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Author(s)

Ordon, Piotr; Tachibana, Akitomo

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Use of nuclear stiffness in search for a maximum hardness principle
and for the softest states along the chemical reaction path: A new
formula for the energy third derivative $\gamma$

Piotr Ordon$^a$ and Akitomo Tachibana
Department of Micro Engineering, Kyoto University, Kyoto 606-8501, Japan

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Nuclear stiffness, expressed as a hardness derivative, appears to be a good measure of the slope of
global hardness. The authors analyze molecular states for which hardness has a maximum value.
Maximum hardness principle (MHP) has been discussed. At the ground state hardness function does
not obtain a maximum value versus spatial coordinates within a constant number of electrons ($N$),
but is so within constant chemical potential ($\mu$) constraint. The authors apply this feature to evaluate
an energy third derivative ($\gamma$). MHP has been analyzed via symmetry considerations of nuclear
stiffness and nuclear reactivity. Nuclear stiffness has been also applied to study the hardness profile
for a chemical reaction. In this case, the authors seek molecular states for which hardness is at a
minimum. They have examined systems for which they have recently obtained regional chemical
potentials [P. Ordon and A. Tachibana, J. Mol. Model. 11, 312 (2005); J. Chem. Sci. 117, 583
(2005)]. The transition state is found not to be the softest along the chemical reaction path. Nuclear
stiffness reflects well the softest conformation of a molecule, which has been found independently
along the intrinsic reaction coordinate profile. Electronic energy-density [A. Tachibana, J. Mol.
Mod. 11, 301 (2005)] has been used to visualize the reactivity difference between the softest state
and the transition state. © 2007 American Institute of Physics. [DOI: 10.1063/1.2741535]

INTRODUCTION

Density functional theory descriptors have become a
unique theoretical approach for an analysis of properties of
theoretical systems. Important chemical properties of mol-
ecules such as electronegativity and hardness have found a
firm theoretical basis.\textsuperscript{4} An excellent review has been given
by Geerlings et al.\textsuperscript{5} Sanderson’s electronegativity equalization
principle, justified by Parr et al.,\textsuperscript{6} has become a tool to
predict charge transfer during chemical reactions. The chemical potential (minus electronegativity) is defined as

$$
\mu = \left( \frac{\partial E(N, \{Q_i\})}{\partial N} \right)_Q = -\chi,
$$

where $N$ is the total number of electrons and $\{Q_i\}$ is a set of
atomic positions. Since it is a Lagrange multiplier for energy
minimization within the constraint of the total number of
electrons ($N$) being constant, $\mu$ has a constant value through-
out the whole system.

The global hardness index\textsuperscript{4} has been used to predict sta-
bility of the system and the possible direction of chemical
reactions. We consider it as a function of nuclear coordinates
and the total number of electrons. It is defined as a second
derivative of the energy (first derivative of the chemical potential) versus $N$,\textsuperscript{9}

$$
\eta = \left( \frac{\partial^2 E(N, \{Q_i\})}{\partial N^2} \right)_Q = \left( \frac{\partial \mu(N, \{Q_i\})}{\partial N} \right)_Q,
$$

and global softness $S$ is the inverse of global hardness,

$$
S = \frac{1}{\eta} = \left( \frac{\partial N}{\partial \mu} \right)_Q.
$$

Using the hardness index, simple rules of reactivity have
been established. The hard and soft acid and basis principle
states that hard acids react with hard bases and soft acids
prefer soft bases. Recently, a very interesting proof has been
added by Ayers.\textsuperscript{7} In addition, the maximum hardness prin-
ciple (MHP) states that the most stable conformation of a
molecular system is the one for which global hardness is
maximized. Later on, within this paper we present a closer
look into the MHP.

Fuentalba and Parr\textsuperscript{8} defined the third derivative of
energy versus the number of electrons

$$
\gamma = \left( \frac{\partial^3 E(N, \{Q_i\})}{\partial N^3} \right)_Q = \left( \frac{\partial^2 \mu(N, \{Q_i\})}{\partial N^2} \right)_Q
= \left( \frac{\partial \eta(N, \{Q_i\})}{\partial N} \right)_Q,
$$

One of our results presented here is a new expression for $\gamma$
derived from MHP.

