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Vibrational softening of diatomic molecules

Ludwik Komorowski, Piotr Ordon

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

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Abstract. An analysis of a model molecular oscillator is presented: a vibrating diatomic molecule carrying N_0 electrons. The energy derivatives over the number of electron (N) and the deformation (Q), $\partial^n/\partial N^n$ and $\partial^n/\partial \mathbf{Q}^n$ have been analyzed up to second order ($n = 2$), including the appropriate mixed derivatives. The effect of coupling between distortion of the electron density induced by ΔN and the vibrational deformation of the molecule has been studied. Anharmonicity of the oscillator has been shown to be a possible result of that coupling; new relations between the parameters characterizing the anharmonicity of the oscillator and the energy derivatives at density functional theory level have been obtained. *Ab initio* calculations for a set of diatomic molecules have been performed, yielding values for all the derivatives discussed and demonstrating the effect of coupling with vibrations.

Key words: Electronegativity – Hardness – Vibrations – Anharmonicity

1 Introduction

Density functional theory (DFT) has offered a unique theoretical approach for analysis of properties of molecular systems [1]. Important chemical properties of atoms and molecules introduced intuitively have found firm theoretical ground in this theory (electronegativity, chemical hardness). Characterization of the actual reactivity of molecules has been a target of numerous studies aimed at a description of parameters of atoms in molecules [2]. Quantum-chemical methods of calculation of such atomic indices, such as the Fukui function index, and local softness have been proposed [3]. Recently, a number of novel quantities of the nuclear character have been proposed, as a prospective tool for the description of the effect of mechanical deformation on a molecule. Cohen et al. [4] introduced the concept of nuclear reactivity as

$$\Phi_i = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{v(\mathbf{r})}. \tag{1}$$

The same authors also defined another derivative as the nuclear softness [4],

$$\sigma_i = \left(\frac{\partial \mathbf{F}_i}{\partial \mu}\right)_{v(\mathbf{r})}. \tag{2}$$

The inverse of this quantity has been discussed by De Proft et al. [5]; it was given the name nuclear hardness. Ordon and Komorowski [6] demonstrated that the nuclear reactivity is simply the derivative of the chemical electronegativity; they also proposed a simple approximation leading to numerical values thereof:

$$\Phi_i = \left(\frac{\partial \chi}{\partial \mathbf{Q}_i}\right)_N \cong \frac{1}{2}\left(\mathbf{F}_i^{+} - \mathbf{F}_i^{-}\right). \tag{3}$$

The same authors introduced another derivative under the name of nuclear stiffness [6]

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = -\frac{1}{2}\left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2}\right)_{v(\mathbf{r})} \cong -\frac{1}{2}\left(\mathbf{F}_i^{+} + \mathbf{F}_i^{-}\right). \tag{4}$$

$\mathbf{F}_\mathrm{i}$ is the Hellman–Feynman force acting on the *i*th nucleus [7]. $\mathbf{F}^{+}{}_\mathrm{i}$ and $\mathbf{F}^{-\mathrm{i}}$ in Eqs. (3) and 4 are total electrostatic forces acting on the *i*th nucleus within the structure of a molecular ion with the number of electrons increased ($N_0 + 1$) and decreased ($N_0 - 1$), respectively, while the structure of the molecular skeleton is kept unchanged. χ is the electronegativity, $\mu = -\chi$ is the chemical potential, η is the global hardness of the electronic system [1], and $\mathbf{Q}_\mathrm{i} = \mathbf{R}_\mathrm{i} - \mathbf{R}_{\mathrm{i},0}$ is the displacement vector of atom “i” from an equilibrium position $\boldsymbol{R}_{\mathrm{i,o}}$.

This present work provides the detailed analysis of the following problems:

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1. The entire body of derivatives $\partial^{\mathrm{n}}/\partial N^{\mathrm{n}}$ and $\partial^{\mathrm{n}}/\partial \mathbf{Q}^{\mathrm{n}}$ has been analyzed up to second order for a harmonic oscillator: a vibrating diatomic molecule carrying N_0 electrons. Novel Maxwell relations between the derivatives are demonstrated.
2. The response of a molecular oscillator to the change in the number of electrons, N, has been studied including the effect of coupling between the vibrations and ionization.
3. The anharmonicity of an oscillator is shown to be a direct effect of coupling with vibrations.
4. Qualitative properties of the derivatives are discussed as well as relations between them resulting from the analysis of anharmonicity.
5. The effect of anharmonic deformations on the DFT derivatives (electronegativity and hardness) is analyzed for selected diatomic molecules.

