

Hardness and softness kernels, and related indices in the spin polarized version of density functional theory

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Abstract

In this Letter, the mathematical expressions corresponding to the kernel, local and global spin softness have been derived, and their relationship with other indices have been explored. Introducing various spin kernels, the mathematical framework of the spin polarized version of the chemical reactivity indices have been completed. Furthermore, new linear response functions have been defined and their relationship with the softness hierarchy are exposed. Finally, the importance of some of these indices has been illustrated for the reactivity pattern of open shell molecules.

1. Introduction

Density functional theory has provided a more formal mathematical framework to many empirical chemical reactivity concepts like electronegativity [1], hardness [2] and the Fukui function [3]. The model has a thermodynamics-like mathematical structure [4] which facilitates its interpretation and extensions to other more complex situations. This area of research, which has been called conceptual density functional theory, has recently been exhaustively reviewed [5]. In the last time, there have been a continuous interest in applying all these concepts to reactions where the spin polarization plays a significant role [6–10]. This has been possible because Galván et al. [11–14] have developed the main equations for some of those indices in the spin-polarized density functional theory. They defined the spin chemical potential, various spin dependent hardness quantities and a set of general-

ized Fukui functions. However, at this stage the thermodynamics-like structure of the original model is not complete because the spin polarized version of the respective hardness and softness kernels have not been defined. Hence, it seems natural to generalize the model in order to obtain the whole reactivity picture in the spin polarized version.

In the case of the density functional theory, the Hohenberg–Kohn theorem establishes an one-to-one mapping between ground-state density $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$, apart from an additive constant. However, long time ago von Barton and Hedin [15] recognized that in spin-density functional theory the map from spin densities $\rho_S(\mathbf{r})$ to external potentials is not guaranteed. Recently Kohn et al. [16] have clarified this situation, showing that for non-degenerate ground states in the presence of magnetic field $B(\mathbf{r})$ with spin magnetism, the practical spin-density functional theory do not have problems. The Hohenberg–Kohn theorem guarantees that any property of the system is a functional of the electron density $\rho(\mathbf{r})$ and spin density $\rho_S(\mathbf{r})$, without explicit recourse to the external potential $v(\mathbf{r})$ and external magnetic fields $B(\mathbf{r})$ [16]. The implications of non-uniqueness for practical

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spin-density functional theory calculations are still under study [16,17].

In this work we derived the expressions corresponding to global, local and non-local spin softness and their relations with other indices. A set of molecules, which display different chemical reactivities in different spin multiplicities, have been selected to test the validity of the new reactivity indices.

2. Theory

In the presence of a magnetic field $B(\mathbf{r})$ in the z -direction the functional of the energy can be expressed in terms of the electron density $\rho(\mathbf{r})$, the spin density $\rho_S(\mathbf{r})$, the external potential $v(\mathbf{r})$ and the magnetic field $B(\mathbf{r})$. The spin density is defined as $\rho_S(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$, α and β refer to the spin-up or -down [15,18]:

$$E[\rho(\mathbf{r}), \rho_S(\mathbf{r}), v(\mathbf{r}), B(\mathbf{r})] = F[\rho(\mathbf{r}), \rho_S(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) - \beta_e \times \int d\mathbf{r} B(\mathbf{r})\rho_S(\mathbf{r}) \quad (1)$$

β_e is the electron Bohr magneton. Now, this expression has to be minimized with respect to both, the electron density and the spin density, respecting the constraints that the electron density integrates to the number of electrons, N , and the spin density integrates to the spin number, $N_S = N_\alpha - N_\beta$. The corresponding Lagrange multipliers have been defined by Galván et al. [11] as:

$$\mu_N = \left[\frac{\delta E}{\delta \rho(\mathbf{r})} \right]_{\rho_S(\mathbf{r}), v(\mathbf{r}), B(\mathbf{r})} = v(\mathbf{r}) + \left[\frac{\delta F}{\delta \rho(\mathbf{r})} \right]_{\rho_S(\mathbf{r}), v(\mathbf{r}), B(\mathbf{r})} \quad (2)$$

$$\mu_S = \left[\frac{\delta E}{\delta \rho_S(\mathbf{r})} \right]_{\rho(\mathbf{r}), v(\mathbf{r}), B(\mathbf{r})} = -\beta_e B(\mathbf{r}) + \left[\frac{\delta F}{\delta \rho_S(\mathbf{r})} \right]_{\rho(\mathbf{r}), v(\mathbf{r}), B(\mathbf{r})} \quad (3)$$

where μ_N is the analog of the standard chemical potential in the case of spin restricted systems except for the fact that the derivative is carried out at a fixed value of N_S and μ_S is the spin chemical potential. This last quantity measures the spin density tendency to change and alike the electron chemical potential it is not necessarily negative. Hence, the functional to be minimized is

$$\Omega = F[\rho(\mathbf{r}), \rho_S(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) - \mu_N \int d\mathbf{r} \rho(\mathbf{r}) - \beta_e \times \int d\mathbf{r} B(\mathbf{r})\rho_S(\mathbf{r}) - \mu_S \int d\mathbf{r} \rho_S(\mathbf{r}) \quad (4)$$

