Philicity indices within the spin-polarized density-functional theory framework

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The electrophilicity index is analyzed within the framework of spin-polarized density-functional theory. In this context, constrained philicities, $\omega_N \equiv (\mu_N)^2/(2\eta_{NN})$, are introduced in order to define the capability of a system to acquire or donate electrons in a process at constant spin number. The spin-philicity/spin-donicity indices, $\omega_S^\pm \equiv (\mu_S^\pm)^2/(2\eta_{SS})$, are examined and rationalized here as the *philicity* of a given system to change its *spin-polarization* state, as being defined through the spin potential μ_S and spin hardness η_{SS} for a process at constant number of electrons. The local extension of these indices has been also outlined and numerical results have been discussed on the analysis of the electrophilic nature of some simple carbene systems both in the singlet and triplet states.

I. INTRODUCTION

Parr *et al.* proposed in 1999 a model leading to an operational definition for the concept of *electrophilicity*, i.e., the capability of a system to acquire an optimal amount of electrons.[1] Electrons will instantaneously saturate a system embedded within an ideal zero-temperature sea of free electrons until the chemical potential of the system increases to zero, and hence, within a canonical ensemble representation, the energy change ΔE_ν can be written up to second order as

$$\Delta E_\nu = \mu \Delta N + \frac{1}{2}\eta \Delta N^2, \tag{1}$$

at constant external potential $\nu(\mathbf{r})$, which is created by M nuclei α located at positions $\{\mathbf{R}_\alpha\}$, i.e., $\nu(\mathbf{r}) = \Sigma_\alpha^M Z_\alpha/|\mathbf{r}-\mathbf{R}_\alpha|$, and where μ and η are the (electronic) chemical potential and hardness for the molecular system,

$$\mu \equiv \left[\frac{\partial E}{\partial N}\right]_{\nu(\mathbf{r})}, \quad \eta \equiv \left[\frac{\partial \mu}{\partial N}\right]_{\nu(\mathbf{r})}. \tag{2}$$

ΔN in Eq. (1) refers to the number of electrons incoming from this sea toward the system. Under the hypothesis that ΔE_ν could become stationary with respect to ΔN, the critical value for this electron flow is

$$\Delta N_{\max} = -\frac{\mu}{\eta} > 0, \tag{3}$$

that leads to a lowering in the electronic energy ($\mu < 0$, $\eta > 0$),

$$\Delta E_{\nu,\max} = -\frac{\mu^2}{2\eta} \equiv -\omega < 0, \tag{4}$$

being therefore identified as the negative of the electrophilicity, ω, of such system. This model for an electrophilicity index of Eq. (4) thus measures the maximum energy stabilization of a given system when it is being solvated by electrons at constant external potential. High values of ω are naturally associated to species that have a high acquaintance for electrons, i.e., "electrophilic" systems.[1] It is clear, however, that for the constrained variational procedure described in Eqs. (1)–(4) the electron-spin property is not explicitly considered for such reactivity. Electron-spin changes are assumed to occur instantaneously.

Conceptual spin-polarized density-functional theory (SP-DFT) provides a more general framework for the theoretical treatment of chemical reactivity.[2–4] In fact, it enables the constrained analysis of both *charge-transfer* and *spin-polarization* processes.[5–9] The general SP-DFT formalism comprising global and local (i.e., $\mathbf{r}$ dependent) electronic chemical reactivity descriptors was first presented by Galván *et al.* in 1988.[5] Some applications of the related quantities were used to describe atomic systems,[7] chemical binding,[10] charge redistribution between states of different multiplicities,[11] and forbidden singlet-triplet transitions.[12] A comprehensive review of these applications is available.[6] Global and local descriptors of the SP-DFT within an ensemble $E[N, N_S, \nu(\mathbf{r})]$ were also used in the discussion of the hydrogenation reaction of the succinimidyl radical and also in the analysis of the Bergman cyclization process.[13]

More recent examples of application of the SP-DFT

quantities have been reported by some of us in the study of regioselectivity of [2+2] photocycloaddition of enones to substituted alkenes,[14] and in the so-called two-state reactivity framework on the examination of cycloaddition reactions of triplet methylene.[15] Some of the present authors have presented a simple implementation scheme for the calculation of the condensed-to-site Fukui functions within such SP-DFT framework.[16] We have also discussed in detail an extension of nuclear reactivity descriptors within such SP-DFT context, stressing its importance and relation to other electronic descriptors and its connection to the Berlin theorem of chemical binding.[17] In addition, a discussion concerning exact relationships between global, local, and nonlocal descriptors of SP-DFT was recently reported.[18]

Following these ongoing interests in the analysis and extension of conceptual DFT within the framework of SP-DFT,[16–18] and with the aim to complement and examine associated chemical concepts,[14,15] we focus in the present paper on the exploration of the SP-DFT analog for the global electrophilicity index given in Eq. (4). This paper is organized as follows. After briefly reviewing some basic principles of reactivity analysis within a SP-DFT framework, we present in Sec. II A a constrained extension of the electrophilicity index given in Eq. (4). Section II B discusses the related concept of a philicity of a given system to experience spin polarization and Sec. II C presents the local related indices. A computational example of the usefulness of these quantities is given in Secs. III and IV.