Hardness dependence on molecular deformation has
been studied extensively. Atomic reactivity indices have been
analyzed. The derivative of global hardness ($\eta$) has been
introduced by Ordon and Komorowski as nuclear stiffness,\textsuperscript{9}
Torrent-Succarrat amined the chemical potential’s dependence on Cartesian co-
total force acting on the force is given by the interaction of the electronic density 
total number of electrons, force acting on the is the Hellmann-Feynman force.\textsuperscript{11} The electronic part of this 
change computed via nuclear reactivity.\textsuperscript{14} From a variational 
tial’s change given by the Fukui function correlates with the 
Nuclear reactivity indices 
Nuclear reactivity indices have been introduced by Ordon 
and A. Tachibana J. Chem. Phys. \textbf{126} \textsuperscript{23,41,15-2} P. Ordon and A. Tachibana J. Chem. Phys. \textbf{126} \textsuperscript{20} The direction of the largest \textsuperscript{16} Theoretical features of this index\textsuperscript{22,35} justified the concept of local metallization.\textsuperscript{19} Using this idea the properties of RDX (hexahydro-1,3,5-
trinitro-1,3,5-triazine) molecule dissociation has been described.\textsuperscript{20} The direction of the largest \textbf{G} (or \textit{G}_\text{io}) gives the direction of maximal increase of reactivity, and this way, the 
experimental data for the bond cleavage of the RDX mole-
ecule have been confirmed. The issue of renormalization of 
the energy function, due to the coupling with oscillatory mo-
tion of nuclei, has been first raised by Luty.\textsuperscript{21} The role of 
nuclear stiffness within the whole set energy derivatives re-
sults in vibrational softening of molecules.\textsuperscript{16,22} An anhar-
monic behavior of diatomic molecules has been described by 
virtue of nuclear stiffness and another derivative\textsuperscript{23,24} (a mode 
softening index):

\begin{equation}
\lambda_{ij} = -\left(\frac{\partial \Phi_j}{\partial Q_i}\right)_N = \left(\frac{\partial k_{ij}}{\partial N}\right)_Q.
\end{equation}

**MAXIMUM HARDNESS PRINCIPLE**

The most complete description and survey on the MHP is 
given by Geerlings \textit{et al.}\textsuperscript{5} They give, except for a theoretical 
sketch, a very detailed review of all papers that tested 
MHP in a variety of chemical reactions.

There have been several attempts to formulate MHP. The idea from Pearson\textsuperscript{25} was very broad. He suggested that mole-
cules arrange themselves so as to be as hard as possible. 
This statement encouraged researchers to examine MHP by 
geometry optimization. The results were ambiguous. This 
caused the need for a rigorous proof of MHP. The proof has 
been proposed by Chattaraj and Parr.\textsuperscript{26,27} Result of their 
pub-
llication was that (for the ground state) hardness function has 
a maximum within the constraint of constant chemical poten-
tial \(\mu\) and constant temperature \((T)\). This result provided

