

## Investigation of the role of the C–PCM solvent effect in reactivity indices

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**Abstract.** It has been shown recently, how the coupling between electronic degrees of freedom and vibrational modes is reflected in the properties of molecules. The necessary derivatives have been analyzed and their thermodynamic relations were demonstrated. This present work is focused on the analysis of a molecular system, under the influence of C–PCM induced solvent effect. The analysis is based on reactivity indices derived from DFT. The shift of frequency for diatomic molecules has been obtained. It has been identified as chemical force effect. The role of nuclear reactivity indices has been emphasized. This concept has been extended to obtain regional chemical potential values within C–PCM model for polyatomic molecules.

**Keywords.** Chemical potential; hardness; nuclear reactivity indices; regional DFT; C–PCM solvation model.

### 1. Introduction

Chemists tend to discover theories which govern chemical reactivity. DFT has become a very unique theoretical approach for analysis of properties of molecular systems. Important chemical properties of molecules such electronegativity and hardness have found firm theoretical basis.<sup>1</sup> Excellent review has been given by Geerlings *et al.*<sup>2</sup> Chemical potential (minus electronegativity) is defined as:

$$\mathbf{m} \equiv (\partial E(N, \{\mathbf{Q}_i\}) / \partial N)_{\mathbf{Q}, \mathbf{a}^{ext}(\mathbf{r})=0} = -\mathbf{c}, \quad (1)$$

where  $N$  is total number of electrons and  $\{\mathbf{Q}_i\}$  is a set of atomic positions. Constraint  $\mathbf{Q}$  indicates constant molecular geometry.  $\mathbf{a}^{ext}(\mathbf{r}) = 0$  indicates that the electric field external to the molecule is set to zero.  $\mathbf{m}$  has constant value throughout the whole system, since it is Lagrange multiplier of energy minimization within the constraint of total number of electrons being constant. Global hardness is defined as a second derivative of energy versus  $N$ :

$$\mathbf{h} \equiv (\partial^2 E(N, \{\mathbf{Q}_i\}) / \partial N^2)_{\mathbf{Q}, \mathbf{a}^{ext}(\mathbf{r})=0}, \quad (2)$$

The complete set of energy derivatives versus  $\{\mathbf{Q}, N\}$  parameters (up to third order) has been recently presented and analyzed by Ordon and Komorowski.<sup>3</sup> They also present set of grand canonical potential derivatives versus  $\{\mathbf{Q}, \mathbf{m}\}$  parameters. Analysis up to second order in energy derivatives has been given by Torrent-Sucarrat *et al.*<sup>4</sup> Independent approach is due to Nalewajski.<sup>5</sup> These approaches focus on static force as the origin of all (nuclear reactivity) indices. (Recent analysis published by Chattaraj and Sarkar<sup>6</sup> uses reactivity indices to describe time dependent process.) It is well known since the work of Feynman<sup>7</sup> that force is one of the most important descriptors for molecular processes:

$$\mathbf{F}_i \equiv - \left( \frac{\partial E(N, \{\mathbf{Q}_i\})}{\partial \mathbf{Q}_i} \right)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} = \int \mathbf{r}(\mathbf{r}) \mathbf{\epsilon}_i(\mathbf{r}) d\mathbf{r} + \mathbf{F}_i^{n-n}. \quad (3)$$

thus the derivatives of force play very important role in our formalism.

First of all, the set of force constants, describe vibrational harmonic oscillations:<sup>8</sup>

$$k_{ij} \equiv \left( \frac{\partial^2 E(N, \{\mathbf{Q}_i\})}{\partial \mathbf{Q}_i \partial \mathbf{Q}_j} \right)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} = - \left( \frac{\partial \mathbf{F}_i}{\partial \mathbf{Q}_j} \right)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} \quad (4)$$

\*For correspondence

and (when diagonalized) give normal mode patterns with corresponding vibrational energies. Then, nuclear reactivity index<sup>9</sup> is the derivative of force acting on the given atomic nuclei, with respect to the total number of electrons. Due to Maxwell relation<sup>10</sup> it gives also the dependence of chemical potential versus the Cartesian displacement of the same nuclei:

$$\Phi_i \equiv -(\partial \mathbf{m} / \partial \mathbf{Q}_i)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} = (\partial \mathbf{F}_i / \partial N)_{\mathbf{Q}, \mathbf{a}^{ext}(\mathbf{r})=0}. \quad (5)$$