II. THEORETICAL FRAMEWORK AND DISCUSSION

Within a spin-polarized DFT framework both the electron $\rho(\mathbf{r})$ and spin $\rho_S(\mathbf{r})$ densities are explicitly considered in terms of the spin-up $\rho^\uparrow(\mathbf{r})$ and spin-down $\rho^\downarrow(\mathbf{r})$ components, $\rho(\mathbf{r})=\rho^\uparrow(\mathbf{r})+\rho^\downarrow(\mathbf{r})$ and $\rho_S(\mathbf{r})=\rho^\uparrow(\mathbf{r})-\rho^\downarrow(\mathbf{r})$. Minimization of the energy functional, $E=F[\rho(\mathbf{r}),\rho_s(\mathbf{r})]+\int\rho(\mathbf{r})\nu(\mathbf{r})d\mathbf{r}-\mu_B\int\mathbf{B}(\mathbf{r})\rho_s(\mathbf{r})d\mathbf{r}$, with respect to $\rho(\mathbf{r})$ and $\rho_s(\mathbf{r})$ under the normalization constraints, $\int\rho(\mathbf{r})d\mathbf{r}=N=N^\uparrow+N^\downarrow$ and $\int\rho_S(\mathbf{r})d\mathbf{r}=N_S=N^\uparrow-N^\downarrow$, yields the fundamental equations,

$$\mu_N \equiv \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_{\rho_s,\mathbf{B}(\mathbf{r})} = \left[\frac{\delta F}{\delta\rho(\mathbf{r})}\right]_{\rho_s,\mathbf{B}(\mathbf{r})} + \nu(\mathbf{r}), \qquad (5)$$

and

$$\mu_S \equiv \left[\frac{\delta E}{\delta\rho_s(\mathbf{r})}\right]_{\rho(\mathbf{r}),\nu(\mathbf{r})} = \left[\frac{\delta F}{\delta\rho_s(\mathbf{r})}\right]_{\rho(\mathbf{r}),\nu(\mathbf{r})} - \mu_B\mathbf{B}(\mathbf{r}),$$

for an N-electron system with spin number N_S, in the field of external, $\nu(\mathbf{r})$, and magnetic, $\mathbf{B}(\mathbf{r})$, potentials. μ_B is the Bohr magneton, and $F[\rho(\mathbf{r}),\rho_s(\mathbf{r})]$ is the universal functional, standing for the sum of the total kinetic electronic energy $T_e[\rho,\rho_S]$ and the total electron-electron repulsion $V_{ee}[\rho,\rho_S]$. Simultaneously solving Eqs. (5) allows us to obtain the ground-state electron and spin densities that are consistent with the selected values of N and N_S. The Lagrange multipliers μ_N and μ_S, of Eqs. (5) have been identified as the *constrained chemical* and *spin potentials*, respectively,[5–9] with μ_N being analogous to the chemical potential of the spin-restricted DFT theory except that it should be also evaluated at constant spin number, and μ_S is related to the

capability of such system to undergo spin polarization,[5–9] at constant number of electrons,

$$\mu_N \equiv \left[\frac{\partial E}{\partial N}\right]_{N_S,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}, \qquad \mu_S \equiv \left[\frac{\partial E}{\partial N_S}\right]_{N,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}, \qquad (6)$$

These *global* quantities do not depend on the spatial position $\mathbf{r}$ within the molecular framework, but characterize the entire system as an entity. They describe responses of the entire system against global perturbations. Other examples are the constrained hardnesses[5–9] $\eta_{NN}\equiv[\partial\mu_N/\partial N]_{N_S,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}$, $\eta_{NS}\equiv[\partial\mu_N/\partial N_S]_{N,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}\equiv[\partial\mu_S/\partial N]_{N_S,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}\equiv\eta_{SN}$, and $\eta_{SS}\equiv[\partial\mu_S/\partial N_S]_{N,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})}$, describing changes in μ_N and μ_S with respect to variations in the number of electrons N at constant N_S (i.e., constrained charge transfer), or in the spin number N_S at constant N (i.e., spin-polarization processes). Note that as a natural extension to the spin-restricted case, a complete hierarchy of global, local (i.e., one spatial coordinate $\mathbf{r}$ dependent), and nonlocal (i.e., two or more spatial coordinates $\mathbf{r},\mathbf{r}'$-dependent) descriptors can be set up through the coefficients of Taylor series functional expansions of the energy functional in terms of ground-state variables in such a system. Within such an ensemble perturbative description of chemical reactivity, the changes between different selected ground states can be described in terms of the spin-up and spin-down numbers of electrons, $(N^\uparrow,N^\downarrow)$,[10] or equivalently, in terms of the variables $N,N_S,\nu(\mathbf{r})$, and $\mathbf{B}(\mathbf{r})$,[5–9] or any suitable Legendre-transformed ensemble.[18] On the other hand, *local* descriptors (i.e., $\mathbf{r}$ dependent) are associated with global/local responses of the system against local/global perturbations. The electron density $\rho(\mathbf{r})$ and spin density $\rho_S(\mathbf{r})$, as well as the generalized SP-DFT Fukui functions, $f_{NN}(\mathbf{r}),f_{SN}(\mathbf{r}),f_{NS}(\mathbf{r})$, and $f_{SS}(\mathbf{r})$,[5,6] are examples of local quantities, which can be associated to regional responses of a reacting system determining, e.g., regioselectivity in reactions. Global, local, and nonlocal SP-DFT descriptors constitute the basic ingredients to discuss the electronic[18] and nuclear reactivities[17] in processes that involve both charge transfer and/or spin polarization.[5–9]

