delta v(\vec{r})\,d\vec{r}$$
$$+ \int f_{SN}(\vec{r})\delta B(\vec{r})\,d\vec{r} + \int f_{SS}(\vec{r})\delta B(\vec{r})\,d\vec{r}, \tag{A.6}$$

where $\eta_{i,j}$ $(i,j = N, S)$ are the spin polarized hardnesses [23]. Now, the variation of the force on atom α in terms of the basic variables takes the following form:

$$\delta\vec{F}_\alpha = \left(\frac{\partial\vec{F}_\alpha}{\partial N}\right)_{N_s,v,B}dN + \left(\frac{\partial\vec{F}_\alpha}{\partial N_s}\right)_{N,v,B}dN_s + \int\left(\frac{\delta\vec{F}_\alpha}{\delta v(\vec{r})}\right)_{N,N_s,B}$$
$$\times \delta v(\vec{r})\,d\vec{r} + \int\left(\frac{\delta\vec{F}_\alpha}{\delta B(\vec{r})}\right)_{N,N_s,v}\delta B(\vec{r})\,d\vec{r}. \tag{A.7}$$

Introducing Eq. (A.6) into Eq. (A.4) and comparing with Eq. (A.7) leads to:

$$\vec{\phi}_\alpha^N = \int \vec{S}_\alpha^{N,s}(\vec{r})(\eta_{NN} + \eta_{SN})\,d\vec{r}, \tag{A.8}$$

$$\vec{\phi}_\alpha^s = \int \vec{S}_\alpha^{N,s}(\vec{r})(\eta_{NS} + \eta_{SS})\,d\vec{r}, \tag{A.9}$$

$$\left(\frac{\partial\vec{F}_\alpha}{\delta v(\vec{r}')}\right)_{N,N_s,B} = \vec{S}_\alpha^{N,s}(f_{NN}(\vec{r}') + f_{NS}(\vec{r}')) - \vec{S}_\alpha^{N,s}(\vec{r}'), \tag{A.10}$$

$$\left(\frac{\delta\vec{F}_\alpha}{\delta B(\vec{r}')}\right)_{N,N_s,v} = \vec{S}_\alpha^{N,s}[f_{SN}(\vec{r}') + f_{SS}(\vec{r}')] - \vec{S}_\alpha^{N,s}(\vec{r}'), \tag{A.11}$$

where $\vec{S}_\alpha^{N,s} = \int \vec{S}_\alpha^{N,s}(\vec{r})\,d\vec{r}$.

On the other hand, replacing $\delta\vec{F}_\alpha$ in (A.5) and comparing with $\delta u_s(\vec{r})$, we obtain

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\vec{\phi}_\alpha^N = (\eta_{NN} + \eta_{SN}), \tag{A.12}$$

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\vec{\phi}_\alpha^s = (\eta_{NS} + \eta_{SS}), \tag{A.13}$$

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left[\frac{\delta\vec{F}_\alpha}{\delta v(\vec{r}')}\right]_{N,N_s,B}d\vec{r}' = f_{NN}(\vec{r}') + f(\vec{r}')_{NS} - \delta(\vec{r}-\vec{r}'), \tag{A.14}$$

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left[\frac{\delta\vec{F}_\alpha}{\delta B(\vec{r}')}\right]_{N,N_s,v}d\vec{r}' = f_{SN}(\vec{r}') + f(\vec{r}')_{SS} - \delta(\vec{r}-\vec{r}'). \tag{A.15}$$

