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Nuclear reactivity indices within regional density functional theory

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Abstract Regional chemical potential values- μ_R have been obtained with the use of nuclear reactivity indices. Perturbational formulae use values of reactivity indices of isolated molecular fragments. The changes of the parameters ($\Delta N_R, \{ \Delta \mathbf{Q}_i \}_{i \in R}$) within each fragment determine the value of the regional chemical potential after a chemical reaction. The computational scheme has been tested numerically along the chemical reaction path. We have studied a set of chemical reactions to obtain regional chemical potentials (μ_R^{ts}) and regional transfer potentials (τ_R^{ts}) for transition states of the following chemical reactions: $\text{HF} + \text{CO} = \text{HFCO}$, $\text{HCl} + \text{CO} = \text{HCICO}$, $\text{HF} + \text{SiO} = \text{HFSiO}$ and $\text{HF} + \text{GeO} = \text{HFGeO}$. The results are reasonable and encouraging. Values of these indices show the possible reactivity directions of the transition states examined.

Keywords Regional DFT · Nuclear reactivity indices · Transition state

Introduction

Nuclear reactivity indices

Density functional theory (DFT) has become a unique theoretical approach for the analysis of properties of theoretical systems. Important chemical properties of molecules such as electronegativity and hardness have found a firm theoretical basis [1]. An excellent review has

been given by Geerlings et al. [2]. The chemical potential (minus electronegativity) is defined as:

$$\mu \equiv \left(\frac{\partial E(N, \{\mathbf{Q}_i\})}{\partial N} \right)_{\mathbf{Q}} = -\chi \quad (1)$$

where N is total number of electrons and $\{\mathbf{Q}_i\}$ is a set of atomic positions. Constraint \mathbf{Q} denotes constant molecular geometry. Since it is a Lagrange multiplier of energy minimization within the constraint of the total number of electrons being constant, μ has a constant value throughout the whole system.

Global hardness is defined as the second derivative of the energy versus N :

$$\eta \equiv \left(\frac{\partial^2 E(N, \{\mathbf{Q}_i\})}{\partial N^2} \right)_{\mathbf{Q}} \quad (2)$$

Fuenalba and Parr [3] defined the third derivative of the energy vs the number of electrons:

$$\gamma \equiv \left(\frac{\partial^3 E(N, \{\mathbf{Q}_i\})}{\partial N^3} \right)_{\mathbf{Q}} = \left(\frac{\partial^2 \mu(N, \{\mathbf{Q}_i\})}{\partial N^2} \right)_{\mathbf{Q}} \quad (3)$$

The description of chemical reactivity has been a target of numerous studies aimed at parameters of atoms in molecules [4]. Various quantum chemical methods [5] have been proposed to obtain such atomic indices as the Fukui function:

$$f(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{\mathbf{Q}} \quad (4)$$

and local softness:

$$s(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{\mathbf{Q}} \quad (5)$$

The analysis of the effect of nuclear displacement on the electronic energy of a molecule was not introduced into DFT until the work by Cohen et al. [6] who first proposed the nuclear reactivity function as a derivative of the Hell-

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man–Feynman [7] force over the number of electrons $\Phi_i \equiv (\partial \mathbf{F}_i / \partial N)_{\mathbf{Q}}$, also known as the nuclear Fukui function [8]. Ordon and Komorowski [9] obtained a Maxwell relation, which proves that nuclear reactivity is the change of electronegativity vs molecular deformation:

$$\Phi_i \equiv \left(\frac{\partial \mathbf{F}_i}{\partial N} \right)_{\mathbf{Q}} = - \left(\frac{\partial \mu}{\partial \mathbf{Q}_i} \right)_{\mathbf{Q}} \quad (6)$$

