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Spin-Philicity and Spin-Donicity as Auxiliary Concepts To Quantify Spin-Catalysis Phenomena

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For molecular systems susceptible to undergo a change of their spin state as a result of a chemical reaction with a given reactant, the spin-polarized density functional theory is used to define the concepts of "spin-philicity" (ω_S^+) and "spin-donicity" (ω_S^-) as global reactivity indexes. They are defined as the maximum energy change when a molecular system acquires or donates a spin number ΔN_S to increase (ω_S^+) or decrease (ω_S^-) its spin multiplicity. The spin transformation of chemically reactive species induced by the interaction of these molecules with external spin carriers—a phenomenon known as spin catalysis—is discussed on the basis of an absolute scale for ω_S^+ and ω_S^-. As an illustration of the method, a selection of paramagnetic and diamagnetic molecules, commonly used as spin catalyst, is classified within this scale and the hierarchy obtained is compared with the available experimental information.

1. Introduction

Theoretical descriptions of chemical reactivity are normally based on the idea of spin conservation along the reaction path. Frontier orbital concept and current DFT based reactivity indexes assume the reactions to proceed on surfaces of uniform spin. Shaik and co-workers[1] classify these reactions in terms of single-state reactivity (1-SR) and of two-state reactivity (2-SR) where two spin surfaces connect reactants and products.

For 1-SR cases a number of reactivity indexes have been proposed and used. Recently, local and global reactivity indexes defined in the density functional theory (DFT) approach using Kohn−Sham orbital approach have been defined by us.[2] For chemical reactions implying intermediate bond snipping (breaking), and further bond knitting (making), such as "rotation" around a double bond or free-radical recombination reactions,[3] the mechanism may involve spin number changes in the corresponding partners that can be related to n-SR surfaces. In this paper we extend the definitions to spin-dependent DFT with the aim to cope with reactivity indexes for n-SR in radical and nonradical systems.

Spin catalysis, a physical phenomenon of spin transformation of chemical species induced by the exchange interaction with external spin carriers,[4,5] is one of the most relevant problems in modern spin chemistry literature. Spin catalysis deals with the transformation of a spin forbidden nonreactive state of a system into another chemically reactive spin allowed state of different multiplicity. The photosynthetic assisted triplet oxygen ($^3O_2$) fixation to D-ribulose 1,5-bisphosphate is a clear example showing the biologic and atmospheric importance of this electronic property.[6]

For spin catalysis, the commonly accepted idea is that the spin transformation of the interacting radical pair is induced either by the nonmagnetic exchange interaction with the electron spin of the radical pair or the electron spin of an external spin-carrier (the catalyst), which usually is a paramagnetic (ionic or neutral) species.[4,5,7] Even though the first direct experimental demonstration of spin catalysis by radicals has been obtained rather recently,[8,9] the reaction rate enhancement induced by the presence of paramagnetic molecules in a reacting system was observed long ago.[10−14] A classic example is the di-deutero-ethylene thermal cis−trans isomerization presented by Douglas, Rabinovitch, and Looney[15] in the mid 1950s. This experimental study reported on the catalysis of the isomerization process by oxygen, nitric oxide, free radicals, and some olefins.

Dickinson et al.[16] also looked at the catalytic effects of paramagnetic species on the cis-trans isomerization phenomena (photochemical iodine-sensitized cis−trans isomerization of di-chloro-ethylene). Harman and Eyring, in a seminal work,[11] suggested that paramagnetic substances could catalyze isomerization by providing a nonhomogeneous magnetic field which selectively acts on the two magnetic dipoles associated to the spin of the two electrons in the π-system of the substrate.[11] This magnetic-induced explanation of spin catalysis[11] was criticized by McConnell.[17] It was argued that the spin−spin and spin−orbit interactions between the spin component of one electron with the orbit of the other, as compared with the already small spin−spin and spin−orbit contributions referred to the same electron was expected to be too small to provide a sound explanation. McConnell persuasively gave arguments in favor of a qualitative explanation involving the interaction of a catalyst in a doublet spin-state with the singlet and triplet spin states of the substrate.[17] The spin space is increased now. Standard spin angular momentum sum rules produce two doublet states

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together with a quartet state. According to McConnell, the minimum separation between the two doublet states, as compared to the singlet−triplet energy gap would account for the catalytic effect of paramagnetic molecules. A similar model applies also for catalyst in the triplet state, but such a mechanism is not possible for catalyst in the singlet state.[17] A modern, CASSCF study by Agren et al.[7] in the supermolecule model has given a detailed electronic picture to these ideas.