The derivative of global hardness ( $\mathbf{h}$ ) has been introduced by Ordon and Komorowski<sup>3</sup> as nuclear stiffness:

$$\mathbf{G}_i \equiv (\partial \mathbf{h} / \partial \mathbf{Q}_i)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} = -(\partial^2 \mathbf{F}_i / \partial N^2)_{\mathbf{Q}, \mathbf{a}^{ext}(\mathbf{r})=0}. \quad (6)$$

The Maxwell relation grants that the second derivative of force acting on given atomic nuclei, with respect to the total number of electrons, is equal to the global hardness dependence on the Cartesian displacement of the same nuclei. Higher derivatives are also possible.<sup>11</sup> Within this paper we will use the following derivative of the force constant:<sup>12</sup>

$$\mathbf{I}_{ij} \equiv -(\partial \Phi_i / \partial \mathbf{Q}_j)_{N, \mathbf{a}^{ext}(\mathbf{r})=0} = (\partial k_{ij} / \partial N)_{\mathbf{Q}, \mathbf{a}^{ext}(\mathbf{r})=0}. \quad (7)$$

Another set of derivatives is obtained for grand canonical potential  $-\Omega$ .<sup>3,13</sup> The varying parameters are atomic positions and chemical potential  $-\{\mathbf{Q}, \mathbf{m}\}$ . The derivative of grand canonical potential versus chemical potential gives the negative value of the total number of electrons:

$$\left( \frac{\partial \Omega(N, \{\mathbf{Q}_i\})}{\partial \mathbf{m}} \right)_{\mathbf{Q}, \mathbf{e}^{ext}(\mathbf{r})=0} = -N \quad (8)$$

and versus atomic coordinate equals the negative value of force:

$$\left( \frac{\partial \Omega(N, \{\mathbf{Q}_i\})}{\partial \mathbf{Q}_i} \right)_{\mathbf{m}, \mathbf{e}^{ext}(\mathbf{r})=0} = -\mathbf{F}_i. \quad (9)$$

Thus a Maxwell relation defines another reactivity index:

$$\sigma_i \equiv (\partial N / \partial \mathbf{Q}_i)_{\mathbf{m}, \mathbf{e}^{ext}(\mathbf{r})=0} = (\partial \mathbf{F}_i / \partial \mathbf{m})_{\mathbf{Q}, \mathbf{e}^{ext}(\mathbf{r})=0} \quad (10)$$

which is the change of the total number of electrons versus nuclear position. This happens to be equal to force derivative over chemical potential. Global softness is the second derivative of grand canonical potential:

$$S \equiv - \left( \frac{\partial^2 \Omega(N, \{\mathbf{Q}_i\})}{\partial \mathbf{m}^2} \right)_{\mathbf{Q}, \mathbf{e}^{ext}(\mathbf{r})=0} = \left( \frac{\partial N}{\partial \mathbf{m}} \right)_{\mathbf{Q}, \mathbf{e}^{ext}(\mathbf{r})=0} = \frac{1}{\mathbf{h}}. \quad (11)$$

In this paper we intend to study the influence of solvent effect on reactivity indices. We achieve it two-fold. First we obtain reactivity indices for isolated diatomic molecules (HF, HCl, CO, SiO, GeO) within CPC–M induced field. Then we use these indices to evaluate regional chemical<sup>14</sup> potentials for diatomic fragments corresponding to isolated molecules within the transition states of the following reactions: HF + CO = HFCO, HCl + CO = HCICO, HF + SiO = HFSiO and HF + GeO = HFGeO.

