DFT Analysis of Fluctuations in Electronegativity and Hardness of a Molecular Oscillator

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ABSTRACT: This work extends application of the density functional theory apparatus to the analysis of thermal fluctuations. It focuses on expectations concerning the role of molecular deformation in changing the global hardness and electronegativity (chemical potential), and hence, the affinity for an intermolecular electron exchange. Molecular harmonic oscillations, the most common molecular deformations, have been analyzed in detail to discover the circumstances, leading to significant modifications in electronegativity and hardness of the molecule. The mean fluctuations of electronegativity and global hardness have been analyzed for a harmonic oscillator. The nuclear reactivity and nuclear stiffness indices have been explored in calculation of thermal fluctuations for any system, harmonic as well as anharmonic. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 91: 398–403, 2003

Key words: chemical electronegativity; fluctuations; global hardness; harmonic oscillator; thermal excitations

Introduction

Conceptual density functional theory (DFT) has offered important tools for the analysis of chemical reactivity of molecules [1]. The affinity toward intermolecular electron transfer has been related to global thermodynamically based quantities: electronegativity (χ) (negative chemical potential), and global hardness (η). However, applications of the DFT to actual molecules have been typically limited to 0 K limit [2–4]. Profound thermodynamic analysis proposed by Nalewajski [5] has not yet been further explored in practice.

An original new approach has recently been proposed in this laboratory [6, 7], based on the earlier work by Cohen [8]. These studies exposed the role of molecular vibrations and proved that they may lead to substantial changes of molecular parameters (χ, η) and, hence, of the affinity to the intermolec-

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ular electron transfer [9]. Not surprisingly, the more anharmonic are the vibrations, the stronger is the effect on χ, η. For the strictly harmonic oscillator, nontrivial dependence on deformation has been discovered for global hardness only [7, 10]. In all cases, the nature and the character of dependence of χ and η on deformation has been related to specific (chemical) nature of bonds between various atoms.

The current work is focused on the analysis of thermal effects on χ and η through the intramolecular vibrations. A molecule in its equilibrium ground state at constant temperature T is considered. The ensemble formulation of $\langle\chi\rangle$ and $\langle\eta\rangle$ is given first. Then, the role of temperature through the state mixing is shown analytically for a model harmonic oscillator. Finally, specific characteristics of a set of diatomic molecules is provided on the ab initio level, exploring earlier results for nuclear reactivity (Φ) and nuclear stiffness (G), as defined in Ref. [6].

Ensemble Electronegativity and Hardness: Definitions

Two different definitions are possible for electronegativity within canonical ensemble. The number of electrons is fixed, as is external potential $V(\mathbf{r})$; energy fluctuates due to energy reservoir of temperature T; molecule can occupy energy levels E_ν. Let the microstate energy levels E_ν be modified when the total number of electron N in the system changes but the structure and symmetry of the system remains unchanged. Such assumption may not be reasonable for electronic energy levels; only the vibrational levels associated with the ground electronic state will be focused on here. The microstate electronegativity and hardness can be defined as (the conventionally used factor 1/2 in the definition of hardness has been omitted here, for the sake of clarity):

$$\chi_\nu = -\left(\frac{\partial E_\nu}{\partial N}\right)_{V(\mathbf{r})} \quad \text{and} \quad \eta_\nu = \left(\frac{\partial^2 E_\nu}{\partial N^2}\right)_{V(\mathbf{r})} = -\left(\frac{\partial \chi_\nu}{\partial N}\right)_{V(\mathbf{r})} \tag{1}$$

Let the thermodynamic average thereof be $\langle\chi_\nu\rangle$ and $\langle\eta_\nu\rangle$, while the average energy is $\langle E\rangle$. An alternative definition for average electronegativity results by taking the derivative:

$$\langle\chi\rangle = -\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{V(\mathbf{r})} \tag{2}$$

For average hardness, there are two more options:

$$\langle\eta\rangle = \left(\frac{\partial^2\langle E\rangle}{\partial N^2}\right)_{V(\mathbf{r})} = \left(\frac{\partial\mu}{\partial N}\right)_{V(\mathbf{r})} = -\left(\frac{\partial\langle\chi\rangle}{\partial N}\right)_{V(\mathbf{r})} \tag{3}$$

and

$$\langle\eta'_\nu\rangle = -\left(\frac{\partial\langle\chi_\nu\rangle}{\partial N}\right)_{V(\mathbf{r})} \tag{4}$$

The vibrational contribution to the energy and its derivatives is considered in the above equations, other types of the energy being neglected.