McConnell's model of spin catalysis may be reformulated on a more quantitative basis using some previous results developed within the spin polarized density functional theory.[18−21] This method introduces the spin potential and spin hardness concepts. Within this approach, both the catalyst and the substrate may exchange ΔN_S spin units to create new electronic states of different multiplicity. Implicitly, this model entails the existence of a one-to-one mapping between chemical species (represented by the density and the stationary geometry of sources determining the external potential, υ) and electronic state corresponding to the electronic wave function: the density is assumed to be both υ- and N-representable. For each stationary geometry (cis or trans), the υ-sources define a chemical species in the same reference frame. The system is invariant to overall rotations of the laboratory frame, therefore, the general angular momentum ($J = L + S$) is conserved. The cis species transforms according to the $C_{2\upsilon}$ point symmetry group; the trans species does it in the C_{2h} symmetry group. The change from say cis to trans conformation is a more subtle electronuclear problem than an adiabatic change.[22] For this reason, a simple model is used here to discuss issues of reactivity but not of actual mechanistic changes. Note the π-orbitals formed with p_x atomic orbitals for the *cis*-conformer and p_z for the trans-conformer generate orthogonal electronic wave functions for the isomers. Now, an adiabatic change from one point symmetry group to another is not an allowed physical process. Furthermore, a direct change of orbital angular momentum projection of two units is a forbidden process. An intermediate state, usually designated as transition-state, is required to provide the mechanism of isomerization in the present context. This is related to the spin triplet already suggested by Harman and Eyring[11] with some important caveats. The physical quantity conserved in this approach is the generalized angular momentum J.

The catalytic effect may involve either the acceptance of ΔN_S spin units by the catalyst in the spin doublet or donation of ΔN_S spin units by the catalyst in a higher spin state. The energy changes associated to the variation in spin multiplicity can be represented within a static approach by a spin potential defined in the direction of increasing and decreasing multiplicity. It is however of interest to test new global spin reactivity indexes using new concepts named here as spin-philicity (ω_S^+) and spin-donicity (ω_S^-). In this work we present preliminary results on the spin catalytic effects by paramagnetic and diamagnetic catalysts. The following molecular systems have been selected: O_2, S_2, Se_2, NO, NO_2, $CH_3^{\bullet}$, propene, and 2-butene species. Doublet and triplet states are involved. The results are analyzed and compared with the available experimental data. The potential spin catalyst power displayed by the stable free radical 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) is also discussed.

2. Model Equations and Basic Definitions

We start by considering the energy changes from a ground state to a promoted state of different multiplicity within the spin polarized density functional theory. The spin polarized extension of chemical reactivity may be developed in a representation where the independent variables are the number of electrons $N = N_\alpha + N_\beta$ and the number of (unpaired) spins $N_S = N_\alpha - N_\beta$. Within the $\{N, N_S\}$ representation, in the presence of an external potential $\upsilon°(\mathbf{r})$, the total energy of a system can be expanded in a Taylor series around a reference ground state with $N°$ electrons and $N°_S$ unpaired spins, so that the energy difference between the ground-state $E[N°,N°_S,\upsilon°(\mathbf{r})]$ and any promoted state of different multiplicity may be written, up to second order, as

$$\begin{aligned}\Delta E = \mu_S^o \Delta N_S + \mu_N^o \Delta N + \int d\mathbf{r}\, \rho^o(\mathbf{r})\, \Delta\upsilon(\mathbf{r}) + \\ \frac{1}{2}\eta°_{SS}(\Delta N_S)^2 + \frac{1}{2}\eta°_{NN}(\Delta N)^2 + \eta_{NS}^o \Delta N \Delta N_S + \\ \Delta N \int d\mathbf{r}\, f_N^o(\mathbf{r})\, \Delta\upsilon(\mathbf{r}) + \Delta N_S \int d\mathbf{r}\, f_S^o(\mathbf{r})\, \Delta\upsilon(\mathbf{r}) + \\ \frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}')\, \Delta\upsilon(\mathbf{r})\, \Delta\upsilon(\mathbf{r}') + \text{higher order terms} \quad (1)\end{aligned}$$