2 The energy derivatives for a harmonic oscillator

The nuclear reactivity ($\mathbf{\Phi}_{\mathrm{i}}$) and nuclear stiffness ($\mathbf{G}_{\mathrm{i}}$) belong to the group of derivatives of the energy function for a molecule expressed as $E(\mathbf{Q},N)$. For a simple molecular oscillator, the vector indices may be transformed into scalar quantities by taking their projection onto the stretching deformation; the index i will then be dropped. The energy derivatives at constant N have the standard meaning of force (F) and the force constant (k).

$$\left(\frac{\partial E(Q,N)}{\partial Q}\right)_N = -F, \tag{5}$$

$$\left(\frac{\partial^2 E(Q,N)}{\partial Q^2}\right)_N = k. \tag{6}$$

Similarly, the derivatives at constant equilibrium Q, which is equivalent to constant nuclear potential $v(r)$, have well-established meanings of the chemical potential, μ (negative of the chemical electronegativity, χ), and global hardness, η:

$$\left(\frac{\partial E(Q,N)}{\partial N}\right)_Q = \mu = -\chi, \tag{7}$$

$$\frac{1}{2}\left(\frac{\partial^2 E(Q,N)}{\partial N^2}\right)_Q = \eta. \tag{8}$$

The nuclear reactivity and nuclear stiffness are mixed second and third derivatives, respectively:

$$\frac{\partial^2 E(Q,N)}{\partial Q \partial N} = \frac{\partial F}{\partial N} = \frac{\partial \mu}{\partial Q} = -\frac{\partial \chi}{\partial Q} = -\Phi, \tag{9}$$

$$\frac{1}{2}\frac{\partial^3 E(Q,N)}{\partial Q \partial N^2} = \frac{\partial^2 F}{\partial N^2} = \frac{\partial \eta}{\partial Q} = G. \tag{10}$$

The remaining pair of derivatives for a harmonic molecular oscillator has not been discussed so far:

$$\frac{\partial^3 E(Q,N)}{\partial Q^2 \partial N} = -\frac{\partial^2 \chi}{\partial Q^2} = -\frac{\partial \Phi}{\partial Q} = \lambda, \tag{11}$$

Table 1. Energy derivatives as defined by Eqs. (5), (6), (7), (8), (9), (10), (11), (12), (13), and (14) and their Maxwell relations. For the explanation of the symbols, see text, Sect. 2

Energy derivatives	⇒	$\partial/\partial N$	$\partial^2/\partial N^2$
⇓	E (energy)	μ	2η
$\partial/\partial Q$	$-F$	$-\Phi$	$2G$
$\partial^2/\partial Q^2$	k	λ	2τ

$$\frac{1}{2}\frac{\partial^4 E(Q,N)}{\partial Q^2 \partial N^2} = \frac{\partial^2 \eta}{\partial Q^2} = \frac{\partial G}{\partial Q} = \tau \tag{12}$$

The entire list of the derivatives discussed in this section is collected in Table 1, which also indicates the appropriate Maxwell relations. For a harmonic molecular oscillator all derivatives $\partial^{\mathrm{n}}/\partial Q^{\mathrm{n}}$ for $n \geq 3$ are identically zero. The derivatives $\partial^{\mathrm{n}}/\partial N^{\mathrm{n}}$ for $n \geq 3$ have typically been neglected within the DFT consideration. It has been suggested by Fuentalba and Parr [8] that at least $\gamma = 1/6\ \partial^3 E/\partial N^3$ may indeed be negligibly small compared to μ and η. Hence, the derivatives defined by Eqs. (7), (8), (9), (10), (11), and (12) represent a reasonable, minimal set of nonzero energy derivatives for an oscillating system.

Calculation of actual values for all defined derivatives requires solving an everlasting dilemma in applications of the DFT formalism. The $\partial^{\mathrm{n}}/\partial N^{\mathrm{n}}$ derivatives, though well defined, can only be deduced from the data available for physically existing systems: neutral molecule (M) and its ions (M^+, M^-), etc. As has been indicated in previous works, the only available derivatives are averages in the range $[N_0 - 1, N_0 + 1]$, not the true derivatives at N_0 [9, 10, 11]. (An approximate novel calculation scheme for $\partial^{\mathrm{n}}/\partial N^{\mathrm{n}}$ derivatives has been recently proposed at the level of the quantum-chemical Hartree–Fock formalism [3].) This is in contrast to the pure $\partial^{\mathrm{n}}/\partial Q^{\mathrm{n}}$ derivatives that can all be calculated strictly at N_0.

Using the method described in a previous article [6] it is straightforward to derive approximate expressions for λ and τ as average derivatives, strictly analogous to $\mathbf{\Phi}$ and G.

$$\lambda = \frac{\partial^2 \mu}{\partial Q^2} = \frac{\partial}{\partial N}\frac{\partial^2 E}{\partial Q^2} = \frac{\partial k}{\partial N} \cong \frac{1}{2}(k^+ - k^-), \tag{13}$$

$$\tau = \frac{\partial^2 \eta}{\partial Q^2} = \frac{1}{2}\frac{\partial^2}{\partial N^2}\frac{\partial^2 E}{\partial Q^2} = \frac{1}{2}\frac{\partial^2 k}{\partial N^2} = \frac{1}{2}(k^+ + k^-) - k. \tag{14}$$

k^+ and k^- are the force constants for an ionized molecular oscillator with $(N_0 + 1)$ and $(N_0 - 1)$ electrons, respectively.