Defining the effective potentials

$$u_N(\mathbf{r}) = v(\mathbf{r}) - \mu_N \quad (5)$$

and

$$u_S(\mathbf{r}) = -\beta_e B(\mathbf{r}) - \mu_S \quad (6)$$

the functional Ω can be written as

$$\Omega = F[\rho(\mathbf{r}), \rho_S(\mathbf{r})] + \int d\mathbf{r} u_N(\mathbf{r})\rho(\mathbf{r}) + \int d\mathbf{r} u_S(\mathbf{r})\rho_S(\mathbf{r}) \quad (7)$$

Now, the hardness kernel at constant spin density can be defined as follows:

$$\eta_{NN}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta u_N(\mathbf{r})}{\delta \rho(\mathbf{r}')} \right]_{\rho_S(\mathbf{r}), B(\mathbf{r})} = \left[\frac{\delta^2 F}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r})} \right]_{\rho_S(\mathbf{r}), B(\mathbf{r})} \quad (8)$$

and its inverse

$$s_{NN}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta \rho(\mathbf{r})}{\delta u_N(\mathbf{r}')} \right]_{\rho_S(\mathbf{r}), B(\mathbf{r})} \quad (9)$$

is the softness kernel at constant spin density.

Both kernels are the inverse of each other in the sense that

$$\int d\mathbf{r}' s_{NN}(\mathbf{r}, \mathbf{r}') \eta_{NN}(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r}'' - \mathbf{r}). \quad (10)$$

In analogy to the non-spin polarized case, the local softness at constant spin density can be defined as

$$s_{NN}(\mathbf{r}) \equiv \int d\mathbf{r}' s_{NN}(\mathbf{r}, \mathbf{r}') \quad (11)$$

For the case of constant number of electrons the corresponding spin hardness kernel is

$$\eta_{SS}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta u_S(\mathbf{r})}{\delta \rho_S(\mathbf{r}')} \right]_{\rho(\mathbf{r}), v(\mathbf{r})} = \left[\frac{\delta^2 F}{\delta \rho_S(\mathbf{r}') \delta \rho_S(\mathbf{r})} \right]_{\rho(\mathbf{r}), v(\mathbf{r})} \quad (12)$$

Its inverse is the spin softness kernel

$$s_{SS}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta \rho_S(\mathbf{r})}{\delta u_S(\mathbf{r}')} \right]_{\rho(\mathbf{r}), v(\mathbf{r})} \quad (13)$$

and the local spin softness becomes

$$s_{SS}(\mathbf{r}) \equiv \int d\mathbf{r}' s_{SS}(\mathbf{r}, \mathbf{r}') \quad (14)$$

The corresponding crossed terms of spin hardness and softness kernels can be also defined as

$$\eta_{NS}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta u_N(\mathbf{r})}{\delta \rho_S(\mathbf{r}')} \right]_{B(\mathbf{r})} = \left[\frac{\delta^2 F}{\delta \rho_S(\mathbf{r}') \delta \rho(\mathbf{r})} \right]_{B(\mathbf{r})} \quad (15)$$

and

$$\eta_{SN}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta u_S(\mathbf{r})}{\delta \rho(\mathbf{r}')} \right]_{B(\mathbf{r})} = \left[\frac{\delta^2 F}{\delta \rho(\mathbf{r}') \delta \rho_S(\mathbf{r})} \right]_{B(\mathbf{r})} \quad (16)$$

Therefore, $\eta_{NS}(\mathbf{r}, \mathbf{r}') = \eta_{SN}(\mathbf{r}, \mathbf{r}')$ and its inverse is

$$s_{NS}(\mathbf{r}, \mathbf{r}') \equiv - \left[\frac{\delta \rho_S(\mathbf{r})}{\delta u_N(\mathbf{r}')} \right]_{B(\mathbf{r})} = - \left[\frac{\delta \rho(\mathbf{r})}{\delta u_S(\mathbf{r}')} \right]_{B(\mathbf{r})} \equiv s_{SN}(\mathbf{r}, \mathbf{r}') \quad (17)$$