The numerical values thereof have also been determined [9]. Nalewajski [10] has examined the chemical reactivity dependence on Cartesian coordinates within the Born-Oppenheimer approximation. The derivative of global hardness (η) was introduced by Ordon and Komorowski [9] as the nuclear stiffness:

$$\mathbf{G}_i \equiv \left(\frac{\partial \eta}{\partial \mathbf{Q}_i} \right)_{\mathbf{Q}} = - \left(\frac{\partial \Phi_i}{\partial N} \right)_{\mathbf{Q}} = - \left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2} \right)_{\mathbf{Q}} \quad (7)$$

where

$$\mathbf{F}_i \equiv - \left(\frac{\partial E(N, \{\mathbf{Q}_i\})}{\partial \mathbf{Q}_i} \right)_{\mathbf{Q}} \quad (8)$$

is the force [7] acting on i th nucleus. These derivatives were described as quantities that couple electronic and geometrical degrees of freedom [11, 12]. These authors also have presented the analysis of the projection of Φ_i and \mathbf{G}_i indices onto normal vibrational modes [13] and elaborated on the role of these indices in determining fluctuations in chemical potential (electronegativity) and hardness due to molecular oscillations [12, 14]. The possibility of finding still higher derivatives has also been studied:

$$\lambda_{ij} \equiv - \left(\frac{\partial \Phi_i}{\partial \mathbf{Q}_j} \right)_{\mathbf{Q}} = \left(\frac{\partial k_{ij}}{\partial N} \right)_{\mathbf{Q}} \quad (9)$$

The dependence of force constants on the total number of electrons (λ_{ij}) has been obtained and proved useful in analyzing the source of anharmonicity of a molecular oscillator [15].

Regional density functional theory: division into subsystems

Regional density functional theory was introduced to DFT by Tachibana and Parr [16]. Within the simplest version, the system is divided in two subsystems P and Q , so that total energy and total number of electrons split into:

$$E = E_P + E_Q \quad (10)$$

$$N = N_P + N_Q \quad (11)$$

The set of parameters we use to describe a system divided into two subsystems is: $\{N, \Gamma, \{\mathbf{Q}_i\}_P, \{\mathbf{Q}_i\}_Q\}$. It contains the total numbers of electrons and atomic positions within each subsystem. Thus, we can define a regional chemical potential for each region:

$$\mu_R \equiv \left(\frac{\partial E_R}{\partial N_R} \right)_{N_{1-R}} \quad (12)$$

The constant value of N_{1-R} denotes that the number of electrons within all subsystems (other than R) is conserved. The relation of regional chemical potentials to the global chemical potential has been obtained. For a system of two subsystems it reads:

$$\mu = \mu_P + \left(\frac{\partial E_Q}{\partial N_P} \right)_{N_Q} = \mu_Q + \left(\frac{\partial E_P}{\partial N_Q} \right)_{N_P} \quad (13)$$

Equation 13 constitutes the rule of chemical potential inequality [17]:

$$\mu \neq \mu_P \neq \mu_Q \quad (14)$$

The regional chemical potentials- μ_R (μ_P or μ_Q in the case of division into two regions) refer to regional contributions to the global chemical potential- μ . If an electron is withdrawn from a region R , the regional energy E_R changes according to Eq. 12. Thus μ_R is the regional energy change per electron. On the other hand, the exchange of an electron between a particular region R and the environment should influence the energy of the complimentary subsystem(s) and $(\partial E_{R'} / \partial N_R)_{N_{R'(\neq R)}}$ derivatives give the regional energy change per electron, exchanged from other subsystem. Further considerations lead us to the relationship with the thermodynamic concept of the work function [18]. As demonstrated by Volta and Herring and Nichols [19] for a pair of regions P and Q in contact (equilibrium) with each other, the contact potential difference is the difference in regional work functions:

$$v_P - v_Q = W_P - W_Q \quad (15)$$

where v_P , v_Q denote Volta contact potentials and W_P , W_Q denote the local work functions of regions P and Q . Tachibana [18] proved that:

$$\mu = -e(W_P + v_P) = -e(W_Q + v_Q) \quad (16)$$

This leads to relationships between work function and regional chemical potential:

$$v_P = -\frac{1}{e} \left(\left(\frac{\partial E_P}{\partial N_Q} \right)_{N_P} + \left(\frac{\partial E_Q}{\partial N_P} \right)_{N_Q} \right) \quad (17)$$

and finally:

$$W_R = -\frac{\mu_R}{e} \quad (18)$$

There is another set of parameters that describes our system of interest $-\{N, \Gamma, \{\mathbf{Q}_i\}\}$. It contains the total number of electrons, charge transfer function Γ and atomic positions within the whole molecule. Such a description leads to the definition of regional transfer potentials: [20]

$$\tau_R \equiv \left(\frac{\partial E_R}{\partial N} \right)_{\Gamma, \mathbf{Q}} \quad (19)$$

As was described extensively [16], the Γ function measures the electronic density flow between subsystems. In the case of τ_R , no charge is allowed (by the constant value of Γ) to be exchanged. However, the electronic density may vary within the subsystems. This justifies the name-excitation potential. The following rules are fulfilled: the difference rule reads:

$$\mu_P - \mu_Q = \tau_P - \tau_Q \quad (20)$$

and the sum rule:

$$\mu = \tau_P + \tau_Q. \quad (21)$$

The relationship between regional transfer potential, chemical potential and regional chemical potentials is:

$$\tau_R = \frac{\mu + (\mu_R - \mu_{1-R})}{2} \quad (22)$$

Regional chemical potential values from a perturbation scheme

We have obtained the regional chemical potential values for such regions of a molecule, which form isolated molecules at the stage of reactants of the chemical reaction. Let us suppose that electrons flow from region P to region Q , which are at the beginning separated molecules of chemical potentials μ_P^0 and μ_Q^0 , respectively. If we turn the interaction on, these starting values will instantaneously vary according to how the coordinates change and to the values of response functions. According to the definition (Eq. 12), the regional chemical potential is a derivative of the energy of the subsystem E_R over the number of electrons within this subsystem N_R . We expand the chemical potential function of these isolated molecules (subsystems) in a Taylor series in terms of variations of $\{N_P, N_Q, \{\mathbf{Q}_i\}_P, \{\mathbf{Q}_j\}_Q\}$. The new values of Cartesian coordinates and populations of the subsystems in question are obtained after the chemical process is completed. Then we finally obtain the values of the regional chemical potential [11]:

$$\begin{aligned} \mu_R = & \mu_R^0 + \left(\frac{\partial \mu_R}{\partial N_R} \right)_{N_R=N_R^0, \mathbf{Q}} \Delta N_R + \sum_{i \in R} \left(\frac{\partial \mu_R}{\partial \mathbf{Q}_i} \right)_{\mathbf{Q}_i=\mathbf{Q}_i^0, N} \cdot \Delta \mathbf{Q}_i \\ & + \frac{1}{2} \sum_{i,j \in R} \left(\frac{\partial}{\partial N_R} \left(\frac{\partial E_R}{\partial \mathbf{Q}_i \partial \mathbf{Q}_j} \right)_{\mathbf{Q}_i=\mathbf{Q}_i^0, N} \right)_{N_R=N_R^0, \mathbf{Q}} \Delta \mathbf{Q}_i \cdot \Delta \mathbf{Q}_j \\ & + \frac{1}{2} \sum_{i \in R} \left(\frac{\partial}{\partial \mathbf{Q}_i} \left(\frac{\partial \mu_R}{\partial N_R} \right)_{N_R=N_R^0, \mathbf{Q}} \right)_{\mathbf{Q}_i=\mathbf{Q}_i^0, N} \cdot \Delta \mathbf{Q}_i \Delta N_R \\ & + \frac{1}{2} \sum_{i,j \in R} \left(\frac{\partial^2 \mu_R}{\partial N_R^2} \right)_{N_R=N_R^0, \mathbf{Q}} (\Delta N_R)^2 \end{aligned} \quad (23)$$

