DFT Energy Derivatives and Their Renormalization in Molecular Vibrations

PIOTR ORDON, LUDWIK KOMOROWSKI

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

ABSTRACT: Properties of the energy function $E(N, \mathbf{Q})$ and the thermodynamic potential $\Omega(\mu, \mathbf{Q})$ expressed in terms of the number of electrons (N) and the nuclear positions ($\mathbf{Q}$) rather than conventionally, by the electrostatic potential, $\nu(\mathbf{r})$, have been analyzed. The whole body of derivatives up to the third order is presented for each function. Renormalization of the basic derivatives explored in conceptual density functional theory has been demonstrated (chemical potential μ, global hardness η, number of electrons N, global softness S) as a result of coupling between the oscillatory motion of nuclei and the change in N or μ, for E and Ω, respectively. Exact result of renormalization crucially depends on the level of approximation. Extending the analysis beyond the second order was possible by adopting the Liu and Parr–type approximation to the energy function. It has been determined that first derivatives (μ, N) change their values when found beyond the vibrational energy minimum only. Second derivatives (η, S) both get renormalized even at the energy minimum, and they no longer conform to the reciprocity condition ($\eta S \neq 1$). Possible implications for the reactivity of oscillating species have been indicated.   © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 101: 703–713, 2005

Key words: chemical potential; DFT energy derivatives; electronic-vibrational coupling; hardness; softness

Introduction

The analysis of the effect of nuclear displacement on the electronic energy of a molecule was not introduced into the density functional the-

Correspondence to: L. Komorowski; e-mail: ludwik.komorowski@pwr.wroc.p

P. Ordon is currently at the Laboratory of Molecular Modeling, Agricultural Academy, Wrocław, Poland.

ory (DFT) until the work by Cohen et al. [2], who first proposed the nuclear reactivity function as a derivative of the Hellman–Feynman force over the number of electrons $\Phi_i = (\partial \mathbf{F}_i / \partial N)_\nu$. This derivative, also known as the nuclear Fukui function [3], soon attracted attention. Independently, Berkowitz et al. [4], Baekelandt [5], and Ordon and Komorowski [6] proved it to be equal to the derivative of the chemical potential (μ, or the negative of electronegativity, χ) over the nuclear displacement; the numerical values thereof have also been ascribed [6]. Balawender and Geerlings [7] discerned

the nucleophilic and electrophilic Φ_i and provided a computational ab initio scheme for this quantity. The counterpart to the nuclear reactivity, the nuclear softness, was introduced by Cohen et al. [2] as $\sigma_i = (\partial \mathbf{F}_i / \partial \mu)_v$; the numerical values were ascribed to it by De Proft et al. [8]. The derivative of global hardness (η) was introduced by Ordon and Komorowski as the nuclear stiffness: $\mathbf{G}_i = (\partial \eta / \partial \mathbf{Q}_i)_N$ [6]. The authors also presented analysis of Φ_i and $\mathbf{G}_i$ indices for normal vibrational modes [9] and elaborated on the role of these indices in determining the fluctuations in chemical potential (electronegativity) and hardness due to molecular oscillations [9, 10]. The possibility of finding still higher derivatives has also been studied; $\lambda = -(\partial \Phi / \partial \mathbf{Q})_N$ and $\tau = (\partial \mathbf{G} / \partial \mathbf{Q})_N$ for diatomic molecules have been found and proved to be useful in analyzing the source of anharmonicity of a molecular oscillator [11]. The authors have demonstrated connections between these derivatives and the vibrational force constants and thus exposed the need of a unified analysis of the energy function, which should contain the whole body of such derivatives [11, 12]. Here also belongs the derivative first discussed by Fuentalba and Parr [13] as $\gamma = (\partial^3 E / \partial N^3)_v$. The subject is discussed within the conceptual density function theory; its more detailed presentation may be found elsewhere [14]. The complete analysis of couplings between the electronic and geometrical degrees of freedom was presented by Nalewajski [15] in the framework of his charge sensitivity analysis. The issue of renormalization of the energy function due to the coupling with oscillatory motion of nuclei was first raised by Luty [16] and further developed by Komorowski and Ordon [11]. The significance of this approach was indicated within the analysis of a local metallization as a possible source of explosive properties of RDX [17].

The current work is focused on: (1) presenting a comprehensive and complete analysis of all derivatives up to the third order that could possibly have physical significance (and chemical use) for the energy function $E(N, \mathbf{Q}_i)$ as well as for the thermodynamic potential $\Omega(\mu, \mathbf{Q}_i)$; (2) demonstrating the renormalization analysis for E and Ω beyond the second order, thus disclosing the role of the derivatives collected hereby in predicting the chemical reaction effects (electron flow) coupled with the oscillations (displacement of the nuclei).

Energy Function $E(N, Q)$ and Its Derivatives

In order to introduce a coherent formalism for the nuclear derivatives, the convention concerning energy must be introduced first. Instead of typical DFT energy functional $E[N, v(\mathbf{r})]$, the $[N, \mathbf{Q}]$ representation of the energy function will be used, where $\mathbf{Q} \equiv \{\mathbf{Q}_i\}$, and $\mathbf{Q}_i = \mathbf{R}_i - \mathbf{R}_{i,o}$ is the displacement vector for a nucleus whose equilibrium position is $\mathbf{R}_{i,o}$. In the standard Born–Oppenheimer approximation (electronic energy E_e, interaction between the nuclei E_{nn}):

$$E = E_e + E_{nn}. \tag{1}$$

Let the external potential $v(\mathbf{r})$ (electric field $\varepsilon(\mathbf{r})$) be given by the nuclei at fixed positions, exclusively, then:

$$v(\mathbf{r}) = \sum_i \frac{Z_i}{|\mathbf{Q}_i - \mathbf{r}|} \quad \text{and} \quad \nabla v(\mathbf{r}) = -\varepsilon(\mathbf{r}). \tag{2}$$