Now, a small perturbation in the spin density can be written as

$$\begin{aligned}
d\rho_S(\mathbf{r}) &= \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta u_S(\mathbf{r}')} \right]_{\rho(\mathbf{r}),v(\mathbf{r})} \delta u_S(\mathbf{r}') \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta u_N(\mathbf{r}')} \right]_{B(\mathbf{r})} \delta u_N(\mathbf{r}') \\
&= - \int d\mathbf{r}' s_{SS}(\mathbf{r}, \mathbf{r}') [-\beta_e \delta B(\mathbf{r}') - d\mu_S] \\
&\quad - \int d\mathbf{r}' s_{NS}(\mathbf{r}, \mathbf{r}') [\delta v(\mathbf{r}') - d\mu_N] \\
&= \beta_e \int d\mathbf{r}' s_{SS}(\mathbf{r}, \mathbf{r}') \delta B(\mathbf{r}') + \int d\mathbf{r}' s_{SS}(\mathbf{r}, \mathbf{r}') d\mu_S \\
&\quad - \int d\mathbf{r}' s_{NS}(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') + \int d\mathbf{r}' s_{NS}(\mathbf{r}, \mathbf{r}') d\mu_N
\end{aligned} \tag{18}$$

and from Eqs. (2) and (3) it can be concluded that the chemical and spin potentials are functions of the number of electrons, the spin number, the external potential and the magnetic field, then

$$\begin{aligned}
d\mu_N &= \left[\frac{\partial\mu_N}{\partial N} \right]_{N_S, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN + \left[\frac{\partial\mu_N}{\partial N_S} \right]_{N, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN_S \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\mu_N}{\delta v(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} \delta v(\mathbf{r}') \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\mu_N}{\delta B(\mathbf{r}')} \right]_{N, N_S, v(\mathbf{r})} \delta B(\mathbf{r}') \\
&= \eta_{NN} dN + \eta_{NS} dN_S + \int d\mathbf{r}' f_{NN}(\mathbf{r}') \delta v(\mathbf{r}') - \beta_e \\
&\quad \times \int d\mathbf{r}' f_{SN}(\mathbf{r}') \delta B(\mathbf{r}')
\end{aligned} \tag{19}$$

and

$$\begin{aligned}
d\mu_S &= \left[\frac{\partial\mu_S}{\partial N} \right]_{N_S, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN + \left[\frac{\partial\mu_S}{\partial N_S} \right]_{N, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN_S \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\mu_S}{\delta v(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} \delta v(\mathbf{r}') \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\mu_S}{\delta B(\mathbf{r}')} \right]_{N, N_S, v(\mathbf{r})} \delta B(\mathbf{r}') \\
&= \eta_{SN} dN + \eta_{SS} dN_S + \int d\mathbf{r}' f_{NS}(\mathbf{r}') \delta v(\mathbf{r}') - \beta_e \\
&\quad \times \int d\mathbf{r}' f_{SS}(\mathbf{r}') \delta B(\mathbf{r}')
\end{aligned} \tag{20}$$

where the hardnesses, η_{NN} , η_{NS} , η_{SN} , and η_{SS} , and the Fukui functions, $f_{NN}(\mathbf{r}')$, $f_{SN}(\mathbf{r}')$, $f_{NS}(\mathbf{r}')$ and $f_{SS}(\mathbf{r}')$ have been previously defined by Galván et al. [11].

Putting the last two equations into Eq. (18) the following expression is obtained:

$$\begin{aligned}
d\rho_S(\mathbf{r}) &= [\eta_{SN} s_{SS}(\mathbf{r}) + \eta_{NN} s_{NS}(\mathbf{r})] dN + [\eta_{SS} s_{SS}(\mathbf{r}) \\
&\quad + \eta_{NS} s_{NS}(\mathbf{r})] dN_S + \int d\mathbf{r}' [-s_{NS}(\mathbf{r}, \mathbf{r}') \\
&\quad + s_{SS}(\mathbf{r}) f_{NS}(\mathbf{r}') + s_{NS}(\mathbf{r}) f_{NN}(\mathbf{r}')] \delta v(\mathbf{r}') + \beta_e \\
&\quad \times \int d\mathbf{r}' [s_{SS}(\mathbf{r}, \mathbf{r}') - s_{SS}(\mathbf{r}) f_{SS}(\mathbf{r}') \\
&\quad - s_{NS}(\mathbf{r}) f_{SN}(\mathbf{r}')] \delta B(\mathbf{r}')
\end{aligned} \tag{21}$$