A. Philicity concept in the context of SP-DFT

The energy change of a system can be further examined in a constrained process considered to occur both at constant external potential and spin number N_S. Note that from a generalized canonical ensemble representation, $E[N,N_S,\nu(\mathbf{r}),B(\mathbf{r})]$, the change $\Delta E_{\nu,N_S}$ experienced by such system embedded into a sea of free electrons at zero chemical potential up to second order is

$$\Delta E_{\nu,N_S} = \mu_N\Delta N + \frac{1}{2}\eta_{NN}\Delta N^2, \qquad (7)$$

where μ_N and η_{NN} are the SP-DFT chemical potential and hardness defined in Sec. II,[5–9] and ΔN is the change in the number of electrons experienced by the system due to an electron transfer from such a perfect donor, in a process which occurs both at constant external potential $\nu(\mathbf{r})$ and constant spin number N_S. This is, in fact, a constrained charge-transfer process. Then, under the supposition of a sta-

tionary condition of $\Delta E_{\nu,N_S}$ with respect to ΔN, we have

$$(\Delta N)_{\nu,N_S,\max} = -\frac{\mu_N}{\eta_{NN}} > 0. \tag{8}$$

Henceforth, the corresponding lowering in energy (note that $\mu_N < 0$, $\eta_{NN} > 0$) can be properly rationalized as a measure of the electrophilicity at constant N_S, which we define as ω_N for such a system,

$$\Delta E_{\nu,N_S,\max} = -\frac{(\mu_N)^2}{2\eta_{NN}} \equiv -\omega_N > 0. \tag{9}$$

Note immediately that this constrained electrophilicity, ω_N, measures the capability, both of the spin-up and spin-down spaces of a given system to acquire electronic charge in the exact amount of $(\Delta N)_{\nu,N_S,\max}/2$, i.e., the occupation numbers of the two spin symmetries are changed in an equal amount. This is a natural extension of the Eq. (4) into the SP-DFT, which, in fact, is a proper index for the analysis of open-shell systems.

B. Philicity for spin polarization

By following an analogous procedure with Parr et al.,[1] some of the present authors[19,20] have recently introduced quantities intended to rationalize the *spin-philicity* and *spin-donicity* concepts within the framework of SP-DFT.[5–9] In such initial claim,[19,20] the system of interest was considered to be embedded in a zero-potential *sea of spins*, emphasizing with this name that the spin properties of electrons have to be considered in the treatment. Within a SP-DFT canonical ensemble representation of the energy, the associated energy change $\Delta E_{\nu,N}$ was written up to second order as

$$\Delta E_{\nu,N} = \mu_S \Delta N_S + \frac{1}{2}\eta_{SS}(\Delta N_S)^2, \tag{10}$$

where μ_S and η_{SS} correspond to the above-mentioned spin potential and spin hardness, respectively,[5–9] and ΔN_S refers to a *change in the spin number* at constant external potential $\nu(\mathbf{r})$ and number of electrons N. Hence, the maximum value of ΔN_S in the direction of increasing (+) or decreasing (−) spin number was obtained after assuming a stationary condition of $\Delta E_{\nu,N}$ with respect to ΔN_S,

$$(\Delta N_S^*)^\pm = -\frac{\mu_S^\pm}{\eta_{SS}}, \tag{11}$$

and the corresponding constrained change in energy was identified to be a measure of the spin-philicity ω_S^+ or spin-donicity ω_S^- capabilities of such system,

$$\Delta E_{\nu,N}^* = -\frac{(\mu_S^\pm)^2}{2\eta_{SS}} \equiv -\omega_S^\pm > 0. \tag{12}$$

In contrast to Eq. (4), this change in energy is a positive one since $\mu_S^+ > 0$, $\mu_S^- < 0$, and $\eta_{SS} < 0$. Some of us proposed,[20] consequently, to choose the negative of the energy change as a proper definition for such quantities within the same SP-DFT context. High values for ω_S^+ or ω_S^- were then associated with good spin-acceptor or spin-donor systems, respectively, and claimed to describe *spin transfer* processes.[19,20]