## 2. Induced reactivity by C–PCM solvent effect

Solute–solvent interaction dramatically affects chemical reactivity. Their influence on energies, structures and other properties has been reported and is very well known. To describe this effect, continuum solvation models are often used. The conductor-like polarizable continuum model<sup>15,16</sup> (C–PCM) is a generalization of polarizable continuum model (PCM).<sup>17</sup> This model treats the solvent as a continuum dielectric, which reacts against the solute charge distribution generating reaction field. Thus any change of molecular or electronic structure within solvent induces an external force  $-\mathbf{F}_i^{ext}$ .

$$\begin{aligned} \mathbf{F}_i^{tot} &\equiv \mathbf{F}_i + \mathbf{F}_i^{ext} = - \left( \frac{\partial E(N, \{\mathbf{Q}_i\})}{\partial \mathbf{Q}_i} \right)_{N, \mathbf{e}^{ext}(\mathbf{r})=0} + \mathbf{F}_i^{ext} \\ &= \int \mathbf{r}(\mathbf{r})(\epsilon_i(\mathbf{r}) + \epsilon_i^{ext}(\mathbf{r}))d\mathbf{r} + \mathbf{F}_i^{n-n}. \end{aligned} \quad (12)$$

This force modifies all reactivity indices. Energy differential reads:

$$dE = \mathbf{m}_{\text{tpcm}} dN - \sum_i \mathbf{F}_i \cdot d\mathbf{Q}_i - \sum_i \mathbf{F}_i^{ext} \cdot d\mathbf{Q}_i, \quad (13)$$

and it gives following Maxwell relation:

$$\begin{aligned} -(\partial \mathbf{m}_{\text{tpcm}} / \partial \mathbf{Q}_i)_{N, \mathbf{e}^{ext}(\mathbf{r})=\epsilon} &= (\partial \mathbf{F}_i^{tot} / \partial N)_{\mathbf{Q}} \\ &= \Phi_i + \Phi_i^{ind} = \Phi_i^{tot}. \end{aligned} \quad (14)$$

This is modified nuclear reactivity index. Chemical potential within an induced field is denoted by:

$$\mathbf{m}_{cpcm} = (\partial E / \partial N)_{\mathbf{Q}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} \quad (15)$$

Hardness within the presence of external field has also varied:

$$\mathbf{h}_{cpcm} = (\partial^2 E / \partial N^2)_{\mathbf{Q}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} \quad (16)$$

The values of chemical potential and hardness within the induced field are different from those in the gas phase, which can be illustrated by the fact that energies must change. In particular, induced fields vary ionization potential and electronic affinity, which give (within finite difference approximation) electronegativity and hardness. For chemical potential differential we obtain:

$$d\mathbf{m} = \mathbf{h}_{cpcm} dN - \sum_i (\Phi_i + \Phi_i^{ind}) \cdot d\mathbf{Q}_i \quad (17)$$

Maxwell relation reads:

$$\begin{aligned} \left( \frac{\partial \mathbf{h}}{\partial \mathbf{Q}_i} \right)_{N, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} &= - \left( \frac{\partial^2 \mathbf{F}_i^{tot}}{\partial N^2} \right)_{\mathbf{Q}} = - \left( \frac{\partial (\Phi_i + \Phi_i^{ind})}{\partial N} \right)_{\mathbf{Q}} \\ &= \mathbf{G}_i + \mathbf{G}_i^{ind} = \mathbf{G}_i^{tot} \end{aligned} \quad (18)$$

which gives induced nuclear stiffness. On the other hand, we also can analyze grand canonical potential differential as a function of  $(\mathbf{m}, \{\mathbf{Q}_i\})$  under the influence of induced force:

$$d\Omega = -N d\mathbf{m} - \sum_i \mathbf{F}_i^{tot} \cdot d\mathbf{Q}_i \quad (19)$$

Maxwell relation reads:

$$\boldsymbol{\sigma}_i^{tot} = \left( \frac{\partial N}{\partial \mathbf{Q}_i} \right)_{\mathbf{m}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} = \left( \frac{\partial \mathbf{F}_i^{tot}}{\partial \mathbf{m}} \right)_{\mathbf{Q}} = S_{cpcm} (\Phi_i + \Phi_i^{ind}) \quad (20)$$

and gives the modified reactivity due to variation of atomic positions. Force constant differential as a  $(N, \{\mathbf{Q}_i\})$  function is:

$$dk_{ij}^{cpcm} = \mathbf{I}_{ij}^{cpcm} dN + \sum_k \mathbf{a}_{ijk} \cdot d\mathbf{Q}_k \quad (21)$$