Ensemble Electronegativity, Hardness, and Fluctuations: Relations

Two basic relations are obtained by taking derivative of the partition function:

$$\left(\frac{\partial \ln Q}{\partial N}\right)_{V(\mathbf{r})} = \beta\langle\chi_\nu\rangle. \tag{5}$$

$$\left(\frac{\partial^2 \ln Q}{\partial N^2}\right)_{V(\mathbf{r})} = -\beta\langle\eta'_\nu\rangle. \tag{6}$$

They represent useful, logical counterparts to the basic relations known in statistical thermodynamics:

$$\frac{\partial \ln Q}{\partial\beta} = -\langle E\rangle \quad \text{and} \quad \frac{\partial^2 \ln Q}{\partial\beta^2} = \langle(\delta E)^2\rangle.$$

Equation 5 leads directly to the relation:

$$\langle\chi\rangle = \frac{\partial}{\partial N}\frac{\partial \ln Q}{\partial\beta} = \frac{\partial}{\partial\beta}\frac{\partial \ln Q}{\partial N} = \frac{\partial}{\partial\beta}(\beta\langle\chi_\nu\rangle)$$
$$= \langle\chi_\nu\rangle + \beta\frac{\partial\langle\chi_\nu\rangle}{\partial\beta}. \tag{7}$$

The second derivative over N provides similar relation between two definitions of hardness:

$$\langle\eta\rangle = \langle\eta'_\nu\rangle + \beta\frac{\partial\langle\eta'_\nu\rangle}{\partial\beta}. \tag{8}$$

More insight can be obtained by executing the derivation in the left side of Eq. 6 directly:

$$\left(\frac{\partial^2 \ln Q}{\partial N^2}\right)_{V(\mathbf{r})} = -\beta^2\langle\chi_\nu\rangle^2 - \beta\langle\eta_\nu\rangle + \beta^2\langle\chi_\nu^2\rangle \qquad (9)$$

Using the definition of electronegativity fluctuation and Eq. 5 an interesting novel result is obtained:

$$\langle\eta_\nu\rangle - \langle\eta'_\nu\rangle = \beta\langle(\delta\chi_\nu)^2\rangle \qquad (10)$$

Equations 7, 8, and 10 may serve as a proof that various measures for average electronegativity and average hardness need not be identical. This calls for the interpretation of their meaning in terms conventional for the DFT. The Gibbs equation [11] for the entropy of the system provides a convenient starting point. Free energy functional A is minimized at finite temperatures within canonical ensemble, as demonstrated by Parr [1]; the author's result was based on the earlier work by Mermin [12]. Taking the derivative over N of the Gibbs equation proves $\langle\chi_\nu\rangle$ to be the negative chemical potential as known in thermodynamics:

$$\langle\chi_\nu\rangle = -\left(\frac{\partial A}{\partial N}\right)_{V(\mathbf{r})} = -\mu \qquad (11)$$

Here μ represents the Langrange multiplier as introduced in DFT and has the meaning of the chemical potential of electrons in the system. The absolute global hardness was first introduced in the DFT as the derivative of the chemical potential $\eta = \partial\mu/\partial N$ [13]. In terms of the definition exposed in this work, this corresponds to $\langle\eta'_\nu\rangle$, which then deserves the name of thermodynamical hardness.

Vibrational Contributions to Electronegativity and Hardness for a Harmonic Oscillator

Analysis for a harmonic oscillator is much simplified by noting that the only parameter dependent on N in the energy expression $E_\nu = \hbar\omega(\nu + \frac{1}{2})$ is the frequency ω. Let ω' and ω'' stand for the first and second derivatives of ω over N. Then the microstate values χ_ν and η_ν are simply:

$$\chi_\nu = -\frac{\omega'}{\omega}E_\nu \quad \text{and} \quad \eta_\nu = \frac{\omega''}{\omega}E_\nu \qquad (12)$$