However, as the spin potential μ_S and spin hardness η_{SS} indices describe the response of a system to changes in its spin number (i.e., a process of spin polarization at constant N), the ω_S^+ and ω_S^- indices of Eq. (12) should be considered, in fact, as a measure of *the capability of a system to change its spin polarization*. No external electron transfer is involved in the energy change described by Eq. (10), in view of the constraint of constant N. In fact, examples of the application of Eq. (10), for the evaluation of vertical singlet-triplet gaps in some halocarbene species, have been stressed.[6,12]

The model relationship $\omega_S^\pm$ in Eq. (12) measures the ability of a system to change its spin-polarization state, and such system has not been considered embedded in a sea of electrons or spins, but only in interaction with an electromagnetic field of suitable energy. This is the case for excitation or deexcitation processes occurring both in chemical reactions and spectroscopic experiments. We will refer to these quantities in Eq. (12), $\omega_S^\pm$, as the *philicity for spin polarization* of a given system. Note that in the case of the electrophilicity index of Eq. (4) the chemical potential and hardness of the system, Eq. (2), properly describe responses of the system under constrained charge-transfer processes. The constraint is in that case only the constant external potential. The spin potential μ_S and spin hardness η_{SS}, above defined, involve only spin polarization, indeed at a constant number of electrons. In fact, these quantities have already been found linearly related to vertical transition energies.[19,20] The SP-DFT electrophilicity at constant, N_S, ω_N, in Eq. (9) and the philicity for spin polarization, $\omega_S^\pm$, in Eq. (12) allow us to study and rationalize an electrophilic process in terms of two separate steps, one involving a constrained charge transfer and another one describing a spin-polarization phenomena, respectively.

C. Local considerations

Note that local counterparts (i.e., coordinate $\mathbf{r}$-dependent quantities) for the electrophilicity ω and its SP-DFT constrained relatives, ω_N, and the philicities for spin polarization $\omega_S^\pm$ can readily be defined,

$$\omega^\pm(\mathbf{r}) = \omega f^\pm(\mathbf{r}), \tag{13a}$$

$$\omega_N^\pm(\mathbf{r}) = \omega_N f_{NN}^\pm(\mathbf{r}), \tag{13b}$$

$$\omega_S^\pm(\mathbf{r}) = \omega_S^\pm f_{SS}^\pm(\mathbf{r}), \tag{13c}$$

by using a suitable local normalized-to-unity projector quantity as could be, for instance, the corresponding nucleophilic [i.e., acceptor, (+)] or electrophilic [i.e., donor, (−)] Fukui functions, $f^\pm(\mathbf{r}) \equiv [\delta\mu/\delta\nu(\mathbf{r})]_N^\pm = [\partial\rho(\mathbf{r})/\partial N]_{\nu(\mathbf{r})}^\pm$, or its spin-polarized DFT counterparts $f_{NN}^\pm(\mathbf{r})$ and $f_{SS}^\pm(\mathbf{r})$,
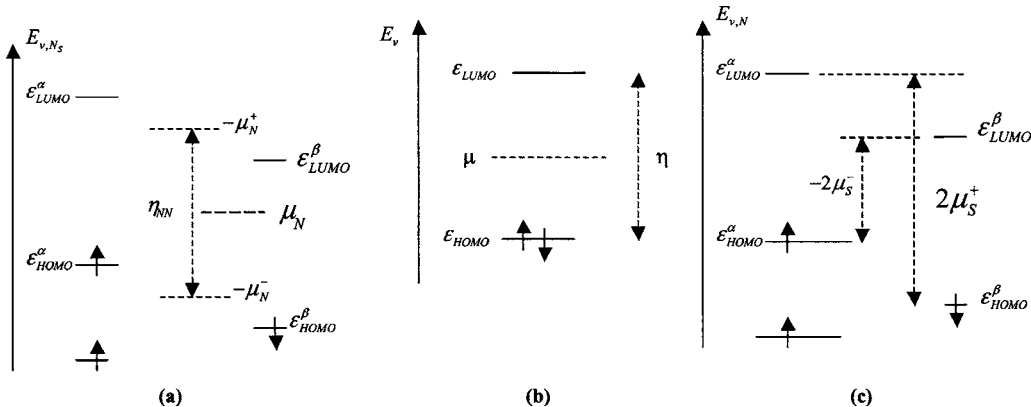
FIG. 1. Schematic representation of chemical potentials and hardnesses within the finite difference frozen-core approximation for the open-shell case (a) and the closed-shell case (b). The spin potentials for the case of spin polarization are shown in (c). The external potential is kept constant in the three cases. The orbital diagrams in (a) and (c) correspond to the carbene series in the triplet ground state.