Additionally, in the canonical ensemble we have $\mu_N = \mu[N, N_s, v(\vec{r}), B(\vec{r})]$, so that

$$d\mu_N = \eta_{NN}\, dN + \eta_{NS}\, dN_s + \int f_{NN}(\vec{r})\delta v(\vec{r}) - \mu_B \int f_{NS}\delta B(\vec{r}), \tag{A.16}$$

$$d\mu_S = \eta_{NS}\, dN_S + \eta_{SS}\, dN_s + \int f_{NS}(\vec{r})\delta v(\vec{r}) - \mu_B \int f_{SS}\delta B(\vec{r}), \tag{A.17}$$

but the explicit dependence of $v(\vec{r})$ on $\vec{R}_\alpha$ allows to write for process at constant Z

$$-\sum_\alpha \vec{\phi}_\alpha^N \delta\vec{R}_\alpha = \int f_{NN}(\vec{r})\delta v(\vec{r})\delta\vec{r}. \tag{A.18}$$

Thus

$$d\mu_N = \eta_{NN}\, dN + \eta_{NS}\, dN_s - \sum_\alpha \vec{\phi}_\alpha^N \delta\vec{R}_\alpha - \mu_B \int f_{NS}\delta B(\vec{r}). \tag{A.19}$$

Similarly

$$-\sum_\alpha \vec{\phi}_\alpha^S \delta\vec{R}_\alpha = \int f_{NS}(\vec{r})\delta v(\vec{r})\delta\vec{r} \tag{A.20}$$

and

$$d\mu_S = \eta_{NS}\, dN_S + \eta_{SS}\, dN_s - \sum_\alpha \vec{\phi}_\alpha^S \delta\vec{R}_\alpha - \mu_B \int f_{SS}\delta B(\vec{r}). \tag{A.21}$$

Eqs. (A.19) and (A.21) reinforce the fact that nuclear Fukui functions are the configurational components of the changes in electronic and spin potentials.

Furthermore, replacing Eq. (A.12) in Eq. (A.8), we obtain an interesting inverse relationship between nuclear hardness and softness kernels

$$\int \vec{S}_\alpha^{N,s}(\vec{r})\vec{\eta}_\beta^{N,S}(\vec{r})\, d\vec{r} = \delta_{\alpha\beta}. \tag{A.22}$$

A.2. Grand canonical ensemble $[\mu_N, \mu_s, v(\vec{r}), B(\vec{r})]$

In the grand canonical ensemble, the variation of the force on atom α is given by

$$\delta\vec{F}_\alpha = \left(\frac{\partial\vec{F}_\alpha}{\partial\mu_N}\right)_{\mu_s,v,B} d\mu_N + \left(\frac{\partial\vec{F}_\alpha}{\partial\mu_s}\right)_{\mu_N,v,B} d\mu_s$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta v(\vec{r})}\right)_{\mu_N,\mu_s,B} \delta v(\vec{r})\, d\vec{r}$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta B(\vec{r})}\right)_{\mu_N,\mu_s,v} \delta B(\vec{r})\, d\vec{r}. \tag{A.23}$$

Since the four basic variables of the ensemble are independent

$$\delta u_s(\vec{r}) = -d\mu_N - d\mu_s + \delta v(\vec{r}) - \delta B(\vec{r})$$
$$= -d\mu_N - d\mu_s + \int \delta(\vec{r}-\vec{r}')\delta v(\vec{r}')\, d\vec{r}'$$
$$- \int \delta(\vec{r}-\vec{r}')\delta B(\vec{r}')\, d\vec{r}'. \tag{A.24}$$

Putting Eq. (A.24) into (A.4) and comparing with Eq. (A.23) yields

$$\left(\frac{\partial\vec{F}_\alpha}{\partial\mu_N}\right)_{\mu_s,v,B} = \left(\frac{\partial\vec{F}_\alpha}{\partial\mu_s}\right)_{\mu_N,v,B} = \vec{S}_\alpha^{N,s}, \tag{A.25}$$

$$\frac{\delta\vec{F}_\alpha}{\delta v(\vec{r})} = \frac{\delta\vec{F}_\alpha}{\delta B(\vec{r})} = \vec{S}_\alpha^{N,s}(\vec{r}). \tag{A.26}$$

On the other hand, replacing $\delta\vec{F}_\alpha$ in Eq. (A.5) and comparing with $\delta u_s(r)$ and using Eqs. (A.25) and (A.26) one obtains

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\vec{S}_\alpha^{N,s} = 1, \tag{A.27}$$

$$\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\vec{S}_\alpha^{N,s}(\vec{r}') = \delta(\vec{r}-\vec{r}'). \tag{A.28}$$

These equations also show that nuclear hardness and softness are inverse quantities.