\begin{table}
\centering
\caption{Global hardness variation caused by lengthening chemical bond of diatomic molecules by \(\Delta Q\) =0.1 Å. Direct calculation [\(\eta(Q^*+\Delta Q) - \eta(Q^*)\)] compared to the hardness change obtained via nuclear stiff-
ness \((\Delta \eta = \textbf{G} \cdot \Delta Q)\). \(\gamma\) is obtained to hold MHP [Eq. (30)]. All quantities are given in eV.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Molecule & \(\eta(Q^*)\) & \(\eta(Q^*+\Delta Q)\) & \(\eta(Q^*+\Delta Q) - \eta(Q^*)\) & \(\Delta \eta = \textbf{G} \cdot \Delta Q\) & \(\gamma\) \\
\hline
BCl & 5.063 & 5.163 & 0.100 & 0.066 & −1.110 \\
BF & 5.928 & 5.968 & 0.040 & 0.037 & −0.775 \\
BH & 4.682 & 4.696 & 0.014 & 0.018 & −1.479 \\
Cl\textsubscript{2} & 5.332 & 5.119 & −0.213 & −0.294 & 3.212 \\
CS & 5.767 & 5.893 & 0.126 & 0.074 & −1.075 \\
HCl & 7.277 & 7.099 & −0.178 & −0.145 & 37.684 \\
HF & 9.465 & 9.068 & −0.397 & −0.368 & 248.794 \\
LiCl & 4.675 & 4.578 & −0.097 & −0.125 & −9.905 \\
CO & 7.899 & 8.356 & 0.457 & 0.439 & −8.562 \\
LiF & 5.592 & 5.736 & 0.144 & 0.127 & −5.592 \\
F\textsubscript{2} & 7.578 & 6.899 & −0.679 & −0.812 & 6.710 \\
FCl & 6.154 & 5.978 & −0.176 & −0.234 & 2.195 \\
SiO & 6.089 & 6.076 & −0.013 & −0.096 & 5.515 \\
NF & 4.421 & 4.538 & 0.117 & 0.015 & −0.102 \\
SO & 3.552 & 3.764 & 0.212 & 0.059 & −0.800 \\
\hline
\end{tabular}
\end{table}
TABLE II. Electronegativity changes caused by lengthening chemical bond of diatomic molecules by \( \Delta Q = 0.1 \) Å. Direct calculation \((\chi' - \chi)\) and via nuclear Fukui function \((\Delta \chi = \Phi \cdot \Delta Q)\).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\chi' = -\mu(Q'))</th>
<th>(\chi' = -\mu(Q' + \Delta Q))</th>
<th>(\chi' - \chi)</th>
<th>(\Delta \chi = \Phi \cdot \Delta Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCI</td>
<td>4.739</td>
<td>5.027</td>
<td>0.288</td>
<td>0.301</td>
</tr>
<tr>
<td>BF</td>
<td>4.864</td>
<td>5.150</td>
<td>0.285</td>
<td>0.283</td>
</tr>
<tr>
<td>BH</td>
<td>4.702</td>
<td>4.761</td>
<td>0.059</td>
<td>0.057</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>6.048</td>
<td>6.528</td>
<td>0.481</td>
<td>0.488</td>
</tr>
<tr>
<td>CS</td>
<td>5.522</td>
<td>5.882</td>
<td>0.360</td>
<td>0.397</td>
</tr>
<tr>
<td>HCl</td>
<td>5.365</td>
<td>5.487</td>
<td>0.122</td>
<td>0.028</td>
</tr>
<tr>
<td>HF</td>
<td>6.913</td>
<td>6.939</td>
<td>0.026</td>
<td>0.014</td>
</tr>
<tr>
<td>LiCl</td>
<td>5.214</td>
<td>5.184</td>
<td>-0.029</td>
<td>-0.059</td>
</tr>
<tr>
<td>CO</td>
<td>5.981</td>
<td>6.974</td>
<td>0.992</td>
<td>0.405</td>
</tr>
<tr>
<td>LiF</td>
<td>5.978</td>
<td>6.131</td>
<td>0.153</td>
<td>0.127</td>
</tr>
<tr>
<td>F(_2)</td>
<td>7.676</td>
<td>8.502</td>
<td>0.826</td>
<td>0.917</td>
</tr>
<tr>
<td>FCl</td>
<td>6.599</td>
<td>7.229</td>
<td>0.629</td>
<td>0.656</td>
</tr>
<tr>
<td>SiO</td>
<td>5.936</td>
<td>6.078</td>
<td>0.142</td>
<td>0.106</td>
</tr>
<tr>
<td>NF</td>
<td>6.066</td>
<td>6.683</td>
<td>0.617</td>
<td>0.652</td>
</tr>
<tr>
<td>SO</td>
<td>5.476</td>
<td>5.623</td>
<td>0.147</td>
<td>0.262</td>
</tr>
</tbody>
</table>

an explanation for the results which show that global hardness depends, more or less linearly, on a totally symmetrical deformation of geometrical parameters such as bond lengths and bond angles. It has been argued that when these parameters are subject to change, the chemical potential \( \mu \) has to change as well. Thus, the constraint of constant \( \mu \) has not been kept. This was confirmed by detailed calculations of ammonia and ethane performed by Pearson and Palke.\(^{28}\) Also, very detailed studies were published by Pal \textit{et al.}\(^{29}\) They also found that hardness is maximized mainly with respect to a nontotally symmetric deformation of a molecule. Then, Sebastian\(^{30,31}\) seemed to find an error in the proof of Chattaraj and Parr.\(^{27}\) He proved that the softness function has no minimum value at chemical potential \( \mu = 0 \). Chattaraj \textit{et al.}\(^{32}\) have pointed out that for the correct value of the chemical potential \((\text{Eq. (1)})\), the proof holds. Later, it has been conclusively shown by Ayers and Parr\(^{33}\) that the original proof (of Chattaraj and Parr\(^{27}\)) was correct. They considered electron density variations that accompanied the minimization of energy. Then, they developed the hardness functional which was earlier constructed by Parr and Gazquez.\(^{35}\) Finally, Ayers and Parr\(^{33}\) noticed that density variations, which minimize the energy functional, maximize (within the constraint of constant \( \mu \)) the hardness functional. The MHP seems to play a central role in the theory of chemical reactivity. In order to lower the hardness and increase the reactivity, one has to change the chemical potential as well. Otherwise, hardness changes with small values of the second order. As Parr and Yang said,\(^{4}\) (p. 101), \( d\mu \) big is good for chemical reactivity.