Results calculated for the entire set of derivatives are shown in Tables 2 and 3.

3 The energy function for a molecular oscillator

The set of derivatives discussed may be used in the Taylor expansion for the energy function $E(N,Q)$. For a molecular harmonic oscillator the energy may be expressed in terms of Q and N as

Table 2. Calculated molecular parameters: electronegativity, χ, chemical hardness (global), η. Φ and G (Eqs. 3, 4, 8) are quoted from Ref. [6]. The energy units are electron volts and the distance is in angstroms

Molecule	$\chi = -\mu = \frac{I+A}{2}$	$\eta = \frac{I+A}{2}$	Φ	G
LiH	4.003	3.729	0.530	−0.928
HF	6.913	9.465	0.139	−3.684
F_2	7.676	7.578	−9.169	−8.120
Cl_2	6.048	5.332	−4.883	−2.939
Li_2	2.595	0.046	0.042	−0.444
FCl	6.599	6.154	−6.562	−2.340
CO	5.981	7.899	−4.054	4.393
LiF	5.978	5.592	−1.272	−1.920
BCl	4.739	5.063	−3.010	0.663
BH	4.702	4.682	−0.570	0.178
CS	5.522	5.767	−3.968	0.740
NF	6.066	4.421	−6.524	0.149
SO	5.476	3.552	−2.619	0.594
HCl	5.365	7.277	−0.280	−1.445
LiCl	5.214	4.675	0.590	−1.248
BF	4.864	5.928	−2.830	0.372
SiO	5.936	6.089	−1.058	−0.958

Table 3. Calculated vibrational force constants for the neutral molecule (k) and its molecular ions, resulting from adding (k^+) or removing (k^-) one electron from the system. The derivatives λ and τ were calculated according to Eqs. (13) and (14), respectively. For the sake of clarity in comparing with other molecular parameters, the units the force constants are electron volts per square angstrom (=0.0624151 N/m])

Molecule	k	k^+	k^-	λ	τ
LiH	8.4235	7.3462	7.9148	−0.2843	−0.7930
HF	67.8714	69.1147	51.5993	8.7577	−7.2647
F_2	68.2721	29.8298	160.8334	−65.5002	27.0595
Cl_2	42.9224	32.1235	48.3226	8.0995	−2.6994
Li_2	2.9684	3.4646	2.7231	0.37074	0.1254
FCl	52.6092	135.2291	49.7169	42.7561	39.8638
CO	224.2665	318.5805	225.1029	46.5888	47.1503
LiF	52.7652	28.4435	23.8230	2.3102	−26.6320
BCl	36.2379	36.2978	35.2036	0.5472	0.4871
BH	23.8993	23.8904	22.4986	0.6959	−0.6984
CS	91.4241	55.9846	88.1368	72.0606	19.3634
NF	92.3158	77.0270	109.4944	−16.2337	0.9094
SO	75.6626	90.2458	105.3819	−7.5680	22.1512
HCl	35.6855	35.5500	9.0719	13.2390	−13.3745
LiCl	11.7901	13.0278	11.2808	0.8735	18.3040
BF	94.9318	98.9950	85.4904	6.7523	−2.6892
SiO	98.1612	75.6620	97.1819	−10.7599	−11.7392

$$\begin{aligned}\Delta E = \mu\Delta N + \frac{1}{2}kQ^2 - \Phi Q\Delta N + \eta\Delta N^2 \\ + \frac{1}{2}\lambda Q^2\Delta N + GQ\Delta N^2 + \frac{1}{2}\tau Q^2\Delta N^2.\end{aligned} \tag{15}$$

All derivatives are numbers calculated at $E(Q = 0, N_0)$; hence, the first energy derivative F (force) is zero. The total energy of a quantum oscillator in any given vibrational state (υ) does not depend on the actual displacement, Q; hence, the energy expression must conform to the condition $\partial\Delta E/\partial Q = 0$. This leads to the following coupling condition between the deformation, Q, and the change in the number of electrons, ΔN:

$$Q = \frac{\Phi\Delta N - G\Delta N^2}{k + \lambda\Delta N + \tau\Delta N^2}. \tag{16}$$

In the limit of small ΔN this result reduces to

$$Q = \frac{\Phi}{k}\Delta N. \tag{17}$$

By inserting this into the energy expansion, the following expression is obtained:

$$\begin{aligned}\Delta E = \mu\Delta N + \left(\eta - \frac{\Phi^2}{2k}\right)\Delta N^2 + \frac{\Phi}{k}\left(\frac{\lambda\Phi}{2k} + G\right)\Delta N^3 \\ + \frac{\Phi^2\tau}{2k}\Delta N^4.\end{aligned} \tag{18}$$