A.3. The isomorphic ensemble $L[N, N_s, \sigma_N(\vec{r}), \sigma_s(\vec{r})]$

The Legendre transform of the variables $v(\vec{r})$ and $B(\vec{r})$ in the canonical ensemble leads to the isomorphic ensemble

$$L = E - \rho(\vec{r})v(\vec{r}) + \mu_\beta\rho_s(\vec{r})B(\vec{r}). \tag{A.29}$$

With the aim that $\rho(\vec{r})$, (ρ_s) and $N(N_s)$ become independent variables, we can write down the isomorphic ensemble in terms of shape factor for $\rho(\vec{r})$ and $\rho_s(\vec{r})$

$$L[N, N_s, \sigma_N(\vec{r}), \sigma_s(\vec{r})]. \tag{A.30}$$

In this ensemble, the variation of the force takes the following form:

$$\delta\vec{F}_\alpha = \left(\frac{\partial\vec{F}_\alpha}{\partial N}\right)_{N_s,\sigma_N,\sigma_s} dN + \left(\frac{\partial\vec{F}_\alpha}{\partial N_s}\right)_{N,\sigma_N,\sigma_s} dN_s$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_N(\vec{r})}\right)_{N,N_s,\sigma_s} \delta\sigma_N(\vec{r})\, d\vec{r}$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_s(\vec{r})}\right)_{N,N_s,\sigma_N} \delta\sigma_s(\vec{r})\, d\vec{r}, \tag{A.31}$$

and the differential of generalized potential

$$\delta u_s(\vec{r}) = \left(\frac{\partial u_s(\vec{r})}{\partial N}\right)_{N_s,\sigma_N,\sigma_s} dN + \left(\frac{\partial u_s(\vec{r})}{\partial N_s}\right)_{N,\sigma_N,\sigma_s} dN_s$$
$$+ \int \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_N(\vec{r}')}\right)_{N,N_s,\sigma_s} \delta\sigma_N(\vec{r}')\, d\vec{r}'$$
$$+ \int \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_s(\vec{r}')}\right)_{N,N_s,\sigma_N} \delta\sigma_s(\vec{r}')\, d\vec{r}'. \tag{A.32}$$

In analogy with De Proft et al. [29], we can define local hardnesses

$$\eta_N(\vec{r}) = \left(\frac{\partial u_s(\vec{r})}{\partial N}\right)_{N_s,\sigma_N,\sigma_s},$$
$$\eta_s(\vec{r}) = \left(\frac{\partial u_s(\vec{r})}{\partial N_s}\right)_{N,\sigma_N,\sigma_s}. \tag{A.33}$$

Thus

$$\delta u_s(\vec{r}) = \eta_N(\vec{r})\, \mathrm{d}N + \eta_s(\vec{r})\, \mathrm{d}N_s$$
$$+ \int \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_N(\vec{r}')}\right)_{N,N_s,\sigma_s} \delta\sigma_N(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \int \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_s(\vec{r}')}\right)_{N,N_s,\sigma_N} \delta\sigma_s(\vec{r}')\, \mathrm{d}\vec{r}' \qquad (A.34)$$

and proceeding in the same way the following equations can be obtained:

$$\left(\frac{\partial\vec{F}_\alpha}{\partial N}\right)_{N_s,\sigma_N,\sigma_s} = -\int \vec{S}_\alpha^{N,s}(\vec{r})\eta_N(\vec{r})\, \mathrm{d}\vec{r}, \qquad (A.35)$$