Force constant differential as a  $(\mathbf{m}, \{\mathbf{Q}_i\})$  function:

$$dk_{ij} = \left( \frac{\partial k_{ij}}{\partial \mathbf{m}} \right)_{\mathbf{Q}} d\mathbf{m} + \sum_k \left( \frac{\partial k_{ij}}{\partial \mathbf{Q}_k} \right)_{\mathbf{m}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} \cdot d\mathbf{Q}_k \quad (22)$$

Using the expression for  $d\mathbf{m}$  (4), as a function of  $(N, \{\mathbf{Q}_i\})$  we obtain:

$$\left( \frac{\partial k_{ij}^{cpcm}}{\partial \mathbf{m}} \right)_{\mathbf{Q}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} = \mathbf{I}_{ij}^{cpcm} S_{cpcm} \quad (23)$$

force constant dependence on chemical potential. The softer the molecule, the bigger is the influence of variation of chemical potential on force constant. The dependence on Cartesian coordinates is just anharmonic constant plus (small) chemical term:

$$\left( \frac{\partial k_{ij}}{\partial \mathbf{Q}_k} \right)_{\mathbf{m}, \boldsymbol{\varepsilon}^{ext}(\mathbf{r})=\boldsymbol{\varepsilon}} = (\Phi_k + \Phi_k^{ind}) \mathbf{I}_{ij}^{cpcm} S_{cpcm} + \mathbf{a}_{ijk} \quad (24)$$

Nuclear reactivity index and softness make this term rather small.  $\mathbf{I}_{ij}^{cpcm}$  usually makes it bigger. See numerical results.

### 3. Regional density functional theory – Division into subsystems

Regional density functional theory has been introduced to DFT by Tachibana and Parr.<sup>14</sup> 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:

$$E = E_P + E_Q, \quad (25)$$

$$N = N_P + N_Q. \quad (26)$$

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

$$\mathbf{m}_R \equiv (\partial E_R / \partial N_R)_{N_{1-R}} \quad (27)$$

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

$$\mathbf{m} = \mathbf{m}_P + (\partial E_Q / \partial N_P)_{N_Q} = \mathbf{m}_Q + (\partial E_P / \partial N_Q)_{N_P} \quad (28)$$

Equation (28) constitutes the rule of chemical potential inequality.<sup>18</sup>

$$\mathbf{m} \neq \mathbf{m}_P \neq \mathbf{m}_Q. \quad (29)$$

Chemical potential inequality is not due to non-equilibrium of the system and does not violate the Sanderson electronegativity equalization principle. Different values of regional chemical potentials reveal differences in regional chemical reactivity for the ground state.

Regional chemical potentials –  $\mathbf{m}_R$  ( $\mathbf{m}_P$  or  $\mathbf{m}_Q$  in case of two regions division) refer to regional contribution to global chemical potential –  $\mathbf{m}$ . If an electron is withdrawn from a region  $R$ , regional energy  $E_R$  changes according to (27). Thus  $\mathbf{m}_R$  is 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 (in case of two regions –  $(\partial E_Q/\partial N_P)_{N_Q}$  and  $(\partial E_P/\partial N_Q)_{N_P}$ ) give the regional energy change per electron, exchanged from other subsystem. Further considerations lead us to the relationship with thermodynamic concept of work function.<sup>19</sup> As demonstrated by Volta *et al*<sup>20</sup> for a pair of regions  $P$  and  $Q$  in contact (equilibrium) with each other, the contact potential difference is the difference of regional work function:

$$v_P - v_Q = W_P - W_Q, \quad (30)$$

where  $v_P$ ,  $v_Q$  denote Volta contact potentials and  $W_P$ ,  $W_Q$  denote local work function of region  $P$  and  $Q$ . Tachibana<sup>19</sup> proved that:

$$\mathbf{m} = -e(W_P + v_P) = -e(W_Q + v_Q). \quad (31)$$

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

$$v_P = 1/e ((\partial E_Q/\partial N_P)_{N_Q} + (\partial E_P/\partial N_Q)_{N_P}), \quad (32)$$

and finally:

$$W_R = -\mathbf{m}_R/e. \quad (33)$$

#### 4. Regional chemical potential values from perturbation scheme

Recently, we have described a scheme of obtaining regional chemical potentials.<sup>21</sup> Regional chemical potential values,  $\mathbf{m}_R$ , have been obtained with the use of

nuclear reactivity indices. Perturbational formulas 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 regional chemical potential after chemical reaction. We expand the chemical potential function of these isolated molecules (subsystems) in 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 achieve the values of regional chemical potential. This time we apply this scheme to molecules in solution with the C-PCM solvation model. Then the formula for region  $P$  reads:

$$\begin{aligned} \mathbf{m}_P = & \mathbf{m}_{P,cpcm}^0 + \mathbf{h}_{P,cpcm}^0 \Delta N_P - \sum_{i \in P} \Phi_i^{tot} \cdot \Delta \mathbf{Q}_i \\ & + \frac{1}{2} \sum_{i,j \in P} I_{ij}^{cpcm} \Delta \mathbf{Q}_i \cdot \Delta \mathbf{Q}_j + \frac{1}{2} \sum_{i \in P} \mathbf{G}_i^{tot} \cdot \Delta \mathbf{Q}_i \Delta N_P. \end{aligned} \quad (34)$$

where  $\mathbf{m}_{P,cpcm}^0$ ,  $\mathbf{h}_{P,cpcm}^0$ ,  $\Phi_i^{tot}$ ,  $I_{ij}^{cpcm}$  and  $\mathbf{G}_i^{tot}$  are global and atomic reactivity indices of isolated molecules within C-PCM induced field. However interaction between subsystems is not taken into account explicitly, it is reflected in  $\Delta N$  and  $\{\Delta \mathbf{Q}_i\}$  values. The values of regional chemical potential do not tend to that of the global chemical potential, the reason for this being (28) and (29). Chemical potential discontinuity has not been taken into account. The change in chemical potential is proportional to the fractional number of electrons and  $\mathbf{m}_P(N)$  is smoothed at integer values of  $N$ .<sup>22,23</sup> Perturbation values for regional chemical potential 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 approxi-

**Table 1.** Gas phase properties: bond length  $Q$ , chemical potential  $\mathbf{m}^0$ , global hardness  $\mathbf{h}^0$ , force constant  $k^0$  and frequency  $\mathbf{w}^0$ .

Molecule	$Q$ [Å]	$\mathbf{m}^0$ [eV]	$\mathbf{h}^0$ [eV]	$k^0$ [eV/Å <sup>2</sup> ]	$\mathbf{w}^0$ [cm <sup>-1</sup> ]
GeO	1.638	-5.746	10.895	64.98	975.1
SiO	1.523	-5.827	11.414	106.96	1239
CO	1.126	-6.437	15.545	241.75	2211.7
HF	0.922	-7.000	18.689	65.30	4096.1
HCl	1.287	-5.560	14.471	32.65	2927.6

**Table 2.** CPC-M properties within gas phase geometry.

Molecule	$\mathbf{m}_{cpcm}^0$ [eV]	$\mathbf{h}_{cpcm}^0$ [eV]	$S_{cpcm}^0$ [1/eV]	$\mathbf{I}^{cpcm}$ [eV/Å <sup>2</sup> ]
GeO	-5.230	5.602	0.178	4.174
SiO	-5.305	5.943	0.168	3.131
CO	-6.015	9.303	0.107	-10.245
HF	-6.564	11.673	0.086	-8.763
HCl	-5.032	8.497	0.118	-12.900

**Table 3.** CPC-M equilibrium geometry properties: bond length, force constant.

Molecule	$Q_{cpcm}$ [Å]	$k_{cpcm}$ [eV/Å <sup>2</sup> ]	$\mathbf{m}_{cpcm}^{eq}$ [eV]	$\mathbf{h}_{cpcm}^{eq}$ [eV]
GeO	1.6594	55.82	-5.250	5.539
SiO	1.5363	95.92	-5.324	5.911
CO	1.1277	240.25	-6.014	9.303
HF	0.9437	50.70	-6.352	11.843
HCl	1.3241	21.07	-5.017	8.586