$$f_{NN}(\mathbf{r}) \equiv \left[\frac{\delta\mu_N}{\delta\nu(\mathbf{r})}\right]_{N,N_S,\mathbf{B}(\mathbf{r})} \equiv \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_{N_S,\nu(\mathbf{r}),\mathbf{B}(\mathbf{r})},$$

$$f_{SS}(\mathbf{r}) \equiv \left[\frac{\delta\mu_S}{\delta\mathbf{B}(\mathbf{r})}\right]_{N,N_S,\nu,(\mathbf{r})} \equiv -\mu_B\left[\frac{\partial\rho_S(\mathbf{r})}{\partial N_S}\right]_{N,\nu,(\mathbf{r}),\mathbf{B},(\mathbf{r})},$$

$$(14)$$

The $f_{NN}^{\pm}(\mathbf{r})$ Fukui function[5,6] is associated with the initial response of the charge density $\rho(\mathbf{r})$ upon removing (−) or adding (+) electronic charge at constant spin number,[5] while the $f_{SS}^{\pm}(\mathbf{r})$ Fukui function measures the changes in the spin density upon a spin-polarization process implying an increasing (+) or decreasing (−) spin number. We must mention here that a generalized local philicity index as defined by Eq. (13a) has been previously discussed by Chattaraj *et al.*[21] in the context of a *condensed-to-atoms* analysis of both electrophilic and nucleophilic reactivities, $\omega_k^{\pm}=\omega f_k^{\pm}$. Such local philicity index $\omega_k^{\pm}$ has been explored in connection with the condensed-to-atoms Fukui functions for the analysis of local reactivity, solvent effects,[22] and intermolecular reactivity trends.[23,24] It has also been found useful, for instance, in the description of regioselectivity in polar Diels-Alder cycloaddition reactions,[25–28] and in the establishment of general electrophilicity scales.[29,30] Simple implementations for condensed-to-atoms models of $f_{NN}^{\pm}(\mathbf{r})$ and $f_{SS}^{\pm}(\mathbf{r})$ have available recently,[16] straightforwardly extending the range of applicability of local SP-DFT philicities, given in Eqs. (13b) and (13c).

III. COMPUTATIONAL DETAILS

In order to test the reliability of the newly defined SP-DFT extensions for electrophilicity ω_N, as well as to discuss the interpretation of $\omega_S^{\pm}$ as the philicity for spin polarization, we have evaluated these quantities for a simple series of carbenes recently studied on Ref. 20. Operational formulas are based on the well-known finite difference and frozen-core approximations[5–9] for the chemical-potential and hardness quantities entering into the definitions of Eqs. (9) and (12),

$$\mu_N^- \approx \frac{1}{2}(\varepsilon_{\text{HOMO}}^{\alpha}+\varepsilon_{\text{HOMO}}^{\beta}), \quad \mu_N^+ \approx \frac{1}{2}(\varepsilon_{\text{LUMO}}^{\alpha}+\varepsilon_{\text{LUMO}}^{\beta}),$$

$$\mu_N \approx \frac{1}{2}(\mu_N^+ + \mu_N^-), \quad \eta_{NN} \approx (\mu_N^+ - \mu_N^-), \quad (15)$$

and

$$\mu_S^- \approx \frac{1}{2}(\varepsilon_{\text{HOMO}}^{\alpha}-\varepsilon_{\text{LUMO}}^{\beta}), \quad \mu_S^+ \approx \frac{1}{2}(\varepsilon_{\text{LUMO}}^{\alpha}-\varepsilon_{\text{HOMO}}^{\beta}),$$

$$\eta_{SS}^{M\rightarrow M'} \approx (\mu_S^{(M')-} - \mu_S^{(M)+})/\Delta N_S, \quad (16)$$

where the $\varepsilon_i^{\alpha,\beta}$ stands for the ith frontier eigenvalue of a given α or β spin state. Note from Eq. (15) that for an open-shell system [Fig. 1(a)], the chemical potential μ_N is positioned between the eigenvalues defining the minimum gap, i.e., $\eta^{\beta-\alpha}=(\varepsilon_{\text{LUMO}}^{\beta}-\varepsilon_{\text{HOMO}}^{\alpha})$, and η_{NN} stands for the gap between the two constrained chemical potentials μ_N^- and μ_N^+. Note also that for a closed-shell system [Fig. 1(b)], i.e., $\varepsilon_{\text{HOMO}}^{\alpha}=\varepsilon_{\text{HOMO}}^{\beta}=\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}^{\alpha}=\varepsilon_{\text{LUMO}}^{\beta}=\varepsilon_{\text{LUMO}}$, we have that $\mu_N=\mu$, $\eta_{NN}=\eta$, and therefore $\omega_N=\omega$. On the other hand, from Eq. (16), the spin potentials $\mu_S^{\pm}$ constitute, in fact, the lowest unoccupied molecular orbital-highest occupied molecular orbital (LUMO-HOMO) gaps among the two spin symmetries (i.e., spin polarization). The spin hardness η_{SS} for the interval (M,M') of spin multiplicities $(M<M')$ was calculated through the spin potentials $\mu_S^-(M')$ and $\mu_S^+(M)$ using the ground-state geometry of multiplicity M. Hence, in the present case, the singlet (ground state)→triplet and the triplet (ground state)→ singlet gaps have been evaluated as $\eta_{SS}^{s\rightarrow t} \approx (\mu_S^{(t)-} - \mu_S^{(s)+})/2$, and $\eta_{SS}^{t\rightarrow s} \approx (\mu_S^{(s)+} - \mu_S^{(t)-})/(-2)$, respectively. All calculations have been carried out at the UB3LYP/6-311++G(d,p) level of theory using the GAUSSIAN 98 package of programs.[31]