Because $(\partial v(\mathbf{r})/\partial N)_\mathbf{Q} = 0$ and $(\partial v(\mathbf{r})/\partial \mu)_\mathbf{Q} = 0$, it follows that:

$$\left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i} \right)_N = \left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i} \right)_\mu = -\varepsilon_i(\mathbf{r}), \tag{3}$$

and the Hellman–Feynman force contains both the electronic and nuclear terms [6]:

$$-\left(\frac{\partial E(N, \mathbf{Q})}{\partial \mathbf{Q}_i} \right)_N = \int \rho(\mathbf{r}) \varepsilon_i(\mathbf{r}) d\mathbf{r} + \mathbf{F}_i^{n-n} = \mathbf{F}_i. \tag{4}$$

Derivatives of force $\mathbf{F}_i$ over $\mathbf{Q}_j$ at constant N have the meaning of force constants k_{ij} (harmonic) and the conventional anarmonicity tensor (cubic force constant) $\mathbf{a}_{ijk}$:

$$k_{ij} = \left(\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial E}{\partial \mathbf{Q}_j} \right)_N \right)_N = -\left(\frac{\partial F_i}{\partial \mathbf{Q}_j} \right)_N, \tag{5}$$

$$\mathbf{a}_{ijk} = \left(\frac{\partial}{\partial \mathbf{Q}_i} \left(\frac{\partial}{\partial \mathbf{Q}_j} \cdot \left(\frac{\partial E}{\partial \mathbf{Q}_k} \right)_N \right)_N \right)_N = \left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k} \right)_N. \tag{6}$$

Because the nuclear term $\mathbf{F}_i^{n-n}$ does not depend on N, derivatives of $\mathbf{F}_i$ over N at constant $\mathbf{Q}$ are just

nuclear reactivity $\mathbf{\Phi}_i$ and nuclear stiffness, $\mathbf{G}_i$, respectively:

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

The nuclear term E_{nn} is independent of N, the derivatives of $E(N, \mathbf{Q})$ over N at constant nuclear positions yield the chemical potential (μ), global hardness (η) and γ:

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

$$\left(\frac{\partial^2 E(N, \mathbf{Q})}{\partial N^2}\right)_{\mathbf{Q}} \equiv \eta, \quad (9)$$

$$\left(\frac{\partial^3 E(N, \mathbf{Q})}{\partial N^3}\right)_{\mathbf{Q}} \equiv \gamma. \quad (10)$$

Hence, the $E(N, \mathbf{Q})$ function derivatives have been proved to be identical to the derivatives of electronic energy as known in the DFT. The differentials of the energy, chemical potential, and global hardness will be used to expose the Maxwell relations in the $[N, \mathbf{Q}]$ representation:

$$dE = \mu dN - \sum_i \mathbf{F}_i \cdot d\mathbf{Q}_i, \quad (11)$$

$$\left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_N \equiv \mathbf{\Phi}_i, \quad (12)$$

$$d\mu = \eta dN - \sum_i \mathbf{\Phi}_i \cdot d\mathbf{Q}_i, \quad (13)$$

$$-\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial \mathbf{\Phi}_i}{\partial N}\right)_{\mathbf{Q}} \equiv -\mathbf{G}_i \quad (14)$$

$$d\eta = \gamma dN + \sum_i \mathbf{G}_i \cdot d\mathbf{Q}_i \quad (15)$$

$$\left(\frac{\partial \gamma}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial \mathbf{G}_i}{\partial N}\right)_{\mathbf{Q}}. \quad (16)$$

The differential of the electron density can also be expressed within the $[N, \mathbf{Q}]$ representation

$$d\rho(\mathbf{r}) = f(\mathbf{r})dN + \sum_i \mathbf{\varpi}_i(\mathbf{r}) \cdot d\mathbf{Q}_i, \quad (17)$$

where the novel linear nuclear response function

$$\mathbf{\varpi}_i(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N \quad (18)$$

is analogous to the linear electronic response function $\omega(\mathbf{r}, \mathbf{r}') = (\delta\rho(\mathbf{r})/\delta v(\mathbf{r}'))_N$, [18], and the Maxwell relation follows:

$$\left(\frac{\partial \mathbf{\varpi}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial f(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N, \quad (19)$$

where $f(\mathbf{r})$ is the Fukui function [18]; a simple exercise with Eqs. (13), (17), and (33), proves $f(\mathbf{r})$ in Eq. (17) to be identical to its standard DFT definition:

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}.$$

An important task is to show how the nuclear derivatives over $\mathbf{Q}_i$ and the local derivatives over $v(\mathbf{r})$ are related:

$$\mathbf{\Phi}_i = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_N = -\int \left(\frac{\delta\mu}{\delta v(\mathbf{r})}\right)_N \left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r}$$

$$= \int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}, \quad (20)$$

$$\mathbf{G}_i = -\left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2}\right)_{\mathbf{Q}} = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = \int \left(\frac{\delta\eta}{\delta v(\mathbf{r})}\right)_N \left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r}$$

$$= -\int h(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}, \quad (21)$$

where $h(\mathbf{r})$ is, according to Fuentalba and Parr [13]:

$$h(\mathbf{r}) \equiv \left(\frac{\delta\eta}{\delta v(\mathbf{r})}\right)_N = \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} = \left(\frac{\delta}{\delta v(\mathbf{r})}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})}\right)_N. \quad (22)$$

The nuclear response function is directly related to the electronic one:

$$\mathbf{\varpi}_i(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N = \int \left(\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_N \left(\frac{\delta v(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r}'$$

$$= \int \omega(\mathbf{r}, \mathbf{r}')\boldsymbol{\varepsilon}_i(\mathbf{r}')d\mathbf{r}'. \quad (23)$$

TABLE I

The energy derivatives in [N, Q] representation in the third order.