**Table 4.** Nuclear reactivity indices for gas phase structures and within C-PCM solvent effect [in eV/Å].

Molecule	$ \Phi_i $	$ \Phi_i^{ind} $	$ \Phi_i^{tot} $	$ \mathbf{G}_i $	$ \mathbf{G}_i^{ind} $	$ \mathbf{G}_i^{tot} $
GeO	0.592	1.521	0.972	3.281	6.196	2.832
SiO	0.962	0.441	1.403	2.826	0.499	2.328
CO	3.710	3.369	0.341	3.106	3.463	0.358
HF	0.199	10.071	9.872	4.204	3.696	7.900
HCl	0.748	0.346	0.402	3.821	1.426	2.395

**Table 5.** Force constant dependence on chemical potential and on bond length.

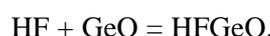
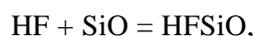
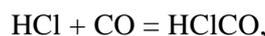
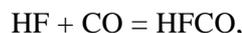
$\mathbf{s}_i^{tot}$  gives tendency of changing the number of electrons due to bond length variation.

Molecule	$(\partial k/\partial \mathbf{m})_{\mathbf{Q}, \epsilon^{ext}(\mathbf{r})=\epsilon}$ [1/Å <sup>2</sup> ]	$(\partial k/\partial \mathbf{Q})_{\mathbf{m}, \epsilon^{ext}(\mathbf{r})=\epsilon}$ [eV/Å <sup>3</sup> ]	$ \mathbf{s}_i^{tot} $ [1/Å]
GeO	0.745	-423.187	0.174
SiO	0.527	-817.390	0.239
CO	-1.101	-879.701	0.037
HF	-0.751	-678.962	0.846
HCl	-1.518	-312.796	0.047

mation depends on how the large change of variables  $\Delta N_R$  and  $\{\Delta \mathbf{Q}_i\}$  is to be obtained to get into the final state.

## 5. Calculations and results

We have studied C-PCM solvent effect on several diatomic molecules and on transition states of the following chemical reactions:



All calculations have been performed by b3lyp/6-311+G\*\* method implemented in Gaussian 03 package.<sup>24</sup> The conductor-like solvation model C-PCM (implemented in Gaussian 03 package) has been introduced by Cossi *et al*<sup>16</sup> We have used this implementation to study reactivity changes. For diatomic molecules: HCl, HF, CO, SiO and GeO we have calculated all reactivity indices and frequency shift. These results are presented in tables 1 to 3. In order to calculate reactivity indices we use finite difference approximation:

for chemical potential:

$$F^0 = (I + A)/2, \quad (35)$$

and for hardness:

$$\eta^0 = (I - A)/2, \quad (36)$$

where  $I(A)$  stands for ionization potential (electron affinity) of a molecule.

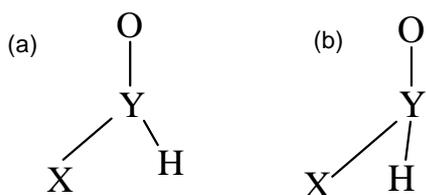
$$\Phi_i = (\mathbf{F}_i^+ - \mathbf{F}_i^-)/2, \quad (37)$$

**Table 6.** Geometry of ground states and transition states (angles in degrees).

Molecule	Bond [ $\text{\AA}$ ]	Bond [ $\text{\AA}$ ]	Bond [ $\text{\AA}$ ]	Distance [ $\text{\AA}$ ]	Angle	Angle
HFCO	C–O	C–F	C–H	H–F	F–C–O	H–C–O
t.s.	1.130	1.885	1.130	1.420	122.2	189.2
t.s. cpcm	1.119	2.058	1.109	1.563	124.0	187.4
HCICO	C–O	C–Cl	C–H	H–Cl	Cl–C–O	H–C–O
t.s.	1.132	2.387	1.119	1.870	122.6	187.6
t.s. cpcm	1.116	2.654	1.101	2.097	125.4	186.0
HFSiO	Si–O	Si–F	Si–H	H–F	F–Si–O	H–Si–O
t.s.	1.520	1.907	1.617	1.276	121.3	197.2
t.s. cpcm	1.530	1.935	1.610	1.299	117.5	200.8
HFGeO	Ge–O	Ge–F	Ge–H	H–F	F–Ge–O	H–Ge–O
t.s.	1.629	2.016	1.597	1.436	122.0	193.0
t.s. cpcm	1.638	2.087	1.586	1.462	117.8	197.8