On the other hand, the spin density is a function of N , N_S , and a functional of the external potential $v(\mathbf{r})$ and the magnetic potential $B(\mathbf{r})$, $\rho_S(\mathbf{r}) \equiv \rho_S[N, N_S, v(\mathbf{r}), B(\mathbf{r})]$. Hence,

$$\begin{aligned}
d\rho_S(\mathbf{r}) &= \left[\frac{\partial\rho_S(\mathbf{r})}{\partial N} \right]_{N_S, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN \\
&\quad + \left[\frac{\partial\rho_S(\mathbf{r})}{\partial N_S} \right]_{N, v(\mathbf{r}), \mathbf{B}(\mathbf{r})} dN_S \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta v(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} \delta v(\mathbf{r}') \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta B(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} \delta B(\mathbf{r}') \\
&= f_{SN}(\mathbf{r}) dN + f_{SS}(\mathbf{r}) dN_S \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta v(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} \delta v(\mathbf{r}') \\
&\quad + \int d\mathbf{r}' \left[\frac{\delta\rho_S(\mathbf{r}')}{\delta B(\mathbf{r}')} \right]_{N, N_S, v(\mathbf{r})} \delta B(\mathbf{r}')
\end{aligned} \tag{22}$$

By comparing the last two equations term-by-term the following equalities follow:

$$f_{SN}(\mathbf{r}) = \eta_{SN} s_{SS}(\mathbf{r}) + \eta_{NN} s_{NS}(\mathbf{r}) = \eta_{NN} s_{NS}(\mathbf{r}) \tag{23}$$

$$f_{SS}(\mathbf{r}) = \eta_{SS} s_{SS}(\mathbf{r}) + \eta_{NS} s_{NS}(\mathbf{r}) = \eta_{SS} s_{SS}(\mathbf{r}) \tag{24}$$

$$\begin{aligned}
\left[\frac{\delta\rho_S(\mathbf{r}')}{\delta v(\mathbf{r}')} \right]_{N, N_S, B(\mathbf{r})} &= -s_{NS}(\mathbf{r}, \mathbf{r}') + s_{SS}(\mathbf{r}) f_{NS}(\mathbf{r}') \\
&\quad + s_{NS}(\mathbf{r}) f_{NN}(\mathbf{r}')
\end{aligned} \tag{25}$$

and

$$\begin{aligned}
\left[\frac{\delta\rho_S(\mathbf{r}')}{\delta B(\mathbf{r}')} \right]_{N, N_S, v(\mathbf{r})} &= \beta_e [s_{SS}(\mathbf{r}, \mathbf{r}') - s_{SS}(\mathbf{r}) f_{SS}(\mathbf{r}') \\
&\quad - s_{NS}(\mathbf{r}) f_{SN}(\mathbf{r}')]
\end{aligned} \tag{26}$$

Note that, alike f_{SS} , f_{SN} does not integrate to the unity but to zero. Hence, from the first equality of Eqs. (23) and (24) it follows that η_{SN} and η_{NS} are necessarily zero. Then integrating Eq. (24) over the whole space, it is found that the inverse of the global spin hardness is the integral of the local spin softness. Hence, one recovers the logical result that the global spin softness S_{SS} is given by

$$S_{SS} = \int d\mathbf{r} s_{SS}(\mathbf{r}) \tag{27}$$

Recognizing the fact that $f_{SS}(\mathbf{r}) = \left[\frac{\partial \rho_S(\mathbf{r})}{\partial N_S} \right]_{N,v(\mathbf{r}),\mathbf{B}(\mathbf{r})}$ and $\eta_{SS} = \left[\frac{\partial \mu_S}{\partial N_S} \right]_{N,v(\mathbf{r}),\mathbf{B}(\mathbf{r})}$ and applying the chain rule, one obtains from Eq. (24)

$$s_{SS}(\mathbf{r}) = \left[\frac{\delta \rho_S(\mathbf{r})}{\delta \mu_S} \right]_{N,v(\mathbf{r}),\mathbf{B}(\mathbf{r})} \quad (28)$$

i.e., the form recently proposed by De Proft et al. [9]. Note that Eq. (28) is analogous to the spin restricted version.

For the electron density, a similar development leads to the expressions:

$$f_{NN}(\mathbf{r}) = s_{NN}(\mathbf{r})\eta_{NN} \quad (29)$$

$$f_{NS}(\mathbf{r}) = s_{NS}(\mathbf{r})\eta_{SS} \quad (30)$$

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_{N,N_S,B(\mathbf{r})} = -s_{NN}(\mathbf{r},\mathbf{r}') + s_{NN}(\mathbf{r})f_{NN}(\mathbf{r}') + s_{NS}(\mathbf{r})f_{NS}(\mathbf{r}') \quad (31)$$

and

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta B(\mathbf{r}')} \right]_{N,N_S,v(\mathbf{r})} = \beta_e [s_{SN}(\mathbf{r},\mathbf{r}') - s_{NN}(\mathbf{r})f_{SN}(\mathbf{r}') - s_{NS}(\mathbf{r})f_{SS}(\mathbf{r}')] \quad (32)$$