Energy derivative	$\mathbf{Q} = const \rightarrow$	$\dfrac{\partial}{\partial N}$	$\dfrac{\partial^2}{\partial N^2}$	$\dfrac{\partial^3}{\partial N^3}$
$N = const \downarrow$	E	μ	η	γ
$\dfrac{\partial}{\partial \mathbf{Q}_i}$	$-\mathbf{F}_i$	$-\mathbf{\Phi}_i$	$\mathbf{G}_i$	
$\dfrac{\partial}{\partial \mathbf{Q}_i} \cdot \dfrac{\partial}{\partial \mathbf{Q}_j}$	k_{ij}	λ_{ij}		
$\dfrac{\partial}{\partial \mathbf{Q}_i}\left(\dfrac{\partial}{\partial \mathbf{Q}_j} \cdot \dfrac{\partial}{\partial \mathbf{Q}_k}\right)$	$\mathbf{a}_{ijk}$			

Collection of all derivatives is given in Table I. The only one not yet defined within the third order is λ the derivative of the force constant

$$\lambda_{ij} = \left(\frac{\partial}{\partial N}\left(\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial E}{\partial \mathbf{Q}_j}\right)_{N}\right)_{N}\right)_{\mathbf{Q}} = \left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}}. \quad (24)$$

By writing the differential of force $\mathbf{F}_i$ in [N, **Q**] representation, the Maxwell relation involving this derivative gives the results:

$$d\mathbf{F}_i = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} dN + \sum_j \left(\frac{\partial \mathbf{F}_i}{\partial \mathbf{Q}_j}\right)_{N} d\mathbf{Q}_j = \mathbf{\Phi}_i dN - \sum_j k_{ij} d\mathbf{Q}_j, \quad (25)$$

$$\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_j}\right)_{N} = -\left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}} = -\lambda_{ij}. \quad (26)$$

Thermodynamic Potential Function $\Omega(\mu, \mathbf{Q})$ and Its Derivatives

Considering Eq. (3), the similar set of derivatives may be expressed in the [μ, **Q**] representation with the thermodynamic potential given as $\Omega = E - \mu N$. The total differential thereof becomes [cf. Eq. (11)]:

$$d\Omega = -N d\mu - \sum_i \mathbf{F}_i \cdot d\mathbf{Q}_i. \quad (27)$$

Hence:

$$\left(\frac{\partial \Omega}{\partial \mathbf{Q}_i}\right)_{\mu} = -\mathbf{F}_i, \quad (28)$$

and the Maxwell relation follows, giving the nuclear softness $\boldsymbol{\sigma}_i$:

$$\left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial \mathbf{F}_i}{\partial \mu}\right)_{\mathbf{Q}} \equiv \boldsymbol{\sigma}_i. \quad (29)$$

The thermodynamic potential derivatives over μ belong to the standard of the conceptual DFT and remain unchanged in [μ, **Q**] representation [14, 18]:

$$\left(\frac{\partial \Omega}{\partial \mu}\right)_{\mathbf{Q}} = -N \quad \text{and} \quad \left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = S. \quad (30)$$

However, the differential of N leads to yet another Maxwell relation, by which the nuclear and electronic softness (S) are related:

$$dN = S d\mu + \sum_i \boldsymbol{\sigma}_i \cdot d\mathbf{Q}_i, \quad (31)$$

$$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_{\mu}. \quad (32)$$

By formulating the differential of the electron density, the electron nuclear softness kernel, $\boldsymbol{\sigma}_i(\mathbf{r})$, appears

$$d\rho(\mathbf{r}) = s(\mathbf{r}) d\mu + \sum_i \boldsymbol{\sigma}_i(\mathbf{r}) d\mathbf{Q}_i, \quad (33)$$

where $s(\mathbf{r}) = (\partial \rho(\mathbf{r})/\partial \mu)_{\mathbf{Q}}$ and

$$\boldsymbol{\sigma}_i(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mu}\left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} = \tilde{f}(\mathbf{r}) \boldsymbol{\sigma}_i; \quad (34)$$

TABLE II _____

Derivatives of the grand canonical thermodynamic potential in the $[\mu, \mathbf{Q}]$ representation in the third order.[a]

Thermodynamic potential derivative	$\mathbf{Q} = const \rightarrow$	$\dfrac{\partial}{\partial \mu}$	$\dfrac{\partial^2}{\partial \mu^2}$	$\dfrac{\partial^3}{\partial \mu^3}$
$\mu = const \downarrow$	Ω	$-N$	$-S$	γS^3
$\dfrac{\partial}{\partial \mathbf{Q}_i}$	$-\mathbf{F}_i$	$-(\boldsymbol{\sigma}_i = S\boldsymbol{\Phi}_i)$	$S^2[\mathbf{G}_i + \gamma S\boldsymbol{\Phi}_i]$	
$\dfrac{\partial}{\partial \mathbf{Q}_i} \cdot \dfrac{\partial}{\partial \mathbf{Q}_j}$	$\tilde{k}_{ij}$	$\tilde{\lambda}_{ij}$		
$\dfrac{\partial}{\partial \mathbf{Q}_i}\left(\dfrac{\partial}{\partial \mathbf{Q}_j} \cdot \dfrac{\partial}{\partial \mathbf{Q}_k}\right)$	$\tilde{\mathbf{a}}_{ijk}$			

[a] The discussion of $\tilde{k}_{ij}$, $\tilde{\mathbf{a}}_{ijk}$, and $\tilde{\lambda}_{ij}$ derivatives is given separately [20].

$\tilde{f}(\mathbf{r})$ is analogous to the Fukui function

$$\tilde{f}(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_\mu. \qquad (35)$$

The Maxwell relation that follows from Eq. (33) reads:

$$\left(\frac{\partial s(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu = \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial \mu}\right)_\mathbf{Q}$$

$$= \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial N}\right)_\mathbf{Q}\left(\frac{\partial N}{\partial \mu}\right)_\mathbf{Q} = \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial N}\right)_\mathbf{Q} S. \qquad (36)$$

The local function $\boldsymbol{\sigma}_i(\mathbf{r})$ produces $\boldsymbol{\sigma}_i$ by integration, as originally proved by Cohen et al. [19]:

$$\int \boldsymbol{\sigma}_i(\mathbf{r})d\mathbf{r} = \int \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu d\mathbf{r}$$

$$= \left(\frac{\partial}{\partial \mathbf{Q}_i}\int \rho(\mathbf{r})d\mathbf{r}\right)_\mu = \left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_\mu = \boldsymbol{\sigma}_i. \qquad (37)$$

The important results of this analysis are again relations between nuclear derivatives within the $[\mu, \mathbf{Q}]$ representation and the local ones in the classical DFT formulation. They are:

$$\left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_\mu = \int \left(\frac{\partial S}{\partial v(\mathbf{r})}\right)_\mu\left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu d\mathbf{r}$$

$$= -\int \left(\frac{\partial S}{\partial v(\mathbf{r})}\right)_\mu \boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = -\int \left(\frac{\partial s(\mathbf{r})}{\partial N}\right)_\mu \boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}, \qquad (38)$$

$$\boldsymbol{\sigma}_i = \left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_\mu = \int \left(\frac{\partial N}{\partial v(\mathbf{r})}\right)_\mu\left(\frac{\partial v(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu d\mathbf{r}$$

$$= \int s(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = S\int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = S\boldsymbol{\Phi}_i, \qquad (39)$$

$$\boldsymbol{\sigma}_i(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu = \int \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')}\right)_\mu\left(\frac{\partial v(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_\mu d\mathbf{r}'$$

$$= \int s(\mathbf{r}, \mathbf{r}')\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}, \qquad (40)$$

where $s(\mathbf{r}, \mathbf{r}')$ is the softness kernel [18].