Within this paper we derive the MHP for atomic coordinates. This gives us a simple relation of nuclear reactivity indices and the third derivative of the energy with respect to the number of electrons. Then, we describe how global hardness changes along the reaction path. We are particularly interested in identifying and analyzing the state on the reaction path for which global hardness has the lowest value. We examine how hardness changes along the reaction path. The obtained curve is the hardness profile of a chemical reaction. We provide a counterexample to the rule that the transition state is the softest within the hardness profile.

**PROPERTIES OF HARDNESS REVEALED BY NUCLEAR STIFFNESS**

If the variation of hardness is caused by chemical reaction (change in \( N \)) accompanied with the transformation of molecular geometry, then the hardness change is given by

\[
d\eta = \sum_i \left( \frac{\partial \eta}{\partial Q_i} \right)_N \cdot dQ_i + \left( \frac{\partial \eta}{\partial N} \right)_Q dN = \sum_i G_i \cdot dQ_i + \gamma dN.
\]

(10)

When the number of electrons is kept constant (e.g., isomerization or charge transfer within the molecule in question), the first order change in the hardness is given by the nuclear stiffness,

\[
d\eta = \sum_i G_i \cdot dQ_i.
\]

(11)

When the deformation is accompanied by the change of chemical potential, the change in hardness reads

\[
d\eta = \sum_i \left( \frac{\partial \eta}{\partial Q_i} \right)_\mu \cdot dQ_i + \left( \frac{\partial \eta}{\partial \mu} \right)_Q d\mu.
\]

(12)

Ordon and Komorowski\(^{16}\) have proven that hardness dependence on molecular deformation within constant \( \mu \) constraint reads

\[
\left( \frac{\partial \eta}{\partial Q_i} \right)_\mu = G_i + \gamma S \Phi_i.
\]

(13)

The hardness derivative versus the chemical potential is given by the product of the global softness \( S \) and the third energy derivative \(-\gamma\)^{16}

\[
\left( \frac{\partial \eta}{\partial \mu} \right)_Q = S \gamma.
\]

(14)

Thus, Eq. (12) reads:

\[
d\eta = \sum_i G_i \cdot dQ_i + \sum_i S \gamma \Phi_i \cdot dQ_i + \gamma S d\mu.
\]

(15)

When the chemical potential is kept constant (which is the case within MHP), then hardness change reads

\[
d\eta = \sum_i (G_i + S \gamma \Phi_i) \cdot dQ_i.
\]

(16)

Projecting vector atomic indices \((\Phi_i \text{ and } G_i)\) onto normal modes\(^{35}\) transforms Eq. (15) into

\[
d\eta = \sum_a (G_a + \gamma S \Phi_a) dQ_a + \gamma S d\mu,
\]

(17)

where \( \Phi_a \) and \( G_a \) denote the \( a \)th normal mode projection of nuclear reactivity and nuclear stiffness,

\[
\Phi_a = \sum_i Q_i^a \cdot \Phi_i,
\]

(18)
Thus, the change of hardness during chemical transformation within the constant $\mu$ constraint is given by

$$d\eta = \sum_{\alpha} (G_{\alpha} + \gamma S_{\alpha}) dQ_{\alpha}.$$  \hfill (20)

Thus, the change of hardness during chemical transformation within the constant $N$ constraint is given by

$$d\eta = \sum_{\alpha} G_{\alpha} dQ_{\alpha}.$$  \hfill (21)

If there is a particular normal mode coordinate $Q_{\alpha}$ along which the molecule is deformed, then hardness can be at its extremum if

$$G_{\alpha} = 0$$  \hfill (22)

at the constant $N$ condition.

The MHP at constant $\mu$ reads

$$G_{\alpha} + \gamma S_{\alpha} = 0.$$  \hfill (23)

This equation is exact, as is that for the MHP. There are two ways to satisfy Eq. (23). The simplest is when $G_{\alpha}$ and $\Phi_{\alpha}$ are zero, which is often the case when $\alpha$ is a nontotally symmetric normal mode.\textsuperscript{16,20} If the Jahn-Teller effect for an ionic state cannot occur, $G_{\alpha}=0$ because of symmetry reasons. The same reasons cause $\Phi_{\alpha}=0$ and Eq. (23) holds automatically. Thus, for nontotally symmetric deformations, the hardness and chemical potential usually remain constant,\textsuperscript{20,35} which supports the MHP concept of Chattaraj and Parr. Earlier, an independent derivation of this result has been given by Makov.\textsuperscript{36}