Now, Eqs. (25), (26), (31) and (32) can be written as

$$\left[\frac{\delta \rho_S(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_{N,N_S,B(\mathbf{r})} = -s_{NS}(\mathbf{r},\mathbf{r}') + \frac{s_{SS}(\mathbf{r})s_{SN}(\mathbf{r}')}{S_{SS}} + \frac{s_{NS}(\mathbf{r})s_{NN}(\mathbf{r}')}{S_{NN}} \quad (33)$$

$$\left[\frac{\delta \rho_S(\mathbf{r})}{\delta B(\mathbf{r}')} \right]_{N,N_S,v(\mathbf{r})} = \beta_e \left[s_{SS}(\mathbf{r},\mathbf{r}') - \frac{s_{SS}(\mathbf{r})s_{SS}(\mathbf{r}')}{S_{SS}} - \frac{s_{NS}(\mathbf{r})s_{NS}(\mathbf{r}')}{S_{NN}} \right] \quad (34)$$

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_{N,N_S,B(\mathbf{r})} = -s_{NN}(\mathbf{r},\mathbf{r}') + \frac{s_{NN}(\mathbf{r})s_{NN}(\mathbf{r}')}{S_{NN}} + \frac{s_{SN}(\mathbf{r})s_{SN}(\mathbf{r}')}{S_{SS}} \quad (35)$$

and

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta B(\mathbf{r}')} \right]_{N,N_S,v(\mathbf{r})} = \beta_e \left[s_{SN}(\mathbf{r},\mathbf{r}') - \frac{s_{NN}(\mathbf{r})s_{NS}(\mathbf{r}')}{S_{NN}} - \frac{s_{SN}(\mathbf{r})s_{SS}(\mathbf{r}')}{S_{SS}} \right] \quad (36)$$

in perfect analogy with the Berkowitz–Parr equation [19]. Eq. (34) is important because it relates empirical chemical concepts like the softness functions with the linear response of the spin density under the presence of a magnetic field. It is, however, not as general as the Berkowitz–Parr equation which is valid for any external perturbation whereas Eq. (34) is only valid for the perturbation due to an external magnetic field in the z -direction. This is due to the initial restriction to the functional of Eq. (1). Note that the four derived response functions of Eqs. (33)–(36) are symmetric with respect to the exchange of \mathbf{r} and \mathbf{r}' , and they integrate to zero, as it should be.

The derived equations close the thermodynamics-like structure of the reactivity indices in the spin-polarized case. The Legendre transforms needed to obtain other ensembles can be now performed [20]. Since all the derived indices are related to empirical chemical concepts, their validation can only be achieved through their comparison with known experimental results.

3. Results and discussion

A set of small molecules have been chosen to test the new proposed indices. They have low-lying excited states of different multiplicity or they are radicals in the ground state. Another set of molecules of the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) family have also been considered to compare with. The geometry of all the molecules has been optimized at the corresponding spin multiplicity using two different basis sets, namely the 6-31G(d) and the 6-311G(d,p), and the B3LYP functional as the method of calculation. In Table 1, the multiplicities, adiabatic and vertical energy separations between the corresponding states, spin chemical potentials, spin hardnesses and softnesses are displayed. Two other quantities are also shown. They are the first- and second-order approximations to the vertical energies. They are calculated as follows:

$$\Delta E_v^{(1)} = \mu_S \Delta N_S \quad (37)$$

and

$$\Delta E_v^{(2)} = \mu_S \Delta N_S + \frac{1}{2} \eta_S \Delta N_S^2 \quad (38)$$

All the indices have been calculated using the frozen orbital approximation based on the working equations given by Galván et al. [11]. The spin potential from above, μ_S^+ , is used when the excited state presents a multiplicity higher than the ground state, and the spin potential from below, μ_S^- , is used in the opposite cases. It can be observed, that while the first-order approximation to the vertical excitation energy yields almost always wrong results, the second-order approximation corrects it. With the only exception of the HSiNa molecule, the deviations are less than 10%. As expected, the spin chemical potential is positive in the cases of raising spin multiplicity and negative in the opposite case. The spin hardness and softness are always negative, in contrast to the spin-restricted version. However, the chemical interpretation remains the same. The greater the absolute value of the spin softness, the more reactive toward a spin change the molecule is. Hence, it can be observed that TEMPO presents the highest value of the spin softness which is in perfect agreement with its known spin catalytic properties. In Table 2, the results obtained for the local quantities, spin Fukui functions and the local spin softnesses are presented. The spin Fukui function gives information about the intramolecular selectivity which determines in each molecule, the most favorable position for a reaction in processes where the spin multiplicity is changed. Hence, in the first 10 molecules, that corresponds to compounds bearing a *NO* group, it can be