It is now possible to complete the set of derivatives of the thermodynamic potential (Table II). The missing derivatives of softness are expressed using derivatives already known from Table I. A simple relation is helpful:

$$\left(\frac{\partial \eta}{\partial \mu}\right)_\mathbf{Q} = \left(\frac{\partial \eta}{\partial N}\right)_\mathbf{Q}\left(\frac{\partial N}{\partial \mu}\right)_\mathbf{Q} = \gamma S. \qquad (41)$$

Let the differential of global hardness be:

$$d\eta = \left(\frac{\partial \eta}{\partial \mu}\right)_\mathbf{Q} d\mu + \sum_i \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_\mu \cdot d\mathbf{Q}_i. \qquad (42)$$

By using Eq. (13), the following is produced:

$$d\eta = \frac{1}{S}\left(\frac{\partial \eta}{\partial \mu}\right)_\mathbf{Q} dN + \sum_i \left(\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_\mu - \gamma S\boldsymbol{\Phi}_i\right) \cdot d\mathbf{Q}_i. \qquad (43)$$

Confronting this result with Eq. (15) provides the first result:

$$\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_\mu = \mathbf{G}_i + \gamma S \mathbf{\Phi}_i. \tag{44}$$

Derivative of softness is now readily obtained:

$$\left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_\mu = \left(\frac{\partial}{\partial \mathbf{Q}_i}\frac{1}{\eta}\right)_\mu = -S^2\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_\mu = -S^2[\mathbf{G}_i + \gamma S \mathbf{\Phi}_i]_\mathbf{Q}. \tag{45}$$

Also:

$$\left(\frac{\partial S}{\partial \mu}\right)_\mathbf{Q} = \left(\frac{\partial S}{\partial N}\right)_\mathbf{Q}\left(\frac{\partial N}{\partial \mu}\right)_\mathbf{Q} = -\gamma S^3. \tag{46}$$

The collection of all derivatives of the thermodynamic potential is given in Table II. When possible, the derivatives have been related to already known energy derivatives in Table I, which then serve as a basis set for numerical studies. The analysis of analogs of the force constant $\tilde{k}_{ij}$ and the tensor of anharmonicity $\tilde{\mathbf{a}}_{ijk}$ (calculated at constant μ), as well as the mixed derivative $\tilde{\lambda}_{ij}$ is presented separately [20].

Renormalization of $E(N, \mathbf{Q})$ and $\Omega(\mu, \mathbf{Q})$ Derivatives for an Oscillating System

The partial derivatives specified in Tables I and II allow writing the energy and thermodynamic potential expansions into the Taylor series up to the third order. Because by definition, $\mathbf{Q}_i = \Delta\mathbf{Q}_i$, the expansions in the kartesian coordinates are, respectively (the first derivative $\mathbf{F}_i = 0$, as the expansion is done at the equilibrium position of the molecule):

$$\Delta E[N, \mathbf{Q}] = \Delta N\mu + \frac{1}{2}(\Delta N)^2\eta - \Delta N \sum_i \mathbf{\Phi}_i\mathbf{Q}_i$$

$$+ \frac{1}{2}\sum_{i,j} k_{ij}\mathbf{Q}_i\mathbf{Q}_j + \frac{1}{6}\sum_{i,j,k} \mathbf{a}_{ijk}\mathbf{Q}_i\mathbf{Q}_j\mathbf{Q}_k + \frac{1}{6}\gamma(\Delta N)^3$$

$$+ \frac{1}{2}(\Delta N)^2 \sum_i \mathbf{G}_i\mathbf{Q}_i + \frac{1}{2}\Delta N \sum_{i,j} \lambda_{ij}\mathbf{Q}_i\mathbf{Q}_j. \tag{47}$$

$$\Delta\Omega[\mu, \mathbf{Q}] = -N\Delta\mu + \frac{1}{2}S(\Delta\mu)^2 - S\Delta\mu \sum_i \mathbf{\Phi}_i\mathbf{Q}_i$$

$$+ \frac{1}{2}\sum_{i,j} \tilde{k}_{ij}\mathbf{Q}_i\mathbf{Q}_j + \frac{1}{6}\sum_{i,j,k} \tilde{\mathbf{a}}_{ijk}\mathbf{Q}_i\Delta\mathbf{Q}_j\mathbf{Q}_k + \frac{1}{6}\gamma S^3(\Delta\mu)^3$$

$$+ \frac{1}{2}(\Delta\mu)^2 \sum_i (\mathbf{G}_i + \gamma S\mathbf{\Phi}_i)\mathbf{Q}_i + \frac{1}{2}\Delta\mu \sum_{i,j} \tilde{\lambda}_{ij}\mathbf{Q}_i\mathbf{Q}_j. \tag{48}$$

Transformations of the expansions to the normal coordinate system of the molecule is readily performed:

$$Q_\alpha = \sum_i \mathbf{Q}_i \cdot \mathbf{l}_i^\alpha \quad \text{where} \quad \sum_i \mathbf{l}_i^\alpha \mathbf{l}_i^\beta = \delta_{\alpha\beta}. \tag{49}$$

The expansion is much simplified by introducing the projection of the vectors onto the normal modes. Practical realization of that transformation is shown in Ref. [9],

$$\sum_i \mathbf{l}_i^\alpha \cdot \mathbf{F}_i = F_\alpha, \quad \sum_i \mathbf{l}_i^\alpha \cdot \mathbf{\Phi}_i = \varphi_\alpha, \quad \sum_i \mathbf{l}_i^\alpha \cdot \mathbf{G}_i = G_\alpha. \tag{50}$$