Corresponding average values and their fluctuations are (C_V has standard meaning of heat capacity):

$$\langle\chi_\nu\rangle = -\frac{\omega'}{\omega}\langle E\rangle \quad \text{and} \quad \langle\eta_\nu\rangle = \frac{\omega''}{\omega}\langle E\rangle \qquad (13)$$

$$\langle(\delta\chi_\nu)^2\rangle = \left(\frac{\omega'}{\omega}\right)^2\langle(\delta E)^2\rangle = \left(\frac{\omega'}{\omega}\right)^2 k_B T^2 C_V \quad \text{and}$$

$$\langle(\delta\eta_\nu)^2\rangle = \left(\frac{\omega''}{\omega}\right)^2\langle(\delta E)^2\rangle = \left(\frac{\omega''}{\omega}\right)^2 k_B T^2 C_V. \qquad (14)$$

The aim of further analysis is to find analytical expressions for the DFT average values of $\langle\chi\rangle$ and $\langle\eta\rangle$, as discussed above. When Eq. (13) for electronegativity is combined with result in Eq. (7), new relation is obtained for the harmonic system

$$\langle\chi\rangle - \langle\chi_\nu\rangle = \beta\frac{\omega'}{\omega}\langle(\delta E)^2\rangle \qquad (15)$$

and

$$\langle\chi\rangle = -\frac{\omega'}{\omega}[\langle E\rangle - TC_V] \qquad (16)$$

Combining Eq. (16) with the standard statistical result for C_V leads to analytical expression for the thermodynamic average $\langle\chi\rangle$, ($u = \hbar\omega/k_B T$).

$$\frac{\langle\chi\rangle}{\hbar\omega} = -\left(\frac{\omega'}{\omega}\right)\left\{\frac{1}{2} + \frac{1}{e^u - 1} - \frac{ue^u}{(e^u - 1)^2}\right\} \qquad (17)$$

Corresponding result for $\langle\eta\rangle$ reads:

$$\langle\eta\rangle = \frac{\omega''}{\omega}[\langle E\rangle - TC_V] + \left(\frac{\omega'}{\omega}\right)^2 T^2\frac{\partial C_V}{\partial T} \qquad (18)$$

$$\frac{\langle\eta\rangle}{\hbar\omega} = \left(\frac{\omega''}{\omega}\right)\left[\frac{1}{2} + \frac{1}{e^u - 1} - \frac{ue^u}{(e^u - 1)^2}\right] - \left(\frac{\omega'}{\omega}\right)^2 u\left[\frac{2e^u}{(e^u - 1)^2} - \frac{ue^u(e^u + 1)}{(e^u - 1)^3}\right] \qquad (19)$$

The way to a similar result for thermodynamical hardness $\langle\eta'_\nu\rangle$ is slightly more complex. Equations (10), (13), and (14) yield, for a harmonic oscillator:

TABLE I
Calculated parameters for a set of diatomic molecules.

Molecule	Φ[a] (eV/Å)	G[a] (eV/Å)	$\hbar\omega$ (eV)	ω'/ω[b] ($\times 10^2$)	ω''/ω[b] ($\times 10^2$)	$\Phi^2/2k$ (eV)	$G^2/2k$ (eV)
LiH	0.530	0.928	0.1764	−8.795	−11.848	0.0167	0.0511
HF	0.139	3.684	0.5173	6.860	−5.946	0.0001	0.1000
F_2	−9.169	8.120	0.1213	−44.118	10.863	0.6157	0.4829
Cl_2	−4.883	2.939	0.0716	−9.792	−3.735	0.2778	0.1006
Li_2	0.042	0.444	0.0420	1.711	−2.460	0.0003	0.0332
FCl	−6.562	2.340	0.0985	31.523	28.729	0.4092	0.0520
CO	−4.054	−4.393	0.2638	9.501	9.700	0.0366	0.0430
LiF	−1.272	1.920	0.1096	4.583	3.497	0.0153	0.0349
BCl	−3.010	−0.663	0.1071	0.760	−0.677	0.1250	0.0061
BH	−0.570	−0.178	0.3022	1.479	−1.466	0.0068	0.0007
CS	−3.968	−0.740	0.1624	−9.966	−11.783	0.0861	0.0030
NF	−6.524	−0.149	0.1563	−8.782	0.129	0.2305	0.0001
SO	−2.619	−0.594	0.1282	−4.404	13.656	0.0453	0.0023
HCl	−0.280	1.445	0.3792	24.691	−24.897	0.0011	0.0293
LiCl	0.590	1.248	0.0779	3.653	1.505	0.0148	0.0661
BF	−2.830	−0.372	0.1737	3.627	−1.055	0.0422	0.0007
SiO	−1.058	0.958	0.1470	−5.853	−6.356	0.0057	0.0047