The important feature of this result is the apparent change in the second derivative of the energy, (the global hardness, $\tilde{\eta}$) with respect to a hypothetical rigid system (η):

$$\tilde{\eta} = \eta - \frac{\Phi^2}{2k}. \tag{19}$$

The global hardness of an oscillator is lower than that of a rigid system owing to the very fact it is oscillating, not owing to the actual deformation. This phenomenon was first discussed by Luty [12]. Surprisingly, oscillations seem to have no effect on the chemical potential of the system. They do, however, change the general character of the energy function: higher energy derivatives (3 and 4), typically neglected at the DFT level for an isolated system, must be taken into consideration.

An insight into the role of coupling with vibrations may be obtained via analysis of the ionization energy ($\tilde{I}$) and the electron affinity ($\tilde{A}$) of an oscillating system compared to a hypothetical rigid one (I, A). When ΔE for $\Delta N = \pm 1$ is calculated from Eq. (18), the following corrections are obtained:

$$\begin{aligned}\tilde{I} &\cong I - \frac{\Phi}{2k}\left(2G + \Phi + \frac{\Phi\lambda}{k} - \tau\right) \\ \tilde{A} &\cong A - \frac{\Phi}{2k}\left(2G - \Phi + \frac{\Phi\lambda}{k} + \tau\right)\end{aligned}. \tag{20}$$

$\tilde{I}$ and $\tilde{A}$ are directly modified not only by the change in hardness, but also by the appearance of the third and fourth powers of ΔN assumed to be zero and not taken into account for a rigid entity. Calculation of the corrections ($\tilde{I} - I$) and ($\tilde{A} - A$) are given in Table 4; the calculated hardnesses, $\tilde{\eta}$, of oscillating molecules are also given. It is important to note that for an oscillating system the global hardness is not necessarily equal to 1/2 ($\tilde{I} - \tilde{A}$), owing to the character of the function $\Delta E(\Delta N)$. Calculated 1/2 ($\tilde{I} - \tilde{A}$) are also shown in Table 4.

4 The anharmonicity of an oscillator

Coupling between Q and ΔN as given by the approximate relation (Eq. 17) allows analysis of further consequences of the molecular deformation. It is, in principle, possible to expect ionization of the molecule induced by sufficiently large deformation (Eqs. 16, 17, 18). At moderate deformations, however, another form of

Table 4. Corrections to the ionization energy and electron affinity induced by the coupling with vibrations as given by Eq. (20). Global hardness of the oscillating molecules ($\tilde{\eta}$) was calculated according to Eq. (19) and compared to the $1/2(\tilde{I} - \tilde{A})$ value. All results in electron volts

Molecule	$\tilde{I} - I$	$\tilde{A} - A$	$\frac{\tilde{I}-\tilde{A}}{2}$	$\tilde{\eta}$
LiH	0.0173	0.100	3.687	3.712
HF	−0.000055	0.0151	9.457	9.465
F_2	−2.932	1.933	5.145	6.962
Cl_2	−0.511	−0.262	5.208	5.054
Li_2	0.00684	0.00565	0.0465	0.0457
FCl	−3.520	2.271	3.259	5.745
CO	−0.391	0.535	7.436	7.862
LiF	0.259	−0.353	5.898	5.577
BCl	−0.0921	0.198	4.918	4.938
BH	0.00558	0.00252	4.684	4.675
CS	−0.542	0.471	5.261	5.681
NF	−0.212	0.314	4.158	4.190
SO	−0.404	0.454	3.123	3.507
HCl	0.0396	−0.0631	7.328	7.276
LiCl	0.504	−0.382	5.118	4.660
BF	0.00599	0.0102	5.926	5.886
SiO	0.0479	−0.0673	6.146	6.083

coupling must be considered. As a consequence of deformation, the electron local density will be modified by $\Delta\rho(\mathbf{r})$, while the total number of electron will remain constant, $\Delta N = \int \Delta\rho(\mathbf{r}) d\mathbf{r} = 0$. Hence, the coupling between Q and $\Delta\rho(\mathbf{r})$ must be discussed rather than coupling between Q and ΔN. This change modifies the meaning of the derivatives μ, η, Φ, and G needed to describe this effect. Instead of $\partial/\partial N$, the functional derivatives $(\delta/\delta\rho)$ at constant N must be found: μ', η', Φ', and G'. In order to complete this present analysis, it is assumed that the general form of Eqs. (15) and (17) can still be used locally, when $\Delta\rho(\mathbf{r})$ replaces ΔN. The integrated energy expression may thus be transformed into much instructive form:

$$\Delta E = \mu' \frac{k}{\Phi'} Q + \left[\eta' \left(\frac{k}{\Phi'} \right)^2 - \frac{k}{2} \right] Q^2 + \frac{k}{2\Phi'} \left(\lambda' + 2k \frac{G'}{\Phi'} \right) Q^3 + \frac{\tau'}{2} \left(\frac{k}{\Phi'} \right)^2 Q^4. \quad (21)$$