However, if the Jahn-Teller effect for an ionic state can occur, then the nuclear stiffness and unclear Fukui function have nonzero values even for nontotally symmetric modes. The general rule states that

$$\Gamma_{\gamma} \times \Gamma_{\alpha} \supset \Gamma_{\gamma'},$$  \hfill (24)

where $\Gamma_{\gamma}$ denotes an irreducible representation of the point group of the $G_{\gamma}$ vector set. $G_{\alpha}$ denotes the irreducible representation of the $\alpha$th normal mode. The most common situation is where one obtains nonzero $G_{\alpha}$ values only for modes which are of molecular symmetry. However, hardness may not be maximal (also versus nontotally symmetric modes) when the set of all $G_{\gamma}$ vectors breaks the molecular symmetry and the irreducible representation $\Gamma_{\gamma}$ of its point group is contained in direct product of $\Gamma_{\gamma}$ and the irreducible representation of the $\alpha$th normal mode $\Gamma_{\alpha}$ [Eq. (24)].

Ordon and co-workers have published examples of such symmetry breaking due to the Jahn-Teller effect.\textsuperscript{20,22} Chemical reaction may cause degeneracy due to the removal of electrons from a fully occupied highest occupied molecular orbital. In such a case, forces driving molecules to lower symmetries happen to occur. These forces are coupled with

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond (Å)</th>
<th>Distance (Å)</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C–O</td>
<td>C–F</td>
<td>C–H</td>
</tr>
<tr>
<td>GS</td>
<td>1.177</td>
<td>1.355</td>
<td>1.0951</td>
</tr>
<tr>
<td>TS</td>
<td>1.130</td>
<td>1.885</td>
<td>1.130</td>
</tr>
<tr>
<td>SS</td>
<td>1.140</td>
<td>1.832</td>
<td>1.0857</td>
</tr>
<tr>
<td></td>
<td>Si–O</td>
<td>Si–F</td>
<td>Si–H</td>
</tr>
<tr>
<td>GS</td>
<td>1.517</td>
<td>1.604</td>
<td>1.466</td>
</tr>
<tr>
<td>TS</td>
<td>1.520</td>
<td>1.907</td>
<td>1.617</td>
</tr>
<tr>
<td>SS</td>
<td>1.520</td>
<td>2.056</td>
<td>2.221</td>
</tr>
<tr>
<td></td>
<td>Ge–O</td>
<td>Ge–F</td>
<td>Ge–H</td>
</tr>
<tr>
<td>GS</td>
<td>1.634</td>
<td>1.759</td>
<td>1.525</td>
</tr>
<tr>
<td>TS</td>
<td>1.629</td>
<td>2.0162</td>
<td>1.597</td>
</tr>
<tr>
<td>SS</td>
<td>1.638</td>
<td>2.202</td>
<td>2.420</td>
</tr>
</tbody>
</table>
the chemical reaction and contribute to $G_i$, which no longer possess molecular symmetry. Numerical observations by Blancafort et al.\textsuperscript{37} may also be explained by Eq. (24). Their results suggest that $G_i$ can break a molecular symmetry due to the interaction of the ground state and low-lying excited states that exhibit degeneracy.

In the case when $G_{a} \neq 0$ and $\Phi_{a} \neq 0$, hardness is maximal due to the product $S_y$ that allows compensation of both terms in Eq. (23). Thus, MHP holds always within constant $\mu$.

**CALCULATIONS AND RESULTS**

We shall illustrate our concepts in several steps. First, we shall numerically prove that the global hardness change caused by geometry variations is approximately predicted by the nuclear stiffness reactivity index

$$\Delta \eta = \sum \mathbf{G}_i \cdot \Delta \mathbf{Q}_i.$$  

(25)

In order to get a complete description, we also present the correlation between the actual change of chemical potential and the one obtained via the nuclear Fukui function. We assume that the following equation holds for moderate geometry changes:

$$\Delta \eta = \sum \mathbf{G}_i \cdot \Delta \mathbf{Q}_i.$$  

(26)

In order to calculate reactivity indices, we use the finite difference approximation. For chemical potential and for hardness,\textsuperscript{4}

$$\mu = \frac{I + A}{2},$$  

(27)

$$\eta = \frac{I - A}{2},$$  

(28)

where $I/A$ stand for the ionization potential/electron affinity of a molecule. Nuclear reactivity indices were obtained by the finite difference approximation as well,\textsuperscript{9}

$$\Phi_i = \frac{F^+_i - F^-_i}{2}$$  

(29)

and

$$G_i = -\frac{F^-_i + F^+_i}{2},$$  

(30)

where $F^+_i$ ($F^-_i$) are the total forces acting on the $i$th nucleus in the negatively (positively) charged molecule, respectively. If a state in question is neither a ground state nor a transition state, we need to modify Eq. (30),

$$G_i = -\frac{F^+_i + F^-_i}{2} + F^o_i,$$  

(31)

where $F^o_i$ is the total force acting on the $i$th nucleus within a neutral molecule.\textsuperscript{9} The approximation for $\Phi_i$ [Eq. (29)] re-