[20,21] μ_N and μ_S are the electronic and spin potential describing the propensity of the system to modify its electronic distribution and its spin polarization, respectively.[20,21] The quantities $\eta°_{NN}$, η_{NS}^o, and $\eta°_{SS}$ (the generalized hardnesses) are the full set of second derivatives of the electronic energies with respect to N and N_S. $f_N^o(\mathbf{r})$ and $f_S^o(\mathbf{r})$ are the generalized Fukui functions. They correspond to the first derivative with respect to N and N_S of the electron density $\rho(\mathbf{r})$, respectively.[20,21] $\chi(\mathbf{r},\mathbf{r}')$ is the linear response function.[23] All quantities bearing the upper index 0 are evaluated at the reference state. Expression 1, for isoelectronic processes, may be significantly simplified. These occur at constant N, thereby reducing the representation of the energy changes to the $\{N_S, \upsilon(\mathbf{r})\}$ plane. If for computing facility we further consider an adiabatic change of multiplicity from N_S to $N_S + \Delta N_S$ (i.e., in the direction of increasing ($\Delta N_S > 0$) or decreasing ($\Delta N_S < 0$), multiplicity at constant external potential), the approximation to the *vertical* change in energy between two states of different multiplicity becomes[20,21]

$$\Delta E_v = \mu_S^o \Delta N_S + \frac{1}{2}\eta°_{SS}(\Delta N_S)^2 \quad (2)$$

Expression 2 is the starting point to define the concepts of spin-donicity and spin-philicity as follows. Consider for instance the maximum change in energy ΔE_{max}, when the system modifies its spin number from N_S to $N_S + \Delta N_S$. A simple variational calculation, similar to that introduced by Parr et al.,[24] to define the electrophilic power of an atom or molecule yields

$$\Delta E_{max} = -\frac{(\mu_S^o)^2}{2\eta_{SS}^o} \quad (3)$$

The set of eqs 1−3 provides the basis to define new spin polarized reactivity indexes, measuring the energy changes as the system exchanges spins with the environment in the direction of increasing (+) and decreasing (−) multiplicity. According to eq 3, these energy changes are directly related to the spin potential and spin hardness in both directions, as we will show below.

If we define the *spin-philicity* power of an atom or a molecule as the energy change when the system acquires an additional spin number ΔN_S, then the natural reference state for the spin potential becomes $\mu_S^o = \mu_S^+$; i.e., the spin potential of the state having lower multiplicity. This leads to increase its multiplicity from $M \rightarrow M'$ ($M' > M$), in the direction where N_S increases[20,21] (e.g. from the singlet to triplet, from doublet to quadruplet, etc), and a possible quantitative definition of the *spin-philicity* power $\omega_S{}^+$ is

$$\omega_S{}^+ \equiv -\frac{(\mu_S{}^+)^2}{2\eta_{SS}^o} \tag{4}$$

If we consider, on the other hand, the change in the direction of decreasing multiplicity, e.g., when the system donates ΔN_S spin units, we may define the *spin-donicity* index $\omega_S{}^-$ as

$$\omega_S{}^- \equiv -\frac{(\mu_S{}^-)^2}{2\eta_{SS}^o} \tag{5}$$

This index is expressed now in terms of the spin potential $\mu_S^o = \mu_S^-$; i.e., the spin potential of the state having higher multiplicity, in the direction where N_S decreases. It should be emphasized that the spin hardness, as well as the spin potential, has to be defined in a particular direction (e.g., $\eta_{SS}^o = \eta_{SS}^+$ in the direction of increasing multiplicity in eq 4, and $\eta_{SS}^o = \eta_{SS}^-$ in the direction of decreasing multiplicity in eq 5). The spin-donicity index is expected to be a useful quantity to describe the spin polarization contributions to spin catalysis within a static reactivity picture. Note that in addition of the spin-philicity and spin-donicity numbers, the spin potential describing the work required to change the spin multiplicity of an electronic state, is by itself a useful descriptor of spin reactivity. It may describe for instance the propensity of a spin catalyst to transfer ΔN_S spin units to a given substrate or to accept ΔN_S spin units from the substrate in a spin catalyzed reaction. While the molecular models that explain the spin catalysis phenomena explicitly introduce the interaction of electronic states with spin multiplicities higher than those present in the ground states of the substrate and the catalyst, the present approach must be understood as a static spin reactivity picture that introduces new reactivity numbers, that accounts for the propensity of the system to change their reference (ground state) multiplicity, to access the new available electronic states defined by the spin angular momentum sum rules.