The prime is added to all derivatives that would change their meaning in the absence of actual ionization. The form of the expression indicates that the coupling between Q and the change in electron density, $\Delta\rho(\mathbf{r})$, is a source of anharmonicity of the oscillator. In the absence of coupling, the energy expression would be that for a harmonic oscillator: $\Delta E = -1/2(kQ^2)$. Equation (21) may be compared to the classical Morse potential [13]:

$$\Delta E = D_e \left(1 - e^{-aQ} \right)^2, \quad (22)$$

where D_e is the dissociation energy and the experimental parameter a is directly related to the force constant k at the energy minimum [14]:

$$a = \left(\frac{k}{2D_e} \right)^{\frac{1}{2}}. \quad (23)$$

Expanding the exponent in Eq. (22) in a power series to the second term results in

$$\Delta E = \frac{k}{2} Q^2 - \frac{ka}{2} Q^3 + \frac{k^2}{16 D_e} Q^4. \quad (24)$$

The role of anharmonic terms defined experimentally is fully exposed in Eq. (24). Since Eqs. (21) and (24) must be identical at all Q, the coefficients at corresponding powers must be equal one by one. This leads to a number of simple and potentially useful conclusions, which are discussed in detail in the last section.

$$\mu' = 0, \quad (25)$$

$$\eta' k = \Phi'^2, \quad (26)$$

$$a = -\left(\frac{\lambda'}{\Phi'} + \frac{2kG'}{\Phi'^2} \right) \cong -\frac{2kG'}{\Phi'^2}, \quad (27)$$

$$D_e = \frac{\Phi'^2}{8\tau'}. \quad (28)$$

5 The role of deformation in changing electronegativity and the global hardness

The analysis given in previous sections unveiled the consequences of the mere fact that the molecule is vibrating. The actual consequence of deformation by the vibrational motion has not yet been shown. It must be noted that for a molecular oscillator in motion only the average quantities can be given a physical meaning. At each vibrational level, the average displacement from the equilibrium position $\langle Q \rangle$ will determine the average change in electronegativity $\langle \Delta\chi \rangle$ and the average change in global hardness $\langle \Delta\eta \rangle$. To a reasonable approximation, for a diatomic molecule (Eqs. 9, 10):

$$\langle \Delta\chi \rangle \cong \langle \phi Q \rangle = \phi \langle Q \rangle. \quad (29)$$

$$\langle \Delta\eta \rangle \cong \langle G Q \rangle = G \langle Q \rangle, \quad (30)$$

For a harmonic oscillator $\langle Q \rangle = 0$ at all vibrational levels; for an anharmonic oscillator, however, $\langle Q \rangle \neq 0$. The properties of the Morse potential (Eq. 21) dictate that $\langle Q \rangle > 0$ and $\langle Q \rangle$ increases with the quantum number, υ, of the oscillation energy levels.

Using the Morse potential, the average amplitude of an oscillator at an energy level υ is

$$\langle Q \rangle = -\frac{1}{2a} \ln \left(1 - \frac{E_\upsilon}{D_e} \right) > 0. \quad (31)$$

D_e is the depth of the potential minimum (dissociation energy), a is the Morse parameter; E_υ is the energy at υth vibrational level below the dissociation limit, typically given by the expression

$$E_\upsilon = \left(\upsilon + \frac{1}{2} \right) \bar{v} - \left(\upsilon + \frac{1}{2} \right)^2 \bar{v} x_e. \quad (32)$$

x_e is the experimental anharmonicity constant. It is now possible to study the overall change in electronegativity

$\langle \Delta\chi \rangle$ and hardness $\langle \Delta\eta \rangle$ due to the anharmonic deformations at all energy levels below the dissociation limit of an oscillator. This is shown in Figs. 1 and 2. Experimental data for the frequency, the anharmonicity constant, and the dissociation energy were used, as given in Table 5. The excitation energy was calculated from Eq. (32); the electronegativity (Fig. 1) and the global hardness (Fig. 2) were calculated from Eqs. (29) and (30), respectively. The average displacement $\langle Q \rangle$ was calculated from Eq. (31). In the case of hardness, the additional effect of oscillations (Eq. 19) has been included ($\tilde{\eta} + \langle \Delta\eta \rangle$).