Table 1

Ground state multiplicity, adiabatic $M - M'$ energy difference ($\Delta E_{M-M'}^{\text{ad}}$),^a vertical energies (ΔE_{ν} , $\Delta E_{\nu}^{(1)}$, $\Delta E_{\nu}^{(2)}$), spin potentials ($\mu_{\uparrow}^{\pm}/\mu_{\downarrow}^{\pm}$), spin hardness ($\eta_{\text{SS}}^{(0)}$) and spin softness (S_{SS}) for the studied compounds^b

Species	GS mult ^c	$\Delta E_{M-M'}^{\text{ad}}$	ΔE_{ν}	$\Delta E_{\nu}^{(1)}$	$\Delta E_{\nu}^{(2)}$	$\mu_{\uparrow}^{\pm}/\mu_{\downarrow}^{\pm}$	$\eta_{\text{SS}}^{(0)\text{d}}$	S_{SS}^{d}
NO ₂	d	76.7	99.2	160.0	99.4	3.47	-1.31	-0.76
		74.8	96.6	157.3	96.9	3.41	-1.31	-0.76
HOONO	s	16.0	69.7	129.8	67.0	2.81	-1.36	-0.73
		-	70.0	128.8	66.7	2.79	-1.35	-0.74
HNO	s	10.0	12.9	86.1	13.4	1.87	-1.58	-0.63
		10.8	13.5	86.6	14.1	1.88	-1.57	-0.64
TEMPO	d	85.6	164.6	170.3	163.0	3.69	-0.16	-6.37
		86.7	182.2	189.4	178.1	4.11	-0.24	-4.10
TEMPO(I)	d	85.5	162.2	171.1	159.2	3.71	-0.25	-3.98
		86.6	179.5	190.0	176.3	4.12	-0.29	-3.41
TEMPO(II)	d	-	175.9	177.4	162.9	3.85	-0.32	-3.17
		-	181.6	199.3	173.3	4.32	-0.56	-1.78
TEMPO(III)	d	-	101.9	145.1	98.5	3.15	-1.01	-0.99
		-	102.2	146.6	99.3	3.18	-1.02	-0.98
TEMPO(IV)	d	94.5	139.7	172.6	132.7	3.74	-0.87	-1.15
		93.9	139.7	180.5	135.5	3.91	-0.98	-1.02
TEMPO(V)	d	-	99.7	146.1	97.6	3.17	-1.05	-0.95
		-	97.9	146.3	96.2	3.17	-1.09	-0.92
TEMPO(VI)	d	91.9	118.1	163.7	116.1	3.55	-1.03	-0.97
		90.9	116.8	156.4	111.8	3.39	-0.97	-1.03
HOOCCH	t	-6.0	-36.2	-94.8	-33.1	-2.06	-1.34	-0.75
		-7.2	-37.1	96.8	-34.3	-2.10	-1.36	-0.73
Cyclopentadienylidene	t	-10.0	-44.8	67.6	-29.0	-1.47	-0.84	-1.20
		-10.3	-32.7	68.3	-20.7	-1.48	-1.03	-0.97
CH ₂ CHN	t	-	-50.3	89.4	-40.6	-1.94	-1.06	0.94
		-	-52.5	91.6	-42.5	-1.99	-1.06	-0.94
HOOCN	t	-13.0	-26.3	92.2	-18.6	-2.00	-1.60	-0.63
		-13.1	-27.0	92.3	-19.0	-1.99	-1.59	-0.63
HSiLi	t	-7.7	-16.7	51.6	-14.2	-1.12	-0.81	-1.23
		-6.8	-16.2	51.2	-13.6	-1.11	-0.82	-1.22
HSiNa	t	-3.7	-9.7	37.4	-4.6	-0.81	-0.71	-1.40
		-3.8	-10.2	37.5	-4.7	-0.81	-0.71	-1.41

First entry corresponds to (U)B3LYP/6-311G(d,p) and second entry corresponds to (U)B3LYP/6-31G(d).

^a Lower multiplicity (M) and upper multiplicity (M').

^b Adiabatic $M - M'$ energy difference and vertical energies in kcal/mol, spin potential values in V, spin-hardness values in V/spin units, spin softness in spin units/V.

^c Singlet = s; doublet = d; triplet = t.

^d The calculations were performed with vertical energies.

observed that the oxygen atom is always more reactive than the nitrogen site. For the last six molecules, the reactivity is centered, as expected, in the carbon, nitrogen and silicon atoms from carbenes, nitrenes and silylenes, respectively, with the only exception of cyclopentadienylidene, which can be explained by the resonance that this compound presents (see Fig. 1). For molecules with a singlet ground state, only $f_{\text{SS},k}^+$ and $s_{\text{SS},k}^+$ are presented. For molecules with triplet ground state, carbenes, nitrenes and silylenes, the indices have been calculated in the direction of the singlet state, hence the Fukui function and the local spin softness from below (-) should be considered. To compare intermolecular reactivity one should look at the values of the corresponding local spin softness. It is clear that TEMPO's family of molecules are the most reactive, in complete agreement with the experimental evidence.