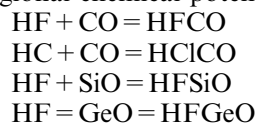
When the previously defined reactivity indices are inserted:

$$\begin{aligned} \mu_R = & \mu_R^0 + \eta_R^0 \Delta N_R - \sum_{i \in R} \Phi_i^0 \cdot \Delta \mathbf{Q}_i + \frac{1}{2} \sum_{i,j \in R} \lambda_{ij}^0 \Delta \mathbf{Q}_i \cdot \Delta \mathbf{Q}_j \\ & + \frac{1}{2} \sum_{i \in R} \mathbf{G}_i^0 \cdot \Delta \mathbf{Q}_i \Delta N_R + \frac{1}{2} \gamma_R^0 (\Delta N_R)^2 \end{aligned} \quad (24)$$

where η_R^0 , Φ_i^0 , λ_{ij}^0 , \mathbf{G}_i^0 and γ_R^0 are global and atomic reactivity indices of isolated molecules. However, the interaction between the subsystems is not taken into account explicitly. It is reflected in ΔN and $\{\Delta \mathbf{Q}_i\}$ values. These are perturbation values for the regional chemical potential. They result from the way the subsystems interact and also from the interaction within the subsystems. No type of interaction is excluded within this phenomenological picture. The results depend only on the model chemistry used. The quality of this approximation depends on how large a change of variables ΔN_R and $\{\Delta \mathbf{Q}_i\}$ is needed to reach the final state. Thus, it is a different approach to obtaining regional DFT indices than that of Tachibana et al. [17] who analyzed the HeH+ system. The latter approach demands evaluating Hellman-Feynman [7] forces and allows only infinitesimal changes of coordinates along the reaction path.

Calculations and results

We have studied a set of chemical reactions to obtain regional chemical potentials for transition states:



All calculations were performed using the B3LYP/6-311+G** method implemented in the Gaussian 98 package [21]. Ground (right hand side of reaction equations) and transition states geometries were optimized. The structures are planar. The details are shown in Table 1. They are sketched in Fig. 1 and are in very

Table 1 Geometry of ground states and transition states (angles given in degrees)

Molecule	Bond (Å)	Bond (Å)	Bond (Å)	Distance (Å)	Angle	Angle	
HFCO	C-O	C-F	C-H	H-F	F-C-O	H-C-O	
	g.s.	1.177	1.355	1.0951	2.0455	122.7	128.4
	t.s.	1.130	1.885	1.130	1.420	122.2	189.2
HClCO	C-O	C-Cl	C-H	H-Cl	Cl-C-O	H-C-O	
	g.s.	1.179	1.796	1.0963	2.397	123.4	127.0
	t.s.	1.132	2.387	1.119	1.870	122.6	187.6
HFSiO	Si-O	Si-F	Si-H	H-F	F-Si-O	H-Si-O	
	g.s.	1.517	1.604	1.466	2.443	126.6	128.1
	t.s.	1.520	1.907	1.617	1.276	121.3	197.2
HFGEO	Ge-O	Ge-F	Ge-H	H-F	F-Ge-O	H-Ge-O	
	g.s.	1.634	1.759	1.525	2.575	123.2	133.7
	t.s.	1.629	2.0162	1.597	1.436	122.0	193.0

good agreement with literature data [22]. Negative frequencies ($-1,384\text{ cm}^{-1}$ for HFClO, $-1,161\text{ cm}^{-1}$ for HClCO, $-1,484\text{ cm}^{-1}$ for HFSiO, $-1,318\text{ cm}^{-1}$ for HFGeO transition state) represent normal modes, which are mainly stretches of the X–H bond (X = F, Cl). We have calculated global reactivity indices using a finite difference approximation:

$$\mu_R^o = \frac{I_R^o + A_R^o}{2}, \quad (25)$$

$$\eta_R^o = \frac{I_R^o - A_R^o}{2} \quad (26)$$

where I_R^o is the ionization potential and A_R^o is the electronic affinity of the isolated diatomic molecules. (We have assumed that γ_R^o is a small value, thus term: $(1/2)\gamma_R^o(\Delta N_R)^2$ can be neglected.) These results for ground states and transition states together with zero point corrected activation energy are shown in Table 2. We show how the chemical potential of the diatomic subsystems changes during the course of the chemical reaction. At the beginning, the subsystems are just isolated molecules—left hand side of the reaction equations. To use Eq. 24, we need reactivity indices for the isolated diatomic molecules. We use the finite difference approximation [9, 13, 14]:

$$\Phi_i^o = \frac{\mathbf{F}_i^- - \mathbf{F}_i^+}{2}, \quad (27)$$

$$\mathbf{G}_i^o = -\frac{\mathbf{F}_i^- + \mathbf{F}_i^+}{2} \quad (28)$$

and

$$\lambda^o = \frac{k^- - k^+}{2}. \quad (29)$$

Table 2 Chemical potential, global hardness for ground states and transition states and zero point corrected activation energy

Molecule	μ_{gs} (eV)	η_{gs} (eV)	μ_{ts} (eV)	η_{ts} (eV)	Activation energy (kcal mol ⁻¹)
HFClO	-5.813	6.930	-6.021	6.212	45.31
HClCO	-5.592	6.142	-5.480	5.323	34.24
HFSiO	-5.704	6.055	-5.896	5.398	62.37
HFGeO	-5.879	5.369	-5.986	5.290	37.76

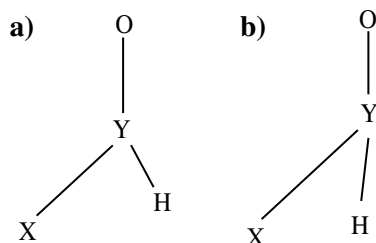


Fig. 1 Ground (a) and (b) transition state for HXYO molecule. X = F, Cl and Y = C, Si, Ge

Table 3 Properties of diatomic isolated molecules

Group-isolated molecule	Q_R^o (Å)	μ_R^o (eV)	η_R^o (eV)	$ \Phi_R^o $ (eV/Å)	$ G_R^o $ (eV/Å)	λ_R^o (eV/Å ²)
HF	0.922	-7.000	9.344	0.199	4.204	-8.411
CO	1.128	-6.437	7.772	3.710	1.553	-10.98
HCl	1.287	-5.560	7.235	0.748	1.910	-12.90
SiO	1.523	-5.827	5.707	0.962	1.413	4.789
GeO	1.638	-5.746	5.448	0.592	1.641	4.222

$\mathbf{F}_i^+/\mathbf{F}_i^-$ are the total forces acting on the i th nucleus in the positively/negatively charged molecule, respectively. k^+/k^- —force constants of positively/negatively charged molecule. The results are shown in Table 3. To use Eq. 24 we also need ΔN_R and $\{\Delta Q_i\}$ values. ΔN_R is just the difference between the Mulliken population in region R in the transition state N_R^{ts} and N_R^o —the total number of electrons within the diatomic molecule that corresponds to region R :

$$\Delta N_R = N_R^{\text{ts}} - N_R^o \quad (30)$$

and

$$\Delta Q_i = \mathbf{Q}_i^{\text{ts}} - \mathbf{Q}_i^o \quad (31)$$

where \mathbf{Q}_i^{ts} are atomic positions within the transition state and \mathbf{Q}_i^o are atomic positions in the diatomic molecule corresponding to the same region. In numerical calculations this can be reduced to the change of interatomic distance within the diatomic region.

From Eq. 24 we have obtained regional chemical potentials μ_R^o for the same molecular fragments within a molecule in the transition state. Then from Eq. 22 we obtain regional transfer potentials— τ_R^{ts} . Subsystem energy derivative versus the change of number of electrons in complimentary subsystem- $(\partial E_R/\partial N_{1-R})_{N_R}$ has been obtained from Eq. 13 via $\mu_{\text{ts}} - \mu_R^{\text{ts}}$. These results are shown in Table 4.