IV. ELECTROPHILICITY AND PHILICITY FOR SPIN POLARIZATION OF SIMPLE CARBENES

Table I reports the relevant SP-DFT quantities for some simple selected carbene systems having both singlet (Table Ia) and triplet (Table Ib) ground states. Properties for the lowest-lying excited state of different multiplicities have

TABLE I. (a) SP-DFT chemical potential μ_N, hardness η_{NN}, electrophilicity ω_N, spin potential μ_S^+, spin hardness η_{SS}, philicity for spin polarization ω_S^+, and vertical $\Delta E^{vt}_{s\to t}$ and adiabatic $\Delta E^{ad}_{s\to t}$ singlet-triplet transition gaps, for some singlet ground-state carbenes. (b) SP-DFT chemical potential μ_N, hardness η_{NN}, and electrophilicity ω_N, spin potential μ_S^-, spin hardness η_{SS}, philicity for spin polarization ω_S^-, and the vertical $\Delta E^{vt}_{t\to s}$ and the adiabatic $\Delta E^{ad}_{t\to s}$ triplet-singlet transition gaps, for some triplet ground-state carbenes.

X–C–Y	2S+1	μ_N(eV)	η_{NN}(eV)[a]	ω_N(eV)[a]	$\Delta E^{vt}_{s\to t}$(kcal/mol)	$\Delta E^{ad}_{s\to t}$(kcal/mol)	$\mu_S^+[\mu_S^{(t)-}]$(eV)[b]	η_{SS}(eV)	ω_S^+(eV)
H–C–OH	1	−3.52	4.55	1.36	34.23	25.67	2.27 (−0.77)	−1.52	−1.70
	3	−3.60(−3.21)	6.88 (2.42)	0.94 (2.13)					
H–C–SH	1	−4.21	4.01	2.21	27.81	18.35	2.00 (−0.73)	−1.37	−1.47
	3	−3.69(−3.77)	5.47 (2.36)	1.52 (3.00)					
H–C–F	1	−4.60	4.05	2.61[c]	19.37	12.13	2.02 (−1.16)	−1.59	−1.29
	3	−4.24(−4.13)	9.17 (3.12)	0.98 (2.72)					
H–C–Cl	1	−5.00	3.40	3.68	10.92	2.23	1.70 (−1.19)	−1.45	−1.00
	3	−4.33(−4.34)	7.01 (3.28)	1.34 (2.87)					
F–C–F	1	−5.10	5.98	2.18[c]	60.36	52.22	2.99 (−0.36)	−1.67	−2.67
	3	−4.34(−4.62)	8.61 (1.53)	1.09 (6.97)					
Cl–C–Cl	1	−5.45	3.81	3.91[c]	24.70	16.57	1.90 (−0.80)	−1.35	−1.34
	3	−4.75(−4.67)	5.70 (2.40)	1.98 (4.55)					
HO–C–OH	1	−3.06	6.13	0.77[c]	70.58	54.54	3.06 (+0.01)	−1.53	−3.07
	3	−3.40(−3.32)	6.50 (2.86)	0.89 (1.93)					
HS–C–SH	1	−3.96	4.20	1.87	37.78	32.89	2.10 (−0.41)	−1.26	−1.76
	3	−3.60(−3.70)	4.27 (1.28)	1.51 (5.33)					
NH$_2$–C–OH	1	−2.32	6.43	0.42	79.82	54.30	3.22 (+0.26)	−1.48	−3.50
	3	−2.76(−2.58)	6.15 (2.52)	0.62 (1.32)					
NH$_2$–C–SH	1	−2.91	5.51	0.77	69.55	39.58	2.76 (+0.16)	−1.30	−2.92
	3	−3.11(−3.22)	5.78 (3.30)	0.83 (1.57)					

X–C–Y	2S+1	μ_N(eV)	η_{NN}(eV)[a]	ω_N(eV)[a]	$\Delta E^{vt}_{s\to t}$(kcal/mol)	$\Delta E^{ad}_{s\to t}$(kcal/mol)	$\mu_S^-[\mu_S^{(s)+}]$(eV)[b]	η_{SS}(eV)	ω_S^-(eV)
H-C-H	3	−4.25(−3.22)	9.59(4.56)	0.94(1.88)	27.25	13.66	−2.28(5.05)	−3.67	−0.71
	1	−4.97	3.32	3.71					
H-C-Me	3	−3.55(−3.43)	8.88(4.05)	0.71(1.45)	21.19	7.86	−2.02(1.12)	−1.57	−1.30
	1	−4.03	3.30	2.46					
H-C-Li	3	−3.39(−2.84)	4.27(3.28)	1.34(1.23)	32.06	32.06	−1.64(0.70)	−1.17	−1.15
	1	−2.92	1.41	3.03					
H-C-AlH$_2$	3	−4.70(−4.77)	5.32(3.42)	2.08(3.32)	22.28	21.26	−1.71(1.00)	−1.36	−1.08
	1	−4.90	2.09	5.74					