3. Computational Details

The spin potentials μ_S^- and μ_S^+ in the direction of decreasing and increasing multiplicity, respectively, were evaluated using the finite difference formulas proposed by Galván et al.[20,21] as

$$\mu_S{}^- = \frac{(\epsilon_H^\alpha(M') - \epsilon_L^\beta(M'))}{2} \tag{6}$$

and

$$\mu_S^+ = \frac{(\epsilon_L^\alpha(M) - \epsilon_H^\beta(M))}{2} \tag{7}$$

TABLE 1: Spin Potential (μ_S^o), Spin Hardness (η_{SS}^o), Spin-Philicity/Spin-Donicity Numbers ($\omega_S^\pm$), Relative Kinetic Parameter (k/k_o), and Vertical Energies (ΔE_v) for Some Active Species[a]

species	GS multiplicity	μ_S^o	μ_S^o	η_{SS}^o	$\omega_S^\pm$	k/k_o	ΔE_v
propene	singlet[b]	μ_S^-	0.59	−1.53	0.12	1.15	98.1 (105.4)
			0.74	−1.50	0.18		103.3 (103.8)
			−3.80	−5.47	1.32		77.0 (83.6)
2-butene	singlet[b]	μ_S^-	0.66	−1.47	0.15	1.15	98.1 (98.9)
			0.72	−1.43	0.18		98.9 (99.8)
			−3.75	−5.28	1.33		70.3 (82.0)
Se_2	triplet	μ_S^-	−1.29	−0.83	1.00		−21.2 (−22.3)
			−1.26	−0.82	0.97		−20.3 (−21.6)
			−4.71	−4.06	2.73		30.2 (30.6)
S_2	triplet	μ_S^-	−1.46	−0.96	1.11		−23.1 (−23.2)
			−1.44	−0.95	1.09		−22.6 (−22.7)
			−5.15	−4.46	2.97		−31.8 (−32.6)
O_2	triplet	μ_S^-	−2.66	−1.81	1.96	1.33	−39.0 (−39.1)
			−2.65	−1.81	1.94		−38.7 (−39.0)
			−9.04	−7.91	5.17		−52.1 (−53.2)
NO_2	doublet	μ_S^+	3.41	−1.31	4.44		96.9 (96.7)
			3.46	−1.31	4.57		99.2 (99.2)
			8.16	−6.56	5.08		74.0 (71.8)
NO	doublet	μ_S^+	4.80	−1.78	6.50	1.41	139.4 (139.1)
			4.78	−1.78	6.42		138.6 (138.3)
			9.92	−7.36	6.69		118.3 (126.6)
$CH_3^\bullet$	doublet	μ_S^+	7.09	−1.14	22.05	1.82	274.5 (276.2)
			6.39	−0.88	23.20		254.4 (257.7)
			9.95	−4.79	10.33		238.2 (251.6)
ethylene	singlet[b]	μ_S^+	3.88	−1.62	4.64		104.2 (104.1)
			3.84	−1.57	4.70		104.7 (104.7)
			7.43	−3.50	7.90		160.9 (202.2)

[a] Spin potential values in Volts, spin hardness in volt/spin units, spin-philicity/spin-donicity values in eV and vertical energies in kcal/mol. k/k_o is the experimental rate constant ratio with reference to the uncatalyzed isomerization reaction of di-deutero-ethylene, taken from ref 15. First entry corresponds to (U)B3LYP/6-31G*; second entry corresponds to (U)B3LYP/6-311G*, and third entry corresponds to (U)HF/6-311G* calculations. [b] Even though the ground state of these compound are singlet states, the catalytic power is evaluated in their promoted triplet state.