The intrinsic reactivity of nitroxyl radicals induced by the change of one electron, which changes the spin number N_{S} , can be analyzed considering the change in the spin den-

sity. From Eq. (22) and at constant external potential $v(\mathbf{r})$ and magnetic potential $B(\mathbf{r})$, the change in the spin density can be expressed as:

$$\Delta\rho_{\text{S}}(\mathbf{r}) = f_{\text{SN}}(\mathbf{r})\Delta N + f_{\text{SS}}(\mathbf{r})\Delta N_{\text{S}} \quad (39)$$

This expression shows that, within a static reactivity picture, the change in the spin density is proportional to changes in the electrons and spin numbers. The quantity f_{SN} , which is related to changes in the spin density with respect to the total number of electrons, is equivalent to the spin Fukui functions, $f_{\uparrow}(\mathbf{r})$ and $f_{\downarrow}(\mathbf{r})$, used by Yang and Parr [21] to explain the reactivity in chemisorption and catalysis of magnetic materials. These last two functions are defined in terms of the spin-up (\uparrow) or α and spin-down (\downarrow) or β densities, which give the spin density, $\rho_{\text{S}}(r) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$. f_{SS} shows the direct relationship which local spin softness through Eq. (24). Nitroxyl radicals like TEMPO have proven to be both, scavengers of free radicals [22–25] and catalysts for alcohol oxidation

Table 2
Local spin Fukui functions ($f_{SS,k}^a$) and local spin softness ($s_{SS,k}^b$) at the site k for the studied compounds at B3LYP/6-31G(d) level

Species	Atom (k)	$f_{SS,k}^+$	$f_{SS,k}^-$	$s_{SS,k}^+$	$s_{SS,k}^-$
NO ₂	N	0.26	0.42	-0.20	-0.32
	O	0.37	0.29	-0.28	-0.22
HOONO	N	0.28		-0.21	
	O	0.21		-0.16	
	O ₁	0.20		-0.15	
	O ₂	0.30		-0.23	
HNO	N	0.46		-0.29	
	O	0.48		-0.30	
TEMPO	N	0.02	0.41	-0.08	-1.67
	O	0.38	0.44	-1.58	-1.81
TEMPO(I)	N	0.02	0.41	-0.07	-1.43
	O	0.38	0.44	-1.35	-1.55
TEMPO(II)	N	0.02	0.40	-0.04	-0.72
	O	0.39	0.44	-0.69	-0.79
TEMPO(III)	N	0.02	0.38	-0.02	-0.38
	O	0.22	0.42	-0.21	-0.41
TEMPO(IV)	N	0.02	0.40	-0.02	-0.41
	O	0.38	0.44	-0.39	-0.45
TEMPO(V)	N	0.01	0.40	-0.01	-0.36
	O	0.22	0.45	-0.21	-0.41
TEMPO(VI)	N	0.02	0.40	-0.02	-0.42
	O	0.37	0.44	-0.38	-0.46
HOOCCH	C	0.12	0.70	-0.09	-0.52
	C ₁	0.33	0.07	-0.24	-0.05
	O ₂	0.45	0.19	-0.33	-0.14
	O ₃	0.09	0.04	-0.07	-0.03
Cyclopentadienylidene	C	0	0.18	0	-0.17
	C ₁	0.27	0.19	-0.26	-0.18
	C ₂	0.22	0.23	-0.22	-0.22
CH ₂ =CHN:	N	0.23	0.37	-0.21	-0.35
	C ₁	0.27	0.19	-0.26	-0.18
	C ₂	0.22	0.23	-0.22	-0.22
HOOCN:	N	0.15	0.50	-0.09	-0.31
	C	0.35	0.05	-0.22	-0.03
	O ₁	0.41	0.40	-0.26	-0.25
	O ₂	0.09	0.05	-0.06	-0.03
HSiLi	Si	0.30	0.61	-0.37	-0.75
	Li	0.57	0.38	-0.70	-0.47
HSiNa	Si	0.39	0.57	-0.54	-0.80
	Na	0.49	0.43	-0.69	-0.60

^a Fukui functions in au.

^b Spin softness in spin units/V.

[26–29]. In both cases, $\Delta N_S = -1$, and $\Delta N = 1$ and -1 for the former and latter cases, respectively. Hence the corresponding expressions are

$$\Delta\rho_S(\mathbf{r}) = f_{SN}(\mathbf{r}) - f_{SS}(\mathbf{r}) \quad (40)$$

$$\Delta\rho_S(\mathbf{r}) = -f_{SN}(\mathbf{r}) - f_{SS}(\mathbf{r}) \quad (41)$$

Note that in the reactivity of radicals, like nitroxyls, the change in the spin density is due to the change in the number of electrons, which exactly matches the definition of f_{SN} . On the other hand, higher values of indices, $f_{SS,k}^-$ and $s_{SS,k}^-$, consistently explain the reactivity trends of nitroxyl radicals, as can be seen in Table 2.