<table>
<thead>
<tr>
<th>TABLE IV. Global hardness $\eta$ (eV) for various states along IRC.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>GS</td>
</tr>
<tr>
<td>TS</td>
</tr>
<tr>
<td>SS</td>
</tr>
<tr>
<td>Separated molecules</td>
</tr>
</tbody>
</table>
mains unchanged for states other than the ground state or the transition state.

### Hardness and chemical potential variations obtained with nuclear stiffness and nuclear reactivity

Calculations were performed using the MP2 method and the 6-311+G(3df,3dp) basis set as implemented in the GAUSSIAN03 code.\(^{41}\) The geometry was optimized for the neutral molecule by a quasi-Newton-Raphson procedure. An ion and cation energies and forces were calculated in the neutral molecular geometry. These quantities were used to obtain chemical potential, hardness [via Eqs. (27) and (28)], nuclear reactivity, and nuclear stiffness [via Eqs. (29) and (30)]. For a set of diatomic molecules, we obtained the chemical potential and hardness for molecules with extended bond length by $\Delta Q = 0.1 \, \text{Å}$ and for molecules of ground state geometry. Equations (27) and (28) have been used. The difference between $\eta(Q^+ + \Delta Q)$ and $\eta(Q^+)$ has been correlated to $G \cdot \Delta Q$. For the sake of completeness, we present similar results for chemical potential variations obtained via the nuclear Fukui function. The results are gathered in Tables I and II and Figs. 1 and 2.

Nuclear stiffness $G$ is the most important parameter predicting the variability of hardness $\eta$ versus molecular deformations $Q$. Data given in Fig. 1 and Table I prove that the index $G$ reflects the change of hardness well. These data also prove that, usually, hardness depends linearly on geometrical coordinate variations. However, one should be certain that $\eta$ depends linearly on $Q$ only within a limited range. Nonzero values of nuclear stiffness indicate that hardness is not maximized at the ground state [within constant $N$ constraint, Eq. (11)]. However, it is maximized within the constraint of constant $\mu$.

#### New formula for $\gamma$

The third derivative of energy versus the number of electrons $\gamma$ gives the hardness change due to the variation in the total number of electrons [Eq. (4)]. Since MHP within constant $\mu$ is established, then Eq. (23) is satisfied. To obtain numerical values of all reactivity indices, we use the finite difference approximation [Eqs. (27)–(30)] which corresponds to the Gyftopoulos-Hatsopoulos three level model\(^{38}\) for which MHP was separately tested.\(^{32}\) Thus, we derive an expression for $\gamma$ from MHP,

$$\gamma = \frac{G}{S \Phi}$$  \hspace{1cm} (32)

We have obtained $\gamma$’s numerical values for a set of diatomic molecules. The results are gathered in Table I. $\gamma$ is provided without the need of calculating a second ionization potential and without any assumption about the $E(N)$ function.\(^{5}\) The results are encouraging. Most often, $\gamma$ is of the same order of magnitude as $\mu$ and $\eta$. The cases of HCl and HF, for which this concept seems to break down, prove that better approximation needs left- and right-hand side derivatives. In these cases $F^+$ and $F^-$ are of very similar value. Thus, $F^+$ and $F^-$ accumulate to form $G$ [Eq. (30)] and almost cancel each other, obtaining $\Phi$ via Eq. (29). Great improvement in $\gamma$ is expected from the separation of nuclear reactivity indices into left- and right-hand side derivatives. Left- and right-hand side derivatives of energy, $\gamma^-$ and $\gamma^+$, would be of similar magnitude as hardness since $G^+/\Phi^+ \equiv 1$.

Fuentalba and Parr\(^{8}\) have obtained $\gamma$ using a model energy function $E(N)$. We, on the other hand, have found $\gamma$ from basic principles. Thus, the precision of the actual $\gamma$ calculation is the same as the ones for hardness, nuclear reactivity, and nuclear stiffness. From our results $\gamma$ is not a small correction to energy. One should also take into account that the sign of $\gamma$ can be positive or negative. Hardness is always positive and chemical potential is always negative.

#### Softest state along the chemical reaction path

Datta\(^{39}\) hypothesized that the transition state (TS) of a chemical reaction should exhibit the lowest hardness along the reaction path. He gave an example of the inversion of the ammonia molecule. This reaction happens to satisfy this hypothesis. However, a counterexample has been given by Kar and Scheiner\(^{40}\) who examined the isomerization of the HCN molecule.