[a]Results in parenthesis have been obtained from the hardness evaluated using the minimum gap, $\eta^{\beta-\alpha}=\varepsilon^\beta_{LUMO}-\varepsilon^\alpha_{HOMO}$, in Eq. (15).
[b]$\mu_S^{(t)-}$ values were obtained from the orbital energies of the triplet state calculated at the singlet ground-state geometry via Eq. (16).
[c]Other data based on a finite difference using calculations for cation and anion systems are available for these systems in Ref. 39. However, these data cannot be compared directly with the present results, but to a model based on kinetics as discussed in Ref. 39.

been calculated in each case, as well as the corresponding vertical and adiabatic transition energy changes. We report responses both at constant spin number (the chemical potential μ_N, the hardness η_{NN}, and the SP-DFT electrophilicity ω_N), and at constant number of electrons (i.e., the philicity for spin polarization $\omega_S^\pm$ and spin hardness η_{SS}).

The carbene intermediates are divalent coordinate carbon species possessing two nonbonding electrons that may have antiparallel spins (singlet state) or parallel spins (triplet state).[32–34] The singlet electronic structure has a low-lying HOMO energy and a high-lying LUMO energy, which allows it to exhibit both electrophilic and nucleophilic reactivities. Triplet carbenes on the other hand are expected to exhibit radical-like reactivity. Singlet carbenes are favored by electron-withdrawing substituents and also by electronic conjugation effects stabilizing the empty orbital. Alkyl groups or electropositive substituents favor triplet states. When the triplet-singlet energy gap is low, the Curtin-Hammett principle[35,36] may apply, and either or both spin states may react. In fact, the global electrophilicity pattern

based on Eq. (4) for singlet carbenes has been analyzed and compared with the experimental scale of philicity[37,38] using electronic reactivity indices.[39]

Direct π-electron donation or conjugation of a substituent with the carbenic center will decrease the intrinsic electrophilic character of carbenes while electron withdrawing will increase it.[20] The model SP-DFT electrophilicity index ω_N of Eq. (9) accounts for these facts, and the following order of increasing electrophilicity is therefore predicted for the singlet ground-state carbenes: $H_2N–C–OH < HO–C–OH < H_2N–C–SH < H–C–OH < HS–C–SH < F–C–F < H–C–SH < H–C–F < H–C–Cl < Cl–C–Cl$. Note also from Table Ia that the first triplet-excited state is predicted to loose its electrophilic power by a factor of about 1.5 times, except for those systems with the lowest electrophilicity for which large "push-pull" effects are involved (i.e., $H_2N–C–OH$, $HO–C–OH$, and $H_2N–C–SH$).[32–34,40] For the triplet ground-state carbenes the order of increasing electrophilicity is correctly predicted to be $H–C–Me < H–C–H < H–C–Li < H–C–AlH_2$, the corresponding singlet-excited state being electrophili-
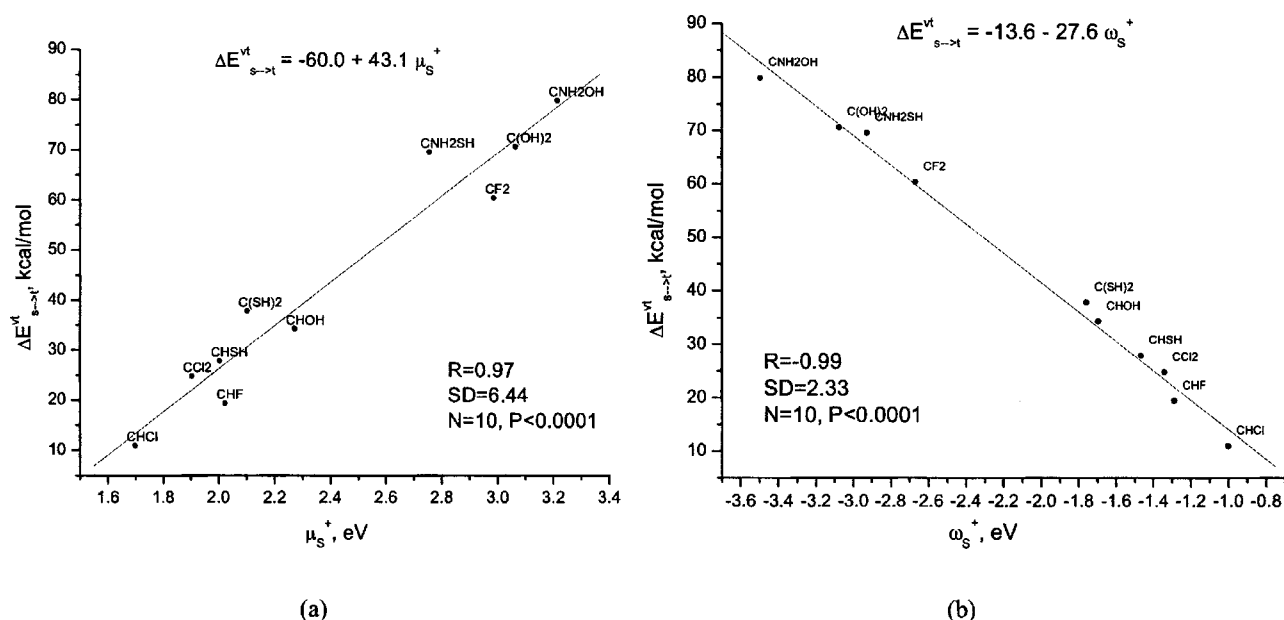
FIG. 2. Vertical triplet-singlet energy gap $\Delta E_{t \to s}^{vt}$ for some simple carbenes vs both (**a**) the spin potential μ_S^+ and (**b**) the philicity for spin-polarization ω_S^+; R=correlation coefficient, SD=Standard deviation, N=Number of data points, and P=the test for the null hypothesis that the overall slope is zero, i.e., the probability that the correlation coefficient is zero. The P values are obtained from the *t* test of the correlation analysis.