$$\left(\frac{\partial\vec{F}_\alpha}{\partial N_s}\right)_{N,\sigma_N,\sigma_s} = -\int \vec{S}_\alpha^{N,s}(\vec{r})\eta_s(\vec{r})\, \mathrm{d}\vec{r}, \qquad (A.36)$$

$$\left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_N(\vec{r})}\right)_{N,N_s,\sigma_s} = -\int \vec{S}_\alpha^{N,s}(\vec{r})\left(\frac{\delta u_s(\vec{r})}{\delta\sigma_N(\vec{r}')}\right)_{N,N_s,\sigma_s} \mathrm{d}\vec{r}', \quad (A.37)$$

$$\left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_s(\vec{r})}\right)_{N,N_s,\sigma_N} = -\int \vec{S}_\alpha^{N,s}(\vec{r})\left(\frac{\delta u_s(\vec{r})}{\delta\sigma_s(\vec{r}')}\right)_{N,N_s,\sigma_N} \mathrm{d}\vec{r}', \quad (A.38)$$

and

$$-\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left(\frac{\partial\vec{F}_\alpha}{\partial N}\right)_{N_s,\sigma_N,\sigma_s} = \eta_N(\vec{r}), \qquad (A.39)$$

$$-\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left(\frac{\partial\vec{F}_\alpha}{\partial N_s}\right)_{N,\sigma_N,\sigma_s} = \eta_s(\vec{r}). \qquad (A.40)$$

Replacing (A.31) into (A.5) and equalizing the $\delta\sigma_N(\vec{r})$ and $\delta\sigma_s(\vec{r})$ coefficients, we obtain

$$-\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_N(\vec{r}')}\right)_{N,N_s,\sigma_s} = \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_N(\vec{r}')}\right)_{N,N_s,\sigma_s}, \qquad (A.41)$$

$$-\sum_\alpha \vec{\eta}_\alpha^{N,s}(\vec{r})\left(\frac{\delta\vec{F}_\alpha}{\delta\sigma_s(\vec{r}')}\right)_{N,N_s,\sigma_N} = \left(\frac{\delta u_s(\vec{r})}{\delta\sigma_s(\vec{r}')}\right)_{N,N_s,\sigma_N}. \qquad (A.42)$$

A.4. The grand isomorphic ensemble $L[N,N_s,\sigma_N(\vec{r}),\sigma_s(\vec{r})]$

In this case, the variations of the force and generalized potential can be written as

$$\delta\vec{F}_\alpha = \left(\frac{\partial\vec{F}_\alpha}{\partial\mu_N}\right)_{\mu_s,\rho,\rho_s} \mathrm{d}\mu_N + \left(\frac{\partial\vec{F}_\alpha}{\partial\mu_s}\right)_{\mu_N,\rho,\rho_s} \mathrm{d}\mu_s$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta\rho(\vec{r})}\right)_{\mu_N,\mu_s,\rho_s} \delta\rho(\vec{r})\, \mathrm{d}\vec{r}$$
$$+ \int \left(\frac{\delta\vec{F}_\alpha}{\delta\rho_s(\vec{r})}\right)_{\mu_N,\mu_s,\rho} \delta\rho_s(\vec{r})\, \mathrm{d}\vec{r}, \qquad (A.43)$$

and

$$\delta u_s(\vec{r}) = -\mathrm{d}\mu_N - \mathrm{d}\mu_s + \left(\frac{\partial v(\vec{r})}{\partial\mu_N}\right)_{\mu_s,\rho,\rho_s} \mathrm{d}\mu_N$$
$$+ \left(\frac{\partial v(\vec{r})}{\partial\mu_s}\right)_{\mu_N,\rho,\rho_s} \mathrm{d}\mu_s$$
$$+ \int \left(\frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s} \delta\rho(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \left(\frac{\delta v(\vec{r})}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho} \delta\rho_s(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \left(\frac{\partial B(\vec{r})}{\partial\mu_N}\right)_{\mu_s,\rho,\rho_s} \mathrm{d}\mu_N + \left(\frac{\partial B(\vec{r})}{\partial\mu_s}\right)_{\mu_N,\rho,\rho_s} \mathrm{d}\mu_s$$
$$+ \int \left(\frac{\delta B(\vec{r})}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s} \delta\rho(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \int \left(\frac{\delta B(\vec{r})}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho} \delta\rho_s(\vec{r}')\, \mathrm{d}\vec{r}'. \qquad (A.44)$$