[a] Taken from Ref. [7].
[b] Calculated according to Eqs. (27) and (28).

$$\langle \eta_\nu' \rangle = \frac{\omega''}{\omega}\langle E \rangle - \left(\frac{\omega'}{\omega}\right)^2 TC_V \tag{20}$$

$$\frac{\langle \eta_\nu' \rangle}{\hbar\omega} = \left(\frac{\omega''}{\omega}\right)\left[\frac{1}{2} + \frac{1}{e^u - 1}\right] - \left(\frac{\omega'}{\omega}\right)^2 \frac{ue^u}{(e^u-1)^2} \tag{21}$$

Fluctuations of Electronegativity and Hardness Expressed by Nuclear Reactivity and Nuclear Stiffness Indices

Within linear response approximations and at fixed number of electrons N, electronegativity and hardness are functions of the atomic displacements, as discussed in Ref. [6]:

$$\Delta\chi \cong -\sum_i \Phi_i \Delta r_i \quad \text{and} \quad \Delta\eta \cong \sum_i G_i \Delta r_i \tag{22}$$

where Δr_i position change of i-th atom. G_i and Φ_i are nuclear stiffness and nuclear reactivity indices (Ref. [6]). Respective fluctuations can be found by averaging these expressions. Straightforward calculus proves that:

$$\begin{aligned}\langle (\delta\chi)^2 \rangle &\cong \left\langle \left(-\sum_i \Phi_i (\delta r_i) \right)^2 \right\rangle \\ &= \left\langle \sum_i (\Phi_i(\delta r_i))^2 + \sum_{ij} \{(1-\delta_{ij})\Phi_i\Phi_j(\delta r_i)(\delta r_j)\} \right\rangle \\ &= \sum_i (\Phi_i^2 \langle (\delta r_i)^2 \rangle) + \sum_{ij} \{(1-\delta_{ij})\Phi_i\Phi_j \langle (\delta r_i) \\ &\quad \times (\delta r_j)\rangle\} = \sum_i (\Phi_i^2 \langle (\delta r_i)^2 \rangle)\end{aligned} \tag{23}$$

Second sum disappears because $\langle (\delta r_i)(\delta r_j) \rangle = 0$ [14]. Hence, for a diatomic molecule [7]:

$$\langle (\delta\chi_\nu)^2 \rangle \cong \Phi^2 \langle (\delta r)^2 \rangle \quad \text{and} \quad \langle (\delta\eta_\nu)^2 \rangle \cong G^2 \langle (\delta r)^2 \rangle \tag{24}$$

Analysis leading to numerical values of Φ and G has been presented in a previous work [6]. It is now sufficient to establish $\langle (\delta r)^2 \rangle$ mean square amplitude of atomic displacements due to thermal vibrations. For a diatomic molecule it is obtained straightforwardly (Ref. [14], p. 77):

$$\langle (\delta r)^2 \rangle = \frac{\hbar}{2M\omega} \operatorname{ctgh} \frac{\hbar\omega}{2k_B T} = \frac{\hbar\omega}{2k} \operatorname{ctgh} \frac{u}{2} \tag{25}$$

Final results for fluctuations are different from Eqs. (14) for harmonic oscillator:

$$\langle(\delta\chi_\nu)^2\rangle = (\hbar\omega)\frac{\Phi^2}{2k}\,\mathrm{ctgh}\,\frac{u}{2} \quad \text{and}$$

$$\langle(\delta\eta_\nu)^2\rangle = (\hbar\omega)\frac{G^2}{2k}\,\mathrm{ctgh}\,\frac{u}{2} \quad (26)$$

Results and Discussion

The necessary data for a set of diatomic molecules have been based on calculations reported in Ref. [7]. Considering $\omega^2 = (k/M)$, the following relations provide a link to previously reported numerical data for the derivatives of the force constant k [7]

$$\frac{\omega'}{\omega} = \frac{\lambda}{2k} \quad \text{and} \quad \frac{\omega''}{\omega} = \frac{\tau}{k} - \left(\frac{\lambda}{2k}\right)^2 \quad (27)$$

where

$$\lambda = \frac{\partial k}{\partial N} \quad \text{and} \quad \tau = \frac{1}{2}\frac{\partial^2 k}{\partial N^2} \quad (28)$$

Results have been collected in Table I. Temperature dependence of the average electronegativity and hardness according to Eqs. (17) and (19) is given in Figures 1 and 2.