We present another counterexample: chemical reactions for which global hardness reaches its minimum at some other state than TS. However, we intend to establish a general approach to the profile of hardness. Thus, we have studied a set of chemical reactions to obtain dependence of global hardness versus the intrinsic reaction coordinate (IRC),

- $\text{HF} + \text{CO} \rightleftharpoons \text{HFCO}$
- $\text{HF} + \text{SiO} \rightleftharpoons \text{HFSiO}$
- $\text{HF} + \text{GeO} \rightleftharpoons \text{HFGeO}$

Calculations have been performed by the b3lyp/6-311+G** method implemented in the GAUSSIAN03 package.\(^{41}\) Ground state (GS)—right-hand side of reaction equations—and transition state geometries were optimized. We used the structures from our previous calculations of the regional chemical potential indices for diatomic regions.\(^{1,2}\) The structures of TS and GS are planar. The details are gathered in Table III. There is a very good agreement with literature data.\(^{42}\) Negative frequencies (−1384 cm$^{-1}$ for HFCO, −1484 cm$^{-1}$ for HFSiO, and −1318 cm$^{-1}$ for HFGeO transition states) represent normal modes, which are mainly F−H bond stretches. The calculated activation energy of the HF–CO dissociation reaction is 45.31 kcal/mol, that of the dissociation reaction of HF–GeO is 37.76 kcal/mol, and that of the dissociation reaction of HF–SiO is 62.37 kcal/mol.

We have examined the set of states along the IRC path to find out if the transition state is the softest. We have calcu-
lated the global hardness index using a finite difference approximation [Eq. (28)]. The results are shown in Figs. 3–5 and in Table IV, which presents hardness values for GS, TS, SS, and the separated molecules limit. We have obtained the state of the lowest hardness SS. The softest state, however, is not the transition state, although the TS is softer than the GS and the separated molecule state reaction path like a mode softening in a phase transition. SS is a state in which the nature of the lowest normal mode changes into H–Y stretching (Y=C, Si, and Ge). The geometry of the softest states has been gathered in Table III.

We are particularly interested in examining those states for which hardness is not subject to change. This is indicated by the lowest-mode projection of $G_i$,

$$G_i = \left( \frac{\partial \eta}{\partial Q_i} \right)_N \approx 0. \quad (33)$$

The fact that SS is the softest state along the reaction path has been confirmed by the global hardness derivative versus the lowest frequency normal coordinate, $G_i$; it is very close to zero. Results [obtained via Eqs. (19) and (31)] are presented in Table V. At the TS, $G_i$ is large and is significantly decreased at the SS. For HF–SiO and HF–GeO it is located
using kinetic energy density, the molecular space has been partitioned into disjoint regions: electronic drop region $R_D$, atmosphere region $R_A$, and the interface $S$. The kinetic energy density $n_T(r)$ is defined as

$$n_T(r) = \frac{1}{2} \sum_i \nu_i \left[ -\frac{\hbar^2}{2m} \Delta \psi_i^*(r) \psi_i(r) + \psi_i^*(r) \right] \times \left[ -\frac{\hbar^2}{2m} \Delta \psi_i(r) \right],$$

(34)

where $m$ is the mass of the electron, $\psi_i(r)$ are the natural orbitals, and $\nu_i$ is the occupation number of $\psi_i(r)$. The kinetic energy density is intentionally not positively defined. In the $R_A \ (n_T(r) < 0)$, the electron density is dried up and the motion of the electrons is classically forbidden. Within the $R_D$ region, the movement of electrons is allowed since $n_T(r) > 0$. The boundary $S$ in between $R_D$ and $R_A$ gives the shape of the reactant atoms and molecules along the course of the chemical reaction coordinate.

Another field has been recently introduced to characterize a chemical reaction. The concept uses stress tensor density to reveal the spindel structure of the chemical bond. This feature of chemical bond appears only under certain circumstances which have been recently extensively discussed. $^{3,45}$

Tension density $\tau^{ij}(r)$ is defined as

$$\tau^{ij}(r) = \{\tau^{11}(r), \tau^{22}(r), \tau^{33}(r)\},$$

(35)

with

$$\tau^{33}(r) = \frac{\hbar^2}{4m} \sum_i \nu_i \left[ \psi_i^*(r) \frac{\partial \psi_i(r)}{\partial x^3} - \frac{\partial \psi_i^*(r)}{\partial x^3} \Delta \psi_i(r) \right] + \frac{\partial \Delta \psi_i(r)}{\partial x^3} \psi_i(r) - \Delta \psi_i^*(r) \frac{\partial \psi_i(r)}{\partial x^3}$$