These indexes are defined in terms of the one electron energies of the frontier molecular orbitals HOMO and LUMO, for the system in the lower and upper *M* and *M′* spin multiplicities, respectively as follows: consider for instance the change in the direction of increasing multiplicity, under the constrain that the total number of electrons *N* must be kept constant. In this case one has to remove $\Delta N_S/2$ electrons from the HOMO-β and place them in the LUMO-α spin−orbital, so that $\mu_\alpha^+ = \epsilon_L^\alpha$ and $\mu_\beta^+ = \epsilon_H^\beta$; which immediately leads to eq 7. For changes in the direction of decreasing multiplicity, a similar procedure leads to eq 6 (see, for instance, ref 19 for further details). With the spin potential values at hand, the spin hardness was evaluated as[21]

$$\eta_{SS}^o = \frac{\mu_S^- - \mu_S^+}{2} \tag{8}$$

The spin-philicity ω_S^+ and spin-donicity ω_S^- indexes were evaluated via eqs 4 and 5, respectively. To show that the spin polarized reactivity indexes are rather independent of the method and basis set used to compute them, we performed three types of calculations including (U)B3LYP/6-31G*, (U)B3LYP/6-311G* and (U)HF/6-311G* levels of theory implemented in the GAUSSIAN98 package of programs.[25] All systems were fully optimized in its ground states (GS). When the GS of the system had the upper multiplicity *M′*, the calculation in its lower multiplicity *M* were performed as single points for the system in the external potential corresponding to the upper multiplicity *M′*. Conversely, if the GS of the system corresponded to the lower multiplicity, the calculation in its upper multiplicity *M′* were performed as single points for the system in the external potential corresponding to the lower multiplicity *M*.

4. Results and Discussion

Table 1 summarizes the global spin properties for a short series of diamagnetic and paramagnetic molecules with recognized spin catalytic power. Ethylene is also included as a well-known substrate in spin catalyzed processes.[15-17] We include the values of vertical energies evaluated as $\Delta E_v = \mu_S^+ + \mu_S^-$.[21] The values in parentheses correspond to the difference in total energy. It may be seen that, in general, the (U)B3LYP functional gives a better description of both, the spin quantities and vertical energies. Note that the predicted ΔE_v values at the (U)B3LYP/6-31G* are within 1−2% error, giving confidence to the spin potential values as global descriptor for the spin multiplicity changes evaluated at this level of theory. Also included in Table 1 are the ratio k/k_o corresponding to the experimental rate constants evaluated by Douglas et al.[15] for the isomerization reaction of di-deutero-ethylene in the absence (k_o) and in the presence (k) of several spin catalyst. In our model, the first five spin catalyst quoted in Table 1 are classified as spin donors. They perform their catalytic effect in the triplet state. While for propene and 2-butene the ground state correspond to singlet states, for the remaining three spin donor catalyst Se_2, S_2, and O_2, their ground states are spin triplets. This feature is reflected in the sign of the corresponding spin potentials, namely μ_S^-. Spin hardness is always negative by construction, but their absolute value may be still regarded as a resistance of the system to change their spin multiplicity. The resulting spin-donicity numbers (ω_S^-) shown in Table 1 display a marginal value when compared to the molecules in the doublet spin state. This is consistent with their moderate spin catalysis activity as evaluated in the work of Douglas et al.:[15] there, these compounds were found to slightly increase the rate constant (10−20% larger than normal) for the isomerization reaction of di-deuterated-ethylene. The triplet spin catalyst Se_2, S_2, and O_2 on the other hand, show larger and negative values of spin potential, thereby showing that the change from triplet to singlet state is energetically favored. Note also that Se_2 and S_2, yet having lower absolute values in spin hardness, are predicted to have a lower spin-donicity number, a result primarily due to their lower values in spin potential as compared to O_2 molecule. The higher spin-donicity number in O_2 molecule, as compared to propene and 2-butene is consistent with the experimental result reported by Douglas et al.:[15] dioxygen was found to increase the rate of isomerization reaction of di-deutero-ethylene 35% above normal.

Also included in Table 1 are the doublet catalyst NO_2, NO, and the methyl radical $CH_3^\bullet$. These molecules are classified as spinphilic species within our model. Note that they were also found to act as efficient spin catalyst.[15] The spin catalytic effect of NO was reported to be similar to that of dioxygen molecule at comparable experimental conditions by Douglas et al.[15] Note that the spin catalytic effect predicted from the ω_S^+ index quoted in Table 1 is consistent with the experimental results, as measured by the ratio k/k_o.