Tensorial derivatives also get transformed as:

$$\sum_{i,j} (\mathbf{l}_i^\alpha \cdot \mathbf{l}_j^\beta)k_{ij} = k_\alpha\delta_{\alpha\beta}, \quad \sum_{i,j} (\mathbf{l}_i^\alpha \cdot \mathbf{l}_j^\beta)\lambda_{ij} = \lambda_\alpha\delta_{\alpha\beta},$$

$$\alpha_{\alpha\beta} = \sum_i \frac{\partial k_\alpha}{\partial \mathbf{Q}_i} \cdot \mathbf{l}_i^\beta. \tag{51}$$

In the normal coordinates, Eq. (47) becomes:

$$\Delta E[N, Q] = \Delta N\mu + \frac{1}{2}(\Delta N)^2\eta - \Delta N \sum_\alpha \varphi_\alpha Q_\alpha$$

$$+ \frac{1}{2}\sum_\alpha k_\alpha Q_\alpha^2 + \frac{1}{6}\sum_{\alpha,\gamma} a_{\alpha\gamma}Q_\alpha^2 Q_\gamma + \frac{1}{6}\gamma(\Delta N)^3$$

$$+ \frac{1}{2}(\Delta N)^2 \sum_\alpha G_\alpha Q_\alpha + \frac{1}{2}\Delta N \sum_\alpha \lambda_\alpha Q_\alpha^2. \tag{52}$$

Transformation of the thermodynamic potential may readily be done by the same manner, but the transformation matrix (and the normal coordinates $\tilde{Q}_\alpha$) will not be the same, as it is evident from the diagonalization of $\tilde{k}_{ij} \neq k_{ij}$ and $\sum_{i,j} (\tilde{\mathbf{l}}_i^\alpha \cdot \tilde{\mathbf{l}}_j^\beta)\tilde{k}_{ij} = \tilde{k}_\alpha\delta_{\alpha\beta}$. Resulting projections of the derivatives ($\tilde{F}_\alpha$, $\tilde{\varphi}_\alpha$, $\tilde{G}_\alpha$, $\tilde{k}_\alpha$, $\tilde{\lambda}_\alpha$, and $\tilde{a}_{\alpha\gamma}$) can be expressed by means of the

derivatives in the normal coordinate system, leading to an interesting description of coupling between the normal vibrational modes [12]. This problem is addressed separately [20], as this current analysis is limited to the energy expansions rather than to the coupling effects. For the sake of completeness, the expansion of $\Omega[\mu, \tilde{Q}_\alpha]$ is presented only:

$$\Delta\Omega[\mu, \tilde{Q}_\alpha] = -N\Delta\mu - \frac{1}{2} S(\Delta\mu)^2 - S\Delta\mu \sum_\alpha \tilde{\varphi}_\alpha \tilde{Q}_{\alpha i}$$

$$+ \frac{1}{2} \sum_\alpha \tilde{k}_\alpha \tilde{Q}_{\alpha i}^2 + \frac{1}{6} \sum_{\alpha,\gamma} \tilde{a}_{\alpha,\gamma} \tilde{Q}_{\alpha i}^2 \tilde{Q}_\gamma + \frac{1}{6} \gamma S^3 (\Delta\mu)^3$$

$$+ \frac{1}{2} (\Delta\mu)^2 \sum_\alpha (\tilde{G}_\alpha + \gamma S\tilde{\varphi}_\alpha)\tilde{Q}_\alpha + \frac{1}{2}\Delta\mu \sum_\alpha \tilde{\lambda}_\alpha \tilde{Q}_{\alpha i}^2. \quad (53)$$

Equations (52) and (53) can get renormalized by introducing the natural coupling conditions at equilibrium: $\mathbf{F}_i = 0$, thus

$$\left(\frac{\partial E}{\partial Q_\alpha}\right)_N = 0$$

and

$$\left(\frac{\partial \Omega}{\partial \tilde{Q}_\alpha}\right)_\mu = 0.$$

Unfortunately, the workable results can be obtained only when the third-order terms are dropped [11], and they are:

$$\Delta E[N, Q_\alpha] = \mu\Delta N + \frac{1}{2} \eta'_{ren} \Delta N^2, \quad (54)$$

$$\Delta\Omega[\mu, \tilde{Q}_\alpha] = -N\Delta\mu - \frac{1}{2} S'_{ren}\Delta\mu^2. \quad (55)$$

This is equivalent to defining the renormalized hardness and softness, respectively, around equilibrium as

$$\eta'_{ren} = \frac{d^2 E}{dN^2} = \eta - \sum_\alpha \frac{\varphi_\alpha^2}{k_\alpha} \quad (56)$$

$$S'_{ren} = \frac{d^2\Omega}{d\mu^2} = S + S^2 \sum_\alpha \frac{\tilde{\varphi}_\alpha^2}{\tilde{k}_\alpha}. \quad (57)$$

The result cannot be extended beyond the equilibrium due both to the limitation of the expansion and to its truncation. Overcoming this limitation is possible using the expansion to the energy proposed by Liu and Parr [1]. The authors showed that the energy functional, if (and only if) limited to the second order of expansion, can be reproduced exactly by the function of the second order. Applying their method to $E(N, Q_\alpha)$ and $\Omega(\mu, Q_\alpha)$ gives, after reworking the expression to their respective normal coordinates [12]:

$$E[N, Q_\alpha] = \mu N - \sum_\alpha F_\alpha Q_\alpha - \frac{1}{2} \eta N^2$$

$$+ N \sum_\alpha Q_\alpha \varphi_\alpha - \frac{1}{2} \sum_\alpha k_\alpha Q_\alpha^2 + const, \quad (58)$$

$$\Omega[\mu, \tilde{Q}_\alpha] = -\mu N - \sum_\alpha \tilde{Q}_\alpha \tilde{F}_\alpha + \frac{1}{2} \mu^2 S$$

$$+ \mu S \sum_\alpha \tilde{Q}_\alpha \tilde{\varphi}_\alpha - \frac{1}{2} \sum_\alpha \tilde{k}_\alpha \tilde{Q}_\alpha^2 + const. \quad (59)$$