Since

$$\mu_N = \left(\frac{\delta E}{\delta\rho(\vec{r})}\right)_{v,B,\rho_s} = v(\vec{r}) + \frac{\delta F}{\delta\rho(\vec{r})}, \qquad (A.45)$$

$$\mu_s = \left(\frac{\delta E}{\delta\rho_s(\vec{r})}\right)_{v,B,\rho} = -\mu_\beta B(\vec{r}) + \frac{\delta F}{\delta\rho_s(\vec{r})}, \qquad (A.46)$$

and using the fact that $\delta F = 0$ for process at fixed ρ and ρ_s

$$\begin{aligned}
\left(\frac{\partial v(\vec{r})}{\partial\mu_N}\right)_{\mu_s,\rho,\rho_s} &= 1, \\
\left(\frac{\partial v(\vec{r})}{\partial\mu_s}\right)_{\mu_N,\rho,\rho_s} &= 0, \\
\left(\frac{\partial B(\vec{r})}{\partial\mu_N}\right)_{\mu_s,\rho,\rho_s} &= 0, \\
\left(\frac{\partial B(\vec{r})}{\partial\mu_s}\right)_{\mu_N,\rho,\rho_s} &= -\frac{1}{\mu_\beta}.
\end{aligned} \qquad (A.47)$$

On the other hand

$$\delta u_s(\vec{r}) = \int \left(\frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s} \delta\rho(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \int \left(\frac{\delta v(\vec{r})}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho} \delta\rho_s(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \int \left(\frac{\delta B(\vec{r})}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s} \delta\rho(\vec{r}')\, \mathrm{d}\vec{r}'$$
$$+ \int \left(\frac{\delta B(\vec{r})}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho} \delta\rho_s(\vec{r}')\, \mathrm{d}\vec{r}', \qquad (A.48)$$

and the following equations can be derived:

$$-\int \vec{S}_\alpha^{N,s}(\vec{r})\left(\frac{\delta(v(\vec{r})+B(\vec{r}))}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s} \mathrm{d}\vec{r} = \left(\frac{\delta\vec{F}_\alpha}{\delta\rho(\vec{r}')}\right)_{\mu_N,\mu_s,\rho_s}, \qquad (A.49)$$

$$-\int \vec{S}_\alpha^{N,s}(\vec{r})\left(\frac{\delta(v(\vec{r})+B(\vec{r}))}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho} \mathrm{d}\vec{r} = \left(\frac{\delta\vec{F}_\alpha}{\delta\rho_s(\vec{r}')}\right)_{\mu_N,\mu_s,\rho}, \qquad (A.50)$$

$$-\sum \vec{\eta}_\alpha^{N,s}(\vec{r}) \left(\frac{\delta \vec{F}_\alpha}{\delta \rho_s(\vec{r}')} \right)_{\mu_N,\mu_s,\rho} = \left(\frac{\delta(v(\vec{r}) + B(\vec{r}))}{\delta \rho_s(\vec{r}')} \right)_{\mu_N,\mu_s,\rho},$$

(A.51)

$$-\sum \vec{\eta}_\alpha^{N,s}(\vec{r}) \left(\frac{\delta \vec{F}_\alpha}{\delta \rho(\vec{r}')} \right)_{\mu_N,\mu_s,\rho_s} = \left(\frac{\delta(v(\vec{r}) + B(\vec{r}))}{\delta \rho(\vec{r}')} \right)_{\mu_N,\mu_s,\rho_s}.$$

(A.52)

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