6 Results and conclusion

Calculations were performed using the second-order Møller–Plesset method and the 6-311 + G(3df, 3dp) basis set for the GAUSSIAN 94 code [15]. The geometry was optimized for a neutral molecule using a quasi Newton–Raphson procedure [16, 17]. The anion and cation energies, the forces, and the force constants were calculated in the neutral molecule geometry. Then, frequencies were obtained. The results of this work are collected in Tables 3 and 4. The calculated vibrational frequencies are shown in Table 5; they fit the experimental data well.

Calculated derivatives of the force constant k (λ and τ) shown in Table 3 are, in most cases, 1 order of magnitude smaller than the force constant itself, though notable exceptions are observed: F_2, FCl, CO, CS. They are certainly not less important numerically than Φ and G derivatives. This is best observed in calculated corrections to the ionization energy and the electron affinity of an oscillator in Table 4 (Eq. 20). Although the corrections are generally small, λ and τ contribute significantly to $\tilde{I}$ and $\tilde{A}$. It is interesting to note that even in an extreme case when the force constant does not depend on N ($\lambda = 0$ and $\tau = 0$), corrections to $\tilde{I}$ and $\tilde{A}$ must still be considered; they would be due to Φ and G only. The $1/2(\tilde{I} - \tilde{A})$ value for an oscillator should be compared to $1/2(I - A)$ in Table 2 in order to estimate the effect of vibration on the global hardness. However, $1/2(\tilde{I} - \tilde{A})$ for an oscillator is not equal to its hardness (second derivative of energy), as indicated by Eq. (18). This is confirmed by calculated $\tilde{\eta}$ in Table 4. The correction to the hardness (Eq. 19), $\Phi^2/2k$, is generally smaller than the correction to $1/2(I - A)$.

The most interesting finding of this work is the role of coupling of the vibrational movement of the nuclei with the deformation of the electron density. Equation 21, albeit approximate, provides an insight into the source of anharmonicity. Consider a molecule (oscillator) where $\lambda = 0$ and $\tau = 0$. From the point of view of the

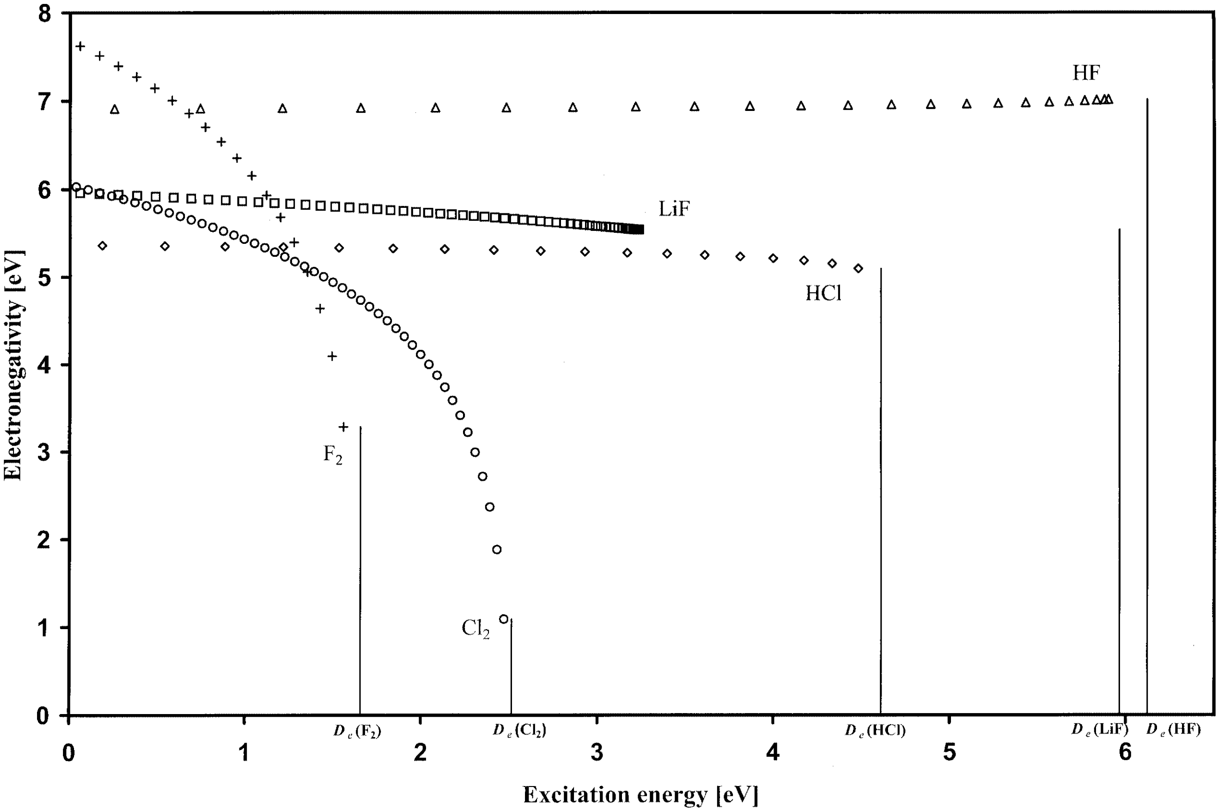

Fig. 1. The change in electronegativity induced by the anharmonic deformation (Eq. 29), $\chi + \langle \Delta\chi \rangle$. The data points were calculated for the series of quantum states given by $\upsilon = 1, 2, 3\ldots$ until the excitation energy calculated from Eq. (32) reached the dissociation limit, D_e, marked by a *vertical line*