Although formally very similar to the Taylor expansions, and still limited to the second order, these equations are remarkably superior in practice, as the coefficients are now functions, not numbers, and hence the use of Eqs. (58) and (59) is not limited to the point of equilibrium. By taking the derivatives over Q_α, the nonzero forces are now obtained, and all functional coefficients in Eqs. (58) and (59) must be differentiated. This order analysis is equivalent to assuming that although the third-order effects may not be important for the energy [Eqs. (58) and (59)], they may well be crucial for its derivative, the force [Eqs. (60) and (61)]:

$$\left(\frac{\partial E}{\partial Q_\alpha}\right)_N = -F_\alpha - \frac{1}{2} N^2 G_\alpha - \lambda_\alpha Q_\alpha N = -F_{\alpha'}$$

$$\text{hence, } Q_\alpha = -\frac{NG_\alpha}{2\lambda_\alpha}; \quad (60)$$

$$\left(\frac{\partial \Omega}{\partial \tilde{Q}_\alpha}\right)_\mu = -\tilde{F}_\alpha + \frac{1}{2} \mu^2 S^2 \tilde{G}_\alpha - \mu\tilde{Q}_\alpha\tilde{\lambda}_\alpha = -\tilde{F}_{\alpha'}$$

$$\text{hence, } \tilde{Q}_\alpha = \mu S^2 \frac{\tilde{G}_\alpha}{2\tilde{\lambda}_\alpha}. \quad (61)$$

Only two simplifications of minor importance have been introduced in the above: $\gamma = 0$ and all anharmonic effects neglected, $a_{\alpha\beta} = 0$. Eliminating $Q_\alpha(\tilde{Q}_\alpha)$ leads to the renormalized functions:

$$E[N, Q_\alpha] = N\mu_{ren} - \frac{1}{2}N^2\eta_{ren} + const., \quad (62)$$

where

$$\mu_{ren} = \frac{dE}{dN} = \mu + \sum_\alpha \frac{G_\alpha F_\alpha}{2\lambda_\alpha}$$

and

$$\eta_{ren} = \frac{d^2E}{dN^2} = \eta + \sum_\alpha \frac{G_\alpha}{\lambda_\alpha}\left(\varphi_\alpha + \frac{G_\alpha k_\alpha}{4\lambda_\alpha}\right),$$

$$\Omega[\mu, \tilde{Q}_\alpha] = -\mu N_{ren} + \frac{1}{2}\mu^2 S_{ren} + const. \quad (63)$$

where

$$N_{ren} = -\frac{d\Omega}{d\mu} = N + \frac{1}{2}S^2\sum_\alpha \frac{\tilde{G}_\alpha}{\tilde{\lambda}_\alpha}\tilde{F}_\alpha$$

and

$$S_{ren} = -\frac{d^2\Omega}{d\mu^2} = S + S^3\sum_\alpha \frac{\tilde{\varphi}_\alpha \tilde{G}_\alpha}{\tilde{\lambda}_\alpha} - \frac{1}{4}S^4\sum_\alpha \tilde{k}_\alpha \frac{\tilde{G}_\alpha^2}{\tilde{\lambda}_\alpha^2}.$$

The importance of this result is in its general character of the renormalized derivatives. It is now possible to analyze how the actual vibrations change the apparent chemical potential and hardness of an oscillating molecule. Results available hitherto were limited to the trivial approximation only, Eq. (56) [9, 11].

Results

The effect of renormalization has been studied numerically for a set of diatomic molecules. Calculations were performed using Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang, and Parr (B3LYP) and 6-311+G(3df, 3dp) basis set for Gaussian 98 code [21]. Geometry was optimized for a neutral molecule by a quasi–Newton-Raphson procedure. Cal-

culations were based on our earlier results obtained within the analysis of thermal fluctuations [9] where the scheme for calculation of thermal average values for the nuclear reactivity and nuclear stiffness has been introduced for each normal mode: $\varphi_\alpha = \varphi_{\alpha,o}\langle Q_\alpha^2\rangle^{1/2}$, and $G_\alpha = G_{\alpha,o}\langle Q_\alpha^2\rangle^{1/2}$. The nuclear reactivity and nuclear stiffness for a rigid structure (unperturbed by oscillation, $\varphi_{\alpha,o}$ and $G_{\alpha,o}$), are readily calculated from the forces, as shown in previous works [6, 9]. In accord with the harmonic level of approximation (neglecting the anharmonicity) the thermal average of force has been introduced as $F_\alpha = -k_\alpha\langle Q_\alpha^2\rangle^{1/2}$, whereas the force constants k_α and the λ_α were assumed to be independent on the nuclear displacements Q_α, well in accord with the map of the derivatives presented in Table I. The average thermal displacement for a normal mode has been used as in Ref. [9].

$$\langle Q_\alpha^2\rangle = \left\langle \sum_{i\in\alpha}(Q_i^\alpha)^2\right\rangle = \frac{\hbar\omega_\alpha}{2k_\alpha}ctgh\frac{\hbar\omega_\alpha}{2k_BT}. \quad (64)$$

The effect of renormalization has been represented as $\Delta\mu = \mu_{ren} - \mu$, and $\Delta\eta = \eta_{ren} - \eta$; the final results expresses changes in the chemical potential and global hardness of an oscillating entity, with respect to its rigid structure:

$$\Delta\mu = -\frac{1}{2}\sum_\alpha \frac{k_\alpha G_{\alpha,o}}{\lambda_\alpha}\langle Q_\alpha^2\rangle, \quad (65)$$

$$\Delta\eta = \sum_\alpha\left[\frac{G_{\alpha,o}\varphi_{\alpha,o}}{\lambda_\alpha} + \frac{k_\alpha G_{\alpha,o}^2}{4\lambda_\alpha^2}\right]\langle Q_\alpha^2\rangle. \quad (66)$$

Considering the property of the *ctgh* function in Eq. (64), the $T \to 0$ limit of $\Delta\mu$ and $\Delta\eta$ can readily be envisaged as:

$$\Delta\mu_o = -\frac{1}{4}\sum_\alpha \hbar\omega_\alpha\frac{G_{\alpha,o}}{\lambda_\alpha}, \quad (67)$$

$$\Delta\eta_o = \frac{1}{2}\sum_\alpha\left[\frac{G_{\alpha,o}\varphi_{\alpha,o}}{k_\alpha\lambda_\alpha} + \frac{G_\alpha^2}{4\lambda_\alpha^2}\right]\hbar\omega_\alpha. \quad (68)$$