(36)

for $k=1, 2, 3$. The stress tensor density $\nabla \cdot \tau(r)$

$$\tau^{ij}(r) = \{\tau^{ij}(r)\}_{ij},$$

(37)

where

$$\tau^{33}(r) = \frac{\hbar^2}{4m} \sum_i \nu_i \left[ \psi_i^*(r) \frac{\partial^2 \psi_i(r)}{\partial x^3 \partial x^3} - \frac{\partial \psi_i^*(r)}{\partial x^3} \frac{\partial \psi_i(r)}{\partial x^3} \right] + \frac{\partial^2 \psi_i(r)}{\partial x^3 \partial x^3} \psi_i(r) - \frac{\partial \psi_i^*(r)}{\partial x^3} \frac{\partial \psi_i(r)}{\partial x^3}$$

(38)

for $k, l=1, 2, 3$. The stress tensor density is diagonalized and its diagonal components satisfy

$$\tau_{33}^{33}(r) \geq \tau_{22}^{33}(r) \geq \tau_{11}^{33}(r).$$

(39)

Tachibana $^{45}$ has proven that the eigenvalue of the stress tensor density gives a measure of the kinetic energy. A positive value for the biggest eigenvalue of the stress tensor-density means tensile stress is exerted at this point on the electronic cloud. When $\tau^{33}(r) < 0$, we observe a compressive stress. The compressive stress gives a positive contribution to the kinetic energy density, while the tensile stress provides a negative contribution because of negative eigenvalues. $^3$

In Figs. 6–11, we present the kinetic energy density, third principal stress, and third principal axis for the transi-

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**Reactivity considerations via energy-density calculations**

Tachibana has introduced field theory into the chemical reactivity analysis. $^{44}$ Using kinetic energy density, the IRC path for HF–CO exhibits the softest state at this side which leads to the molecular ground state GS. This is related to the large volumes of Ge and Si atoms which prevent hardening of the system until the interaction between HF and SiO or GeO fragments is relatively low.
tion states and for the softest states. These results have been obtained with the Molecular Regional DFT program package. In Figs. 6(a), 7(a), 8(a), 9(a), 10(a), and 11(a) white regions denote a negative kinetic-energy density, with gray and black indicating positive-value regions. In Figs. 6(b), 7(b), 8(b), 9(b), 10(b), and 11(b), the deepest blue is −0.2 and the darkest red is +0.2 of stress density in a.u.

The results show that the proton is more tightly bonded within the SS than within the TS since the transition state incorporates nuclear interactions. Higher eigenvalues of stress tensor and spindle structure for the SS indicate a covalent character for the chemical bond. We could call the SS an electronic transition state. In this case, higher values of the stress tensor component and higher kinetic energy density favor lower hardness. The value of stress tensor in the H–F region is greatest within the separated H–F molecule limit. According to our results in Table I, the H–F molecule gets softer when the bond is lengthened. However, such linear response works only near the ground state. After the coordinates change significantly (from the initial state of separated molecules) to form the GS of the product molecule, the interactions with a complementary (to H–F) subsystem harden the product molecule (GS).
The maximum hardness principle via Eqs. (23) and (32) gives $\gamma$ that gives the hardness change due to the variation in the total number of electrons. We tested the new formula for $\gamma$ for a set of diatomic molecules. Obtained results are reasonable; however, further studies are needed to obtain left- and right-hand side derivatives. The main advantage of the new scheme to obtaining $\gamma$ is that no assumption for the $E(N)$ function was needed.

The transition state is not the softest one along the reaction path. Nuclear stiffness reflects well the softest conformation of a molecule during chemical reaction. This has been found independently along the IRC scan for simple examples.

Energy-density considerations reflect differences between structures of similar reactivities. It has been visualized that more reactive structures are of larger values of the components of the stress tensor.

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FIG. 11. CO+HF=COHF reaction path transition state (a) kinetic energy density and (b) stress density and eigenvector.

CONCLUSIONS

It has been demonstrated that nuclear stiffness gives a fair measure for hardness variations. Numerical results for a set of diatomic molecules show that the change of hardness is very well reproduced by nuclear stiffness and that the change in chemical potential can be obtained by nuclear reactivity.
41 M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., GAUSSIAN 03, Revision B01, Gaussian, Inc., Pittsburgh, PA.
46 K. Nakamura, K. Doi, and A. Tachibana, Molecular Regional DFT program package, version 1, Tachibana Laboratory, Kyoto University.