The nitroxyl radicals can be oxidized to N-oxo ammonium salts that are themselves useful oxidants for primary and secondary alcohols. A direct correlation between the measured oxidation potential of the nitroxide and the catalyst efficiency has been found by Rychnovsky et al. [29].

Compounds with the lowest redox potentials are the most effective catalysts. This feature is reflected in the values of the condensed local softness at the oxygen atom in the direction of decreasing multiplicity ($s_{SS,O}^-$). Compounds TEMPO and TEMPO(I) have the higher absolute values of $s_{SS,O}^-$, thereby showing that the change from doublet to singlet state (oxidation) is favored, the corresponding oxidation potentials are 638 mV and 692 mV, respectively. Whereas compounds TEMPO(III), TEMPO(V) and TEMPO(VI), with oxidation potentials 807, 871 and 1091 mV, respectively, are classified as poor catalysts [29], a result consistent with the lower $s_{SS,O}^-$ values. The comparison of the $s_{SS,O}^-$ values between TEMPO(II) and TEMPO(III), and between TEMPO(IV) and TEMPO(V) are consistent with the scavenging effect of persistent nitroxides. If the NO moiety in nitroxide radical is sterically hindered, the reaction rate with the carbon center of the reactive free radical decreases [25].

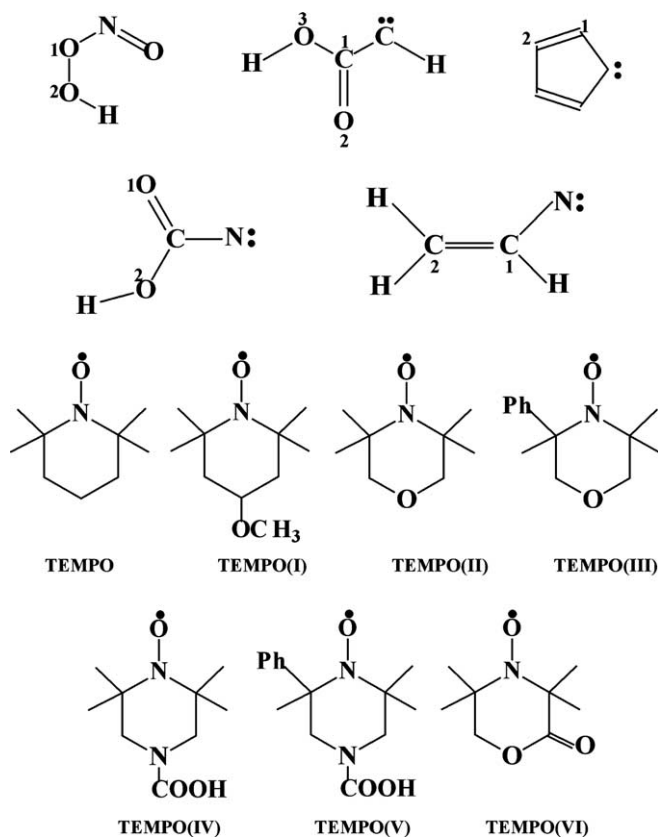


Fig. 1. Molecular structures of the compounds investigated in this work.

Note that TEMPO(II) and TEMPO(IV) having higher absolute values of $s_{\text{SS},\text{O}}$ are predicted to be more reactive than TEMPO(III) and TEMPO(V), respectively.

4. Concluding remarks

The spin-polarized version of the hierarchy of hardnesses and softnesses has been presented. In particular, new equations for the spin softness kernel, spin local softness and spin global softness have been derived. Mixed global spin hardness and softness, η_{NS} and S_{NS} , are consistently normalized to zero, a result that follows from the normalization of the spin Fukui functions. Equations relating the new indices with various response functions have also been derived. Finally, some of these indices have been calculated for a set of molecules to illustrate their reliability and predictive power in the study of chemical processes involving spin polarized systems.

Note added in proof

When this work was finished we learn of a similar paper recently published [30].

Acknowledgments

This work has been supported in part by the Millennium Nucleus for Applied Quantum Mechanics and Computational Chemistry, Grant No. P02-004-F (MIDEPLAN and CONICYT.), Fondecyt Grants 1050294, 1020069, 1030548, and also by Grants DI-15-04, DI-08-05 from Universidad Andrés Bello. D.G. is grateful to Universidad Andrés Bello for a graduate fellowship.

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