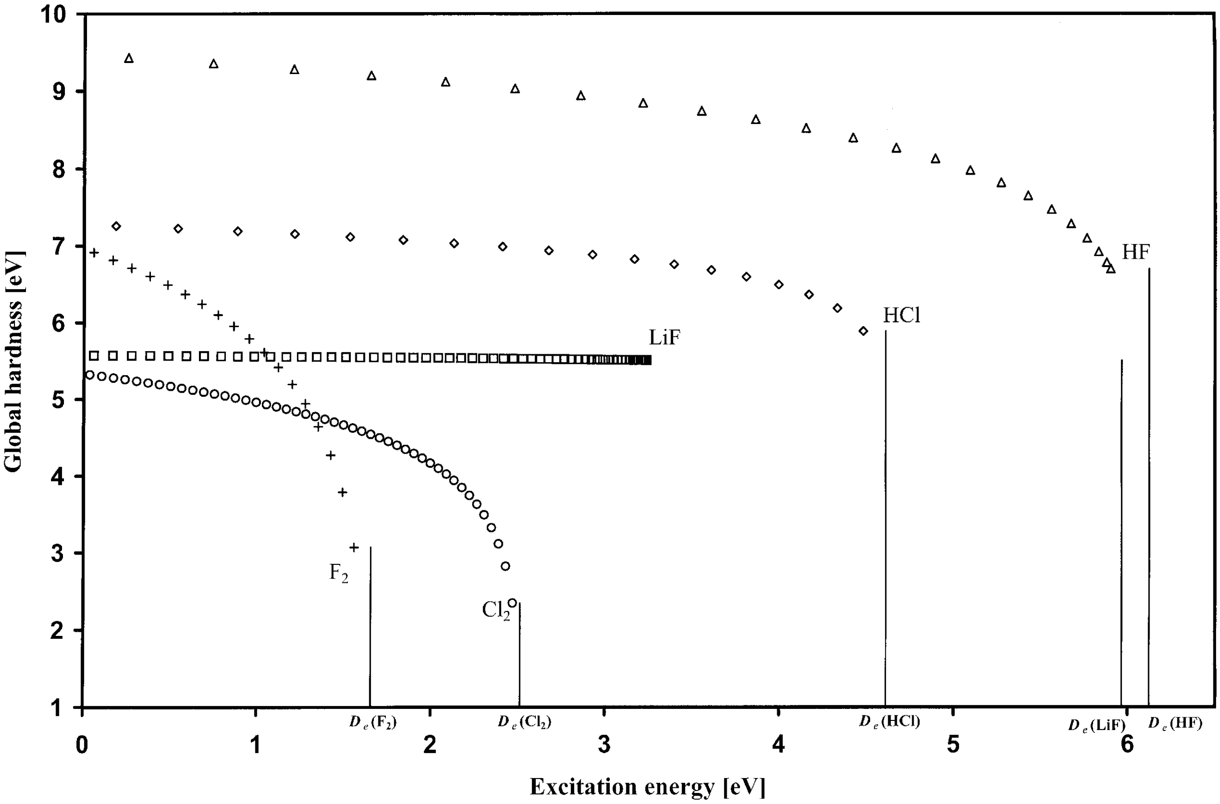

Fig. 2. The change in global hardness induced by the anharmonic deformation (Eq. 30), as well as by the oscillatory motion (Eq. 19), $\tilde{\eta} + \langle \Delta\eta \rangle$. The data points were calculated for the series of quantum states given by $\upsilon = 1, 2, 3\ldots$ until the excitation energy calculated Eq. (32) reached the dissociation limit, D_e, marked by a *vertical line*

Table 5. Experimental data of vibrational frequency ($\bar{\nu}$) and anharmonic constant ($\bar{\nu}x_e$) from Ref. [19]. The dissociation energy (D_e) and the parameter (a) of the Morse potential were calculated using these and other data from the same source (reduced mass, dissociation energy D_0). The calculated vibrational frequency is shown in the last column