These values should contain the essence of a molecule sensitivity to thermal vibration, in terms of its electronegativity $(-\mu)$ and global hardness. They have been calculated for a set of diatomic molecules and collected in Table III. The result is compared

TABLE III _____

Calculated zero temperature limits of renormalizing correction to the electronegativity [$\Delta\chi_o = -\Delta\mu_o$, Eq. (67)] and to the global hardness [$\Delta\eta_o$, Eq. (68)].[a]

Molecule	$\chi = \dfrac{I+A}{2}$	$\eta = I - A$	$\hbar\omega$	$\Delta\chi_o$	$\Delta\eta_o$	$\Delta\eta' \times 10^3$
LiH	4.003	7.458	0.1764	0.2879	0.9760	−0.3497
HF	6.913	18.93	0.5173	−0.1088	0.0453	−0.0008
F$_2$	7.676	15.156	0.1213	0.0075	−0.0011	−1.0939
Cl$_2$	6.048	10.664	0.0716	0.0130	0.0018	−0.4634
Li$_2$	2.595	0.092	0.0420	−0.0251	0.0294	−0.0042
FCl	6.599	12.308	0.0985	−0.0027	0.0008	−0.7661
CO	5.981	15.798	0.2638	0.0124	0.0007	−0.0431
LiF	5.978	11.184	0.1096	−0.0455	0.0400	−0.0318
BCl	4.739	10.126	0.1071	0.0649	0.0679	−0.3694
BH	4.702	9.364	0.3022	0.0386	0.0080	−0.0860
CS	5.522	11.534	0.1624	−0.0037	0.0005	−0.1529
NF	6.066	8.842	0.1563	−0.0007	0.0001	−0.3903
SO	5.476	7.104	0.1282	−0.0050	0.0007	−0.0768
HCl	5.365	14.554	0.3792	−0.0207	0.0026	−0.0117
LiCl	5.214	9.35	0.0779	−0.0556	0.0739	−0.0978
BF	4.864	11.856	0.1737	0.0048	0.0000	−0.0772
SiO	5.936	12.178	0.1470	0.0065	0.0004	−0.0085

[a] The first approximation to renormalization correction resulting from Eq. (56) is also given as $\Delta\eta' = -(\varphi_o^2/2k^2)\hbar\omega$. All values are in electron volts. The necessary data were taken from: Refs. [6] (φ, G, and η), [11] (k, λ, and χ), and [10] ($\hbar\omega$). The G and η values employed here are the derivatives, without the 1/2 factor frequently used in older works, the source data have been multiplied accordingly.

with the analogous crude estimate to renormalized hardness, given by Eq. (56) in the $T \to 0$ limit:

$$\Delta\eta'_o = -\sum_\alpha \frac{\varphi_{\alpha,o}^2}{2k_\alpha^2} \hbar\omega_\alpha.$$

For the sake of clarity, the hardness η as defined in the current work [Eq. (9)] does not contain the (1/2) factor, frequently used in the definition of hardness in the past; the same concerns to the nuclear stiffness G.

Calculation of renormalized values of N and S in Eq. (63) is possible for the diatomic molecules since for one vibration $1_i = \tilde{1}_i$ and, consequently, $F = \tilde{F}$, $\varphi = \tilde{\varphi}$, $G = \tilde{G}$; however, $k \neq \tilde{k}$, $\lambda \neq \tilde{\lambda}$. As demonstrated elsewhere [12, 20] for the diatomic molecule, with the neglect of γ, very simple formulae apply:

$$\tilde{k} = k - S\varphi^2, \text{ and } \tilde{\lambda} = S\lambda + 2S^2\varphi G. \quad (69)$$

The renormalization effects in $\Delta N = N_{ren} - N$ and $\Delta S = S_{ren} - S$ become:

$$\Delta N = \frac{SGF}{2(\lambda + 2S\varphi G)} \quad (70)$$

$$\Delta S = S^2 \frac{(4\lambda\varphi G + 8S\varphi^2 G^2 - kG^2)}{4(\lambda + 2S\varphi G)^2}. \quad (71)$$

Proceeding by the method described above, F, φ, G may be replaced by their thermal average values, and the limit value at $T \to 0$ has been calculated as ΔN_o and ΔS_o in Table IV. However, due to the more complicated functions in Eqs. (70) and (71) as compared with those in Eqs. (65) and (66), these limit values are not necessarily minimal ones. The same concerns apply to the first approximation to the renormalization correction for softness resulting from Eq. (57), $\Delta S' = S'_{ren} - S = S^2(\varphi^2/k - S\varphi^2)$; its $T \to 0$ limit has also been calculated as $\Delta S'_o$. Analysis of the temperature dependence of the renormalization effects as well as their dependence on the frequency ($\hbar\omega$)/force constant (k) is an interesting topic for further studies.

TABLE IV _____

Calculated zero temperature limits of renormalizing correction to number of electrons and softness, ΔN_o and ΔS_o, calculated according to Eqs. (70) and (71).[a]

Molecule	S	$\Delta S_o \times 10^3$	$\Delta S_o' \times 10^3$	$\Delta N_o \times 10^3$
LiH	0.1341	0.2642	0.0063	−38.2312
HF	0.0528	−0.0022	0.0000	5.7479
F$_2$	0.0660	−0.0089	0.0047	−0.4962
Cl$_2$	0.0938	−0.0264	0.0041	−1.2188
Li$_2$	10.8696	−133.5079	0.4967	277.6545
FCl	0.0812	0.0044	0.0050	0.2190
CO	0.0633	−0.0018	0.0002	−0.7848
LiF	0.0894	0.0168	0.0003	4.0706
BCl	0.0988	−0.1120	0.0036	−6.4224
BH	0.1068	−0.0226	0.0010	−4.1290
CS	0.0867	0.0024	0.0011	0.3240
NF	0.1131	0.0013	0.0050	0.0811
SO	0.1408	0.0069	0.0015	0.7081
HCl	0.0687	0.0014	0.0001	1.4218
LiCl	0.1070	−0.0712	0.0011	5.9589
BF	0.0843	−0.0020	0.0005	−0.4036
SiO	0.0821	−0.0010	0.0001	−0.5374

[a] The softness used in calculation is calculated from hardness listed in column 3, Table III, from $\eta S = 1$. The first approximation to renormalization correction for softness, resulting from Eq. (57), is also given, $\Delta S_o' = [S^2 \varphi_o^2 (\hbar \omega)/2k^2 - S\varphi_o^2(\hbar \omega)]$, in the $T \to 0$ limit. The necessary data were taken from Refs. [6] (φ, G, and η), [11] (k and λ), and [10] ($\hbar \omega$).