The results of this work may be considered on three levels of importance: new relations, new concepts, and chemical conclusions.

Basic Eqs. (5) and (6) are crucial and fundamental for all further considerations. Also important is identification of the chemical potential (canonical ensemble) with the average value of the energy derivative, Eq. (11), and the conclusion that among three possible definitions of hardness, only $\langle\eta'_\nu\rangle$ has the DFT meaning. More interesting and potentially useful relations of the thermodynamical character may be readily obtained using equations reported above. Equation (7) is the Gibbs–Helmoltz equation; Eq. (8) is its analogue, hence:

$$\frac{\partial}{\partial T}\left(\frac{\langle\chi_\nu\rangle}{T}\right) = -\frac{\langle\chi\rangle}{T^2} \quad \text{and} \quad \frac{\partial}{\partial T}\left(\frac{\langle\eta'_\nu\rangle}{T}\right) = -\frac{\langle\eta\rangle}{T^2} \quad (29)$$

The basic definitions [Eqs. (2) and (3)] readily give:

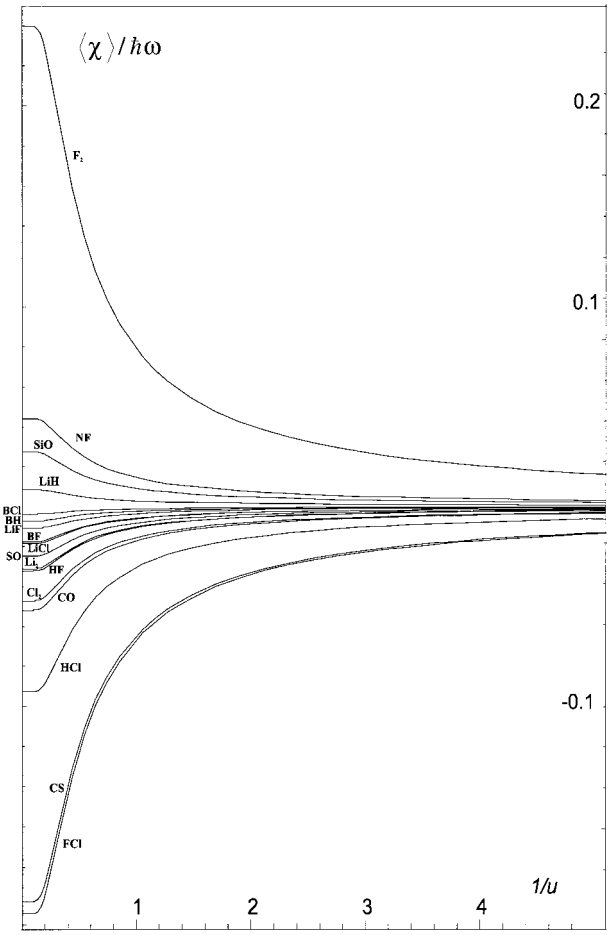

FIGURE 1. Temperature dependence of average molecular electronegativity (in units of $\hbar\omega$, $1/u = k_B T/\hbar\omega$).

$$\frac{\partial\langle\chi\rangle}{\partial T} = -\frac{\partial C_V}{\partial N} \quad \text{and} \quad \frac{\partial\langle\eta\rangle}{\partial T} = \frac{\partial^2 C_V}{\partial N^2} \quad (30)$$

At finite temperatures, there is a choice of DFT parameters that may be considered for a molecule: the thermodynamical ones ($\langle\chi_\nu\rangle$, $\langle\eta'_\nu\rangle$) are not identical to the molecular energy derivatives ($\langle\chi\rangle$, $\langle\eta\rangle$). When expressed as functions of $1/u \propto T$, both $\langle\chi_\nu\rangle$ and $\langle\eta'_\nu\rangle$ are monotonic functions of temperature [Eqs. (13) and (21)]. The thermodynamical global hardness ($\langle\eta'_\nu\rangle$) invariably decreases with temperature (to the moderately negative values at real temperatures), regardless of the signs of (ω'/ω) and (ω''/ω). Electronegativity $\langle\chi_\nu\rangle$ may increase or decrease with temperature, for (ω'/ω) negative or positive, respectively. Bearing in mind that ($\langle\chi_\nu\rangle$, $\langle\eta'_\nu\rangle$) represent only vibrational increments to the total electronegativity and hardness, a significant property of molecular oscillator is discovered: the affinity of a system of molecular oscillators