**Table 7.** Regional chemical potentials for transition states within C–PCM compared to the ones from gas phase.

Molecule	Region	Gas phase			C–PCM		
		$\Delta N_R$	$\Delta Q_R$	$m_R^s$	$\Delta N_R$	$\Delta Q_R$	$m_R^s$
HFGeO	GeO	-0.151	-0.0089	-7.382	-0.233	-0.009	-6.547
	HF	0.151	0.513	-5.512	0.233	0.540	-4.891
HFSiO	SiO	-0.012	-0.0029	-5.961	-0.060	0.007	-5.651
	HF	0.012	0.354	-7.259	0.060	0.377	-6.580
HFCO	CO	-0.154	0.0028	-8.839	-0.346	-0.009	-9.178
	HF	0.154	0.498	-5.389	0.346	0.641	-3.773
HCICO	CO	-0.103	0.0041	-8.047	-0.388	-0.012	-9.552
	HCl	0.103	0.583	-5.949	0.388	0.810	-5.271

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

$$\mathbf{G}_i = -(\mathbf{F}_i^- + \mathbf{F}_i^+)/2 \quad (38)$$

and

$$\mathbf{I} = (k^- - k^+)/2. \quad (39)$$

where  $\mathbf{F}_i^+$  ( $\mathbf{F}_i^-$ ) are the total forces acting on the  $i$ th nucleus in the negatively (positively) charged molecule respectively, and  $k^+$  ( $k^-$ ) the force constants of

negatively (positively) charged molecules. This approximation has been applied to computing reactivity indices of diatomic molecules within gas phase and within C–PCM induced field. These results show that the molecules get softer within C–PCM, however the changes in bond lengths and frequencies are moderate. In table 4 we present C–PCM induced nuclear reactivity indices. Using (23) and (24) we have calculated chemical potential effect on force constant. The results are very reasonable (table 5). Change in chemical potential by 1 eV gives a change in force constant of the same order of magnitude.

We have applied this concept to transition states of chemical reactions. The ground state and transition state structures are shown in figure 1. The details of geometry are presented in table 6. The regional chemical potential values together with charge transfer and bond length change are gathered in table 7.

To use (34) we calculated charge transfer and bond lengths changes, between C-PCM transition state (table 6) and C-PCM diatomic isolated molecules (table 3). Thus we can compare these results to regional chemical potentials of transition states the same reactions within gas phase (table 7). All regions increased their regional chemical potential except for the CO region which seems to be able more likely to attract electrons than in the gas phase. This is since this region lost a lot of electronic charge during chemical reaction within C-PCM. No other parameter matters in the case of CO group. The increase of chemical potential for other groups is easy to explain. It is caused by screening effect of induced polarization charges on the cavity surface.

## 6. Conclusions

We have applied the DFT reactivity indices concept to describe the reactivity properties of molecules within the conductor-like solvation model. The softening of the molecules has been observed. Hardness for diatomic and polyatomic molecules has decreased. The decrease of the force constant has been divided into two parts. One is due to the change of chemical potential. This can be negative or positive. The other one is due to the change of the bond length. This is always negative. This theory has been used to obtain regional chemical potential values for transition states of some chemical reactions under the influence of C-PCM field. Regional chemical potential differentiates subsystems according to energy changes needed to vary numbers of electrons. Due to the rule that big  $\Delta m$  is good (which is also valid for subsystems) we can predict the directions of chemical reactions. The way is just perturbation scheme, where reactivity indices are response functions to parameters changes. These parameters are electronic population and geometry of the subsystems. The procedure in use has been described recently and applied to the transition states of the same reaction in gas phase. The comparison of the results in gas phase and C-PCM is very illustrative. The increase of regional chemical potential for all regions (but C=O) shows that C-PCM model simulates placing the molecule within the higher chemical potential environment.

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