Conclusions

Renormalization of the physically sound derivatives for an oscillating molecule, as performed beyond the trivial second-order procedure, revealed both qualitative and quantitative effects, possibly important for chemical applications. The renormalized values are, from the practical point of view, the only appropriate ones for an oscillating entity at given temperature. Hence, it is of primary importance for a chemist to predict how the properties of a molecule change when temperature rises. This effect can be clearly observed for electronegativity (negative chemical potential) and hardness. Although renormalization corrections are minor (at $T \to 0$), they might become quite important at real temperatures, the effect being dependent primarily on the vibrational frequencies; effects of many vibrations are additive, low frequency modes matter most, and large φ is essential. The sign of the effect can be predicted with some confidence. As discussed before, $G < 0$ is expected [11]. Also, the recent calculations revealed $\lambda < 0$ for the set of molecules studied [20]. Hence, typically $\Delta \mu = \mu_{ren} - \mu < 0$ [Eq. (62)], or $\Delta \chi > 0$;

renormalized electronegativity tends to increase upon vibrations. The change in hardness, $\Delta \eta' = \eta'_{ren} - \eta$, Eq. (56), is always negative and negligibly small in the crude approximation. The more refined, quasi–third-order result [$\Delta \eta = \eta_{ren} - \eta$, Eq. (62)] indicates, however, that the change in hardness may be much larger. Its sign escapes easy predictions, as the sign for φ cannot be a priori determined; however, both $\Delta \chi$ and $\Delta \eta$ increase monotonically with temperature. Variable electronegativity and hardness have very familiar meaning for a chemist, as these parameters have been recognized as stimulating the charge transfer through the simple formula $\Delta N_{AB} = -(\mu_A - \mu_B)/2(\eta_A + \eta_B)$ [18]. Also, the energy gain in this process, known as the charge transfer affinity [22] may be considerably modified by temperature for vibrating molecules.

The change in μ and η may also be a direct consequence of the nuclear displacement, coupled with the actual change in N [Eq. (60)], should the contact time between two entities be sufficiently long to bring them to thermal equilibrium. Such mechanism has been referred to as the "electron preceding" [15]: the initial charge transfer δN induces the change in the equilibrium nuclear posi-

tions $\delta \mathbf{Q}$, and this stimulates changes in $\delta \mu$ and $\delta \eta$, thus coupling the process back to its origin. It is an appealing model for a chemical reaction, as it opens a way to include the N–$\mathbf{Q}$ coupling as an effect enhancing or preventing the charge transfer between molecules. A more reliable method of calculation of the derivatives is now needed in order to assess the importance of the effect in practice.

The renormalization of the derivatives of the thermodynamic potential Ω presented here for the first time has also very interesting physical meaning. Equation $\Delta N \neq 0$ means simply that when chemical potential is an independent variable, the system must be open: one cannot change the global value of μ unless the number of electrons is allowed to change! This electron flow appears here as a direct result of the displacement of nuclei, when a molecule is brought to thermal contact with a reservoir that determines μ (solid surface, large molecule); such mechanism has been referred to as the "electron following" [15]. This in turn must bring a change in softness, very much in accord with the known relation of the softness to the dimension and the polarizability of the system [18]. The renormalization corrections $\Delta N = N_{ren} - N$ and $\Delta S = S_{ren} - S$ are complex functions of temperature [Eq. (63)]; their analysis may be of value in studies of molecules adsorbed on solid surfaces. The actual values of the energy derivatives as collected in Tables I and II allow, at least in principle, one to describe this process quantitatively.

ACKNOWLEDGMENTS

References

1. Liu, S.; Parr, R. G. J Chem Phys 1997, 106, 5578.
2. Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnowsky, J. J Chem Phys 1994, 101, 8988.
3. Baekelandt, B. G.; Cedillo, A.; Parr, R. G. J Chem Phys 1995, 103, 8548.
4. Berkowitz, M.; Ghosh, S. K.; Parr, R. G. J Am Chem Soc 1995, 107, 6811.
5. Baekelandt, B. G. J Chem Phys 1996, 105, 4664.
6. Ordon, P.; Komorowski, L. Chem Phys Lett 1998, 292, 22.
7. Balawender, R.; Geerlings, P. J Chem Phys 2001, 114, 682.
8. De Proft, F.; Liu, S.; Geerlings, P. J Chem Phys 1998, 108, 7549.
9. Komorowski, L.; Ordon, P. J Mol Struct (Theochem) 2003, 25, 630.
10. Komorowski, L.; Ordon, P. Int J Quantum Chem 2003, 91, 398.
11. Komorowski, L.; Ordon, P. Theor Chem Acc 2001, 105, 338.
12. Ordon, P. PhD Thesis; Wrocław University of Technology: Poland, 2003.
13. Fuentalba, P.; Parr, R. G. J Chem Phys 1991, 94, 5559.
14. Geerlings, P.; De Proft, F.; Langenacker, W. Chem Rev 2003, 103, 1793.
15. Nalewajski, R. Comput Chem 2000, 24, 243.
16. Luty, T. Molecular Physics Reports; Institute of Molecular Physics, Polish Academy of Science: Poznań, 1996, 14, 157–167.
17. Luty, T.; Ordon, P.; Eckhardt, C. J. J Chem Phys 2002, 117, 1775.
18. Parr, R. G.; Yang, W. Density Functional Theory of Atoms and Molecules; Oxford University Press: Oxford, 1989.
19. Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnowsky, J. J Chem Phys 1995, 103, 3543.
20. Komorowski, L.; Ordon, P. Int J Quantum Chem 2004, 99, 153.
21. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision A.1; Gaussian: Pittsburgh, 1995.
22. Komorowski, L. Chem Phys 1987, 114, 55.