For fragments where the geometry does not change much, the only effect is charge transfer. This is the case for: C-O, Si-O, Ge-O. For the complimentary subsystem, the situation is more complicated. There is a huge geometry change and terms associated with ΔQ_R tend to decrease the effect of charge transfer on μ_R^{ts} . Thus, in two cases (HFClO and HClCO), the C-O region is more

Table 4 Regional chemical potential for diatomic groups within transition state. Charge transfer and geometrical change has been given as ΔN_R and ΔQ_R

Molecule	Group	ΔN_R	ΔQ_R (Å)	μ_R^{ts} (V)
HFClO	HF	0.154	0.498	-6.666
	CO	-0.154	0.0028	-7.644
HClCO	HCl	0.103	0.583	-6.634
	CO	-0.103	0.0041	-7.250
HFSiO	HF	0.012	0.354	-7.358
	SiO	-0.012	-0.0029	-5.896
HFGeO	HF	0.151	0.513	-6.759
	GeO	-0.151	-0.0089	-6.561

Table 5 Regional DFT indices for transition states

Molecule	μ_{ts} (eV)	Group	μ_R^{ts} (eV)	$\mu_{ts} - \mu_R^{ts}$ (eV)	τ_R^{ts} (eV)
HFCO	-6.021	HF	-6.666	0.645	-2.521
		CO	-7.644	1.623	-3.499
HCICO	-5.480	HCl	-6.634	1.154	-2.432
		CO	-7.250	1.770	-3.048
HFSiO	-5.896	HF	-7.358	1.462	-3.679
		SiO	-5.896	0.000	-2.217
HFGeO	-5.986	HF	-6.759	0.773	-3.092
		GeO	-6.561	0.575	-2.894

electronegative than H-X. In the case of HFSiO and HFGeO, the H-F region stays more electronegative even in the transition state. Exactly the same tendency is reflected by the regional transfer potentials τ_R^{ts} (Table 5). The C-O region within the HXCO molecule has a lower regional transfer potential than the complimentary H-X region. τ_{H-F}^{ts} is lower than τ_{Si-O}^{ts} within HFSiO molecule in a transition state, as is lower than τ_{Ge-O}^{ts} within HFGeO molecule. This tendencies show the possible reactivity directions of examined transition states. Table 5 shows as well (via Eq. 13) that the unit change of the number of electrons in one subsystem causes the increase of the energy of complimentary subsystem by order of magnitude of 1eV. However, there is one exception. The energy of the H-F region (within transition state of HFSiO) will not change if we vary the number of electrons in the Si-O region. The results for hardness (gathered in Table 2) do not show that the transition state is the softest along the reaction path [23]. However, Table 3 shows that η_{ts} is several eV softer than hardness of diatomic isolated molecules (η_R^0). Table 2 shows that hardness of the transition state (η_{ts}) is also significantly lower than hardness of resulting molecule HXYO (η_{gs}).

Conclusions

The regional chemical potential differentiates subsystems according to the energy changes needed to vary numbers of electrons. The analogy to the work function and contact potential is very illustrative. Due to the rule that a large $\Delta\mu$ is good [1] (which is also valid for subsystems), we can predict the directions of chemical reactions. This makes the regional chemical potential one of the most important and potentially useful reactivity indices. Thus, the procedure of actual calculations of regional chemical potential is of great importance. We have proposed a novel method of obtaining regional chemical potentials. The idea is very simple. Once we have values for the regional chemical potential at the beginning of chemical process, we can easily obtain it at the end of chemical process by a simple perturbation

scheme, where reactivity indices are response functions to parameters changes. These parameters are the electronic population and the geometry of the subsystems. This method has been tested on four simple chemical reactions. The results illustrate the principle of chemical potential inequality given by Tachibana [16].

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