The spin catalytic power of O_2 and NO molecules have been recently evaluated from ab initio calculations by Agren et al..[7] These authors reported that the NO catalyst when bounded to ethylene at the N atom end leads to a more pronounced lowering of the activation energy for the isomerization of ethylene than does the dioxygen molecule. The intermolecular exchange interactions led to perturbations not only in the ethylene molecule but also at the catalyst ends. Spin polarization effects were thought to be included within the global catalytic effect evaluated by these authors.[7] Local effects related to the orientation in the catalyst-substrate complex in NO (bound to N or O ends) are not included in the ω_S^+ quantity, so that the global spin catalytic power predicted by the spin-donicity number in Table 1, correctly account for the observed enhancement in the rate constant for the isomerization of di-deutero-ethylene reported by Douglas et al.[15]

The effect of free radicals in the rate of isomerization of di-deutero-ethylene was also investigated by Douglas et al.[15] by adding azomethane. It was found that methyl radicals generated in situ readily accelerated the rate of isomerization in a more efficient way, as compared to O_2 and NO molecules. Note that according to our spin-philicity/spin-donicity scale, methyl radical displays the highest value within the series, in agreement with the observed spin catalytic effect. Note also that the spin-philicity value ω_S^+ predicted for ethylene, as substrate in the spin catalyzed isomerization reaction, is also consistent with the experimental data. For instance, the interaction of ethylene with the catalysts propene, 2-butene, Se_2, S_2, and O_2 will be characterized by a spin transfer from the triplet state of the catalysts toward ethylene in its singlet ground state. Note the high value of $\omega_S^+ \approx 4.7$ eV of singlet ethylene as spin acceptor (at the (U)B3LYP level of theory, see Table 1). On the other hand, the spin catalytic effect performed by NO_2, NO, and $CH_3^\bullet$ as spin acceptors would be upon the triplet state of ethylene as spin donor.

The reliability of the spin reactivity indexes to assess the catalytic effect by paramagnetic molecules was also tested for TEMPO, a well-known free radical scavenger.[9,26] The observation that the recombination probability of triplet sec-phenetyl/sec-phenetylacyl radical pairs generated in the photolysis of *d*, *l* −2,4-diphenylpentan-3-one in benzene increased about three times in the presence of increasing concentration of TEMPO demonstrated the predominance of the catalytic function over the traditional scavenging function of nitroxides.[27] The doublet GS of TEMPO was evaluated at the UB3LYP/6-31G* level of theory. The vertical energy for the doublet quadruplet change evaluated from $\Delta E_v = \mu_S^+ + \mu_S^-$,[21] yielded 175.3 kcal/mol, in good agreement with the value 182.2 kcal/mol (less than 4% error) evaluated from the difference in total energies of the quadruplet-doublet states. According to our model, TEMPO in the doublet GS is classified as a spinphilic species with a spin-philicity power of 28.0 eV, i.e. a more powerful spinphilic species than methyl radical ($\omega_S^+ = 22.05$ eV, see Table 1). The enhanced spinphilic power of TEMPO as compared to that displayed by the methyl radical is almost due to its remarkable lower absolute value of spin hardness ($\eta_{SS}^o = -0.30$ V/spin, compared to the value $\eta_{SS}^o = -1.14$ V/spin for $CH_3^\bullet$ species, see Table 1). The spin potential associated to the doublet GS of TEMPO is 4.10 V, which is less than the value $\mu_S^+ = 7.09$ V evaluated for the methyl radical quoted in Table 1, at the same level of theory.

In summary, the information encompassed in the spin reactivity indexes presented here accounts well for the experimentally observed catalytic effect of paramagnetic and diamagnetic molecules. Paramagnetic species in their doublet ground state performs their catalytic effect as spinphilic species by accepting spins from the environment, thereby lowering the spin multiplicity of the substrate. This effect is to be understood within a static model measuring the propensity of these species to exchange spins with the substrate, but they cannot account for the detailed mechanism of spin transfer (vide infra). Paramagnetic and diamagnetic species in their triplet state on the other hand performs their spin catalytic effects as spin donors species, thereby increasing the spin multiplicity of the substrate. Therefore, while the spin-philicity and spin-donicity indexes, ω_S^+ and ω_S^-, respectively, qualitatively accounts for the observed catalytic effect, the spin potential in the direction of increasing and decreasing multiplicity quantitatively defines the direction and magnitude of the spin transfer process involved in the spin catalysis phenomena. This was checked with the help of a short series of well-known spin catalytic species for which experimental data exist.

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