cally activated by a factor of 2.3–4.0. Note also from both Tables Ia and Ib that the calculation of the SP-DFT chemical potential μ_N and hardness η_{NN} have not been obtained using the smallest gap between the one-electron energies of the frontier molecular orbitals,[41] but instead through the operational formulas given in Eq. (15) which are the natural extensions of these indices in the SP-DFT framework. Note that for the present carbene series in the triplet state (ground or excited states) the use of this smallest gap as the hardness,[41] $\eta_{NN}^{\beta-\alpha}=(\varepsilon_{LUMO}^{\beta}-\varepsilon_{HOMO}^{\alpha})$, yields incorrectly a higher value of electrophilicity for the triplet state (see second entry in parentheses for ω_N reported in Tables Ia and Ib). Note also, on the other hand, that under the present approximations, $\eta_{NN} > \eta^{\beta-\alpha}$, and therefore the triplet state (ground or excited state) is predicted to have a higher constrained hardness η_{NN} than the singlet one.

Regarding the processes involving spin polarization, correlations between the singlet → triplet vertical transition and the spin potential μ_S^+ and philicity ω_S^+ have been observed for the systems listed in Table Ia (singlet ground state), as shown in Fig. 2. It is clear, as was discussed above,[6] that these indices are related to electronic transitions occurring at a constant number of electrons, and not to electron transfer processes. As expected, the philicity for spin polarization $\omega_S^{\pm}$ correlates in good order with the vertical transition energy in all cases for these systems.[16,19,20,42] ω_S^+ is, in fact, a *philicity for spin polarization*. Note also in the present case from Fig. 2(a) and Eq. (12) that a linear relationship between ω_S^+ and $-\mu_S^+$ becomes implicit for this series of carbenes in the singlet ground state because $\mu_S^{(t)-}$ turn out to be small enough as reported in Table Ia. The relative errors in the determination of the $\Delta E_{s \to t}^{vt}$ as the simple sum of $(\mu_S^+ + \mu_S^{-(t)})$, i.e., from Eq. (10), results, in fact, as very small along this series: 0.37% ($H_2N–C–OH$), 0.44% (HO–C–OH), 3.35% ($H_2N–C–SH$), 0.99% (H–C–OH), 3.28% (HS–C–SH), 0.44% (F–C–F),

5.23% (H–C–SH), 3.10% (H–C–F), 7.03% (H–C–Cl), and 3.05% (Cl–C–Cl). These results further stress that, in fact, the $\omega_S^{\pm}$ indices have to be interpreted as philicities for spin-polarization and not as charge-transfer related ones as previously claimed.[19,20,42]

V. CONCLUDING REMARKS AND PERSPECTIVES

In the present work, the electrophilicity index has been further analyzed in the context of a conceptual spin-polarized DFT framework. A new, constrained, version of this index has been introduced [Eq. (9)], and its local extension has been further elaborated.[14,16,21] The previously defined model quantities for $\omega_S^{\pm}$ in Eq. (12) should be associated to the philicity of the system to change its spin polarization as these quantities imply electron charge (or spin) reorganization at constant number of electrons. Computational numerical results for these new quantities can be readily obtained by using, for instance, the approximation scheme first proposed by Galván *et al.*[5] These indices, comprising both philicity for spin polarization $\omega_S^{\pm}$, as well as charge transfer at constant spin number ω_N, yield complementary information for a comprehensive description of chemical reactions involving excited states and open-shell systems. It is expected that the combined use of both indices might allow us to achieve a better description of the initial responses for a chemical reaction involving both spin polarization and charge transfer, analyzed both in the global and local regimes within a SP-DFT framework.[14,16–20]

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