Molecule	$\bar{\nu}(\mathrm{cm}^{-1})$ (experiment)	$\bar{\nu}x_e(\mathrm{cm}^{-1})$	D_e (eV)	a (1/Å)	$\bar{\nu}(\mathrm{cm}^{-1})$ (calculated)
LiH	1405.65	23.20	2.515	1.128	1424.21
HF	4138.32	89.88	6.123	2.218	4176.08
F_2	916.64	11.236	1.658	2.975	978.54
Cl_2	559.72	2.675	2.514	2.002	577.74
Li_2	351.43	2.610	1.068	0.273	339.19
FCl	786.15	6.16	2.666	2.291	794.95
CO	2169.81	13.288	11.226	2.299	2130.27
LiF	910.34	7.929	5.966	1.144	884.79
BCl	839.12	5.11	5.552	1.397	865.01
BH	2366.90	49.39	3.565	1.633	2440.42
CS	1285.08	6.46	7.434	1.888	1310.95
NF	1141.37	8.99	3.620	2.928	1262.06
SO	1149.22	5.63	5.430	2.183	1035.38
HCl	2990.95	52.82	4.612	1.869	3060.51
LiCl	643.31	4.50	5.950	0.864	629.23
BF	1402.13	11.84	7.886	1.787	1408.22
SiO	1241.55	5.966	8.338	1.860	1186.96

vibrational motion such a molecular oscillator might be called "strongly harmonic", as no direct relationship on N of the force constant, k, is assumed. Nevertheless, owing to the coupling with the change in electron density, the anharmonicity term will still be present in the energy expression (Eq. 21), as long as G is finite! Anharmonicity appears to be an intrinsic property of a molecular oscillator. Moreover, experimental parameters describing the anharmonicity through the spectroscopic data can now be related to the DFT descriptors of the molecular system. This requires a comment on the relation between the partial derivatives ($\partial/\partial N$) and functional derivatives ($\delta/\delta\rho$). It is now well established that for the chemical potential

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\upsilon} = \left(\frac{\delta E}{\delta \rho}\right)_{\upsilon} \neq \left(\frac{\delta E}{\delta \rho}\right)_{N} = \mu'. \tag{33}$$

It has been proved that μ and μ′ differ by a constant [1]. Consequently, it might be expected that $\eta = \eta'$, $\Phi = \Phi''$, and $G = G'$. This conclusion is further substantiated by the proof that local and global hardness must be identical [18].

From the result of this present work (Eq. 25) it follows, rather interestingly, that $\mu' = 0$. Other relations given by Eqs. (26), (27), and (28) might be quite useful; they must be dealt with caution, though. Since the derivatives calculated throughout this work are all average values rather that true derivatives, it is not expected that they strictly conform to Eqs.(26) and (27). It is, however, instructive to inspect qualitative requirements introduced through these equations.

From Eq. (26) it follows that the global hardness must be positive number, which is generally accepted, though never formulated as a principle. Confronting Eqs. (19) and (26) it might be expected that $\tilde{\eta}= 1/2\eta$, which is apparently too far reaching, and is not confirmed by the data. Another qualitative hint comes from Eq. (27), which suggests that G is always less than zero since the anharmonic a parameter is, by definition, positive. This conclusion is crucial: it means that in most cases hardness is lowered by deformation; the calculated values of G in Table 2 corroborate this conclusion, with one exception: CO. Unfortunately, the sign of Φ cannot be determined in general. Finally, from Eq. (28) it comes that $\tau > 0$; small τ is associated with a high dissociation energy. The role of Φ and G is again exposed in Eqs. (26), (27), and (28). Even in the strong harmonic limit, $\lambda \to 0$ and $\tau \to 0$, anharmonic properties of a molecular oscillator (a) do not vanish, unless G also becomes insignificantly small or the molecule is extremely hard electronically (Eq. 27). The dissociation energy is determined predominantly by τ, but $\tau \to 0$ does not necessarily mean that the oscillator is harmonic, unless the role of Φ is known (Eq. 28).

A new insight into the properties of the set of molecules under study is opened by the analysis of how electronegativity and hardness are modified by actual deformations (Figs. 1, 2). Here the role of the derivatives λ and τ were neglected in order to study the first-order effects only. A qualitative conclusion born form the analysis of anharmonic properties is confirmed: the global hardness decreases through deformation. For some molecules (F_2, Cl_2) the global hardness may even drop to zero when the molecule approaches the dissociation limit. This property is not general – other molecules change their hardness by a much smaller extent (HCl, HF, LiF). The electronegativity is also modified by deformation, but to a smaller degree. These results may be of value for the chemical reactivity: when deformations introduced through excitations to higher vibronic levels bring the hardness to zero, electron instability may occur and electron transfer follows. The parameters Φ and G offer useful insight into this phenomenon. The role of λ and τ is observed indirectly in Figs. 1 and 2: they determine the anharmonic parameters (a, D_e) whose role in vibrational softening is crucial. All four parameters together, Φ, G, λ, and τ, available now through the quantum-chemical routine calculation, seem to contain rich information about the molecule, especially in the context of its reactivity.

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