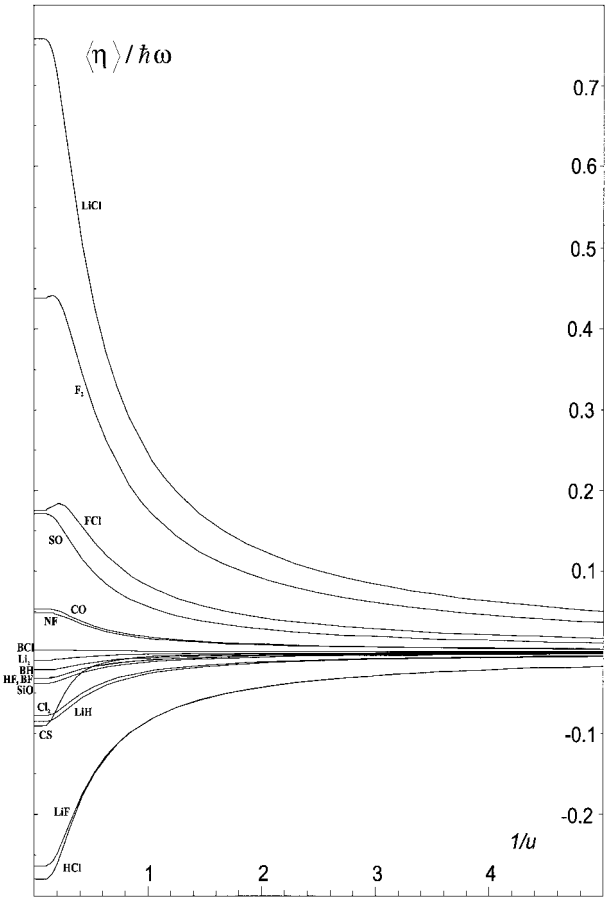

FIGURE 2. Temperature dependence of average molecular hardness (in units of $\hbar\omega$, $1/u = k_BT/\hbar\omega$).

in thermal equilibrium, to the process of exchanging electrons with a partners [9] is considerably modified with temperature, through the variation of $(\langle\chi_v\rangle, \langle\eta'_v\rangle)$.

The meaning of another pair of molecular derivatives $(\langle\chi\rangle, \langle\eta\rangle)$ is not quite clear. They represent temperature averages of energy derivatives for a single molecule rather that ensemble averages. They might prove to be useful in model analysis typical for the chemical reactivity, when collisions of individual species must be considered. The derivatives $(\langle\chi\rangle, \langle\eta\rangle)$ provide a hint on how the single-molecule properties change with temperature. This is illustrated in Figures 1 and 2. The role of vibrational increment to molecular electronegativity $(\langle\chi\rangle)$ and to its global hardness $(\langle\eta\rangle)$ is most important at low temperatures; it vanishes at sufficiently high temperatures, when $k_BT/\hbar\omega > 1$. This is a novel, discovered property of a molecular harmonic oscillator.

The most interesting finding of potential practical importance is represented by Eq. (26), as the temperature dependence of thermal fluctuations. From the property of *ctgh* function, at low temperature limit $(1/u = k_BT/\hbar\omega \to 0)$ fluctuations (in units $\hbar\omega$) have their minimum at nonzero values: $\Phi^2/2k$ and $G^2/2k$, for electronegativity and hardness, respectively. Because this temperature range is typical in chemical situations, the molecular derivatives Φ and G contain crucial information on the sensitivity of chemical species to thermal fluctuations. The most reactive molecules on the list (F_2, FCl, Cl_2) are characterized by the maximum values of $\Phi^2/2k$ and $G^2/2k$. The results in Eq. (26) are more realistic than are the ideal solutions for a harmonic oscillator [Eq. (14)]. By introducing Φ and G parameters, the specific molecular properties of an oscillator are taken into account and results remain valid for any oscillator, harmonic as well as anharmonic.

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