Anharmonicity of a Molecular Oscillator

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ABSTRACT: The phenomenon of anharmonicity has been proved to be an effect of coupling between the change of nuclear positions in molecular vibrations (Q) and the electronic degrees of freedom as represented by the chemical potential (μ) at constant number of electrons (N). The coupling parameters have well-founded meaning in the conceptual density functional theory (DFT), first approximations to their numerical values have recently become available. The effect of coupling between normal vibrational modes also appears to be the direct consequence of the electron-nuclear coupling. To show the pure anharmonic effect, calculations for a collection of diatomic molecules have been presented. The anharmonicity, described in the present work as $d^3E/d\mathbf{Q}^3 \neq 0$, has been proved to be the intrinsic property of every oscillating molecular system. A small anharmonic contribution exists even for the "strong harmonic" oscillator, when for the force constant k both $a = (\partial k/\partial \mathbf{Q})_N = 0$ and $\lambda = (\partial k/\partial N)_Q = 0$. The latter derivative of the force constant appears to be primary factor determining the anharmonic property of a molecule. An estimate of its values has been provided from the experimental data on the anharmonicity of diatomic molecules. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 99: 153–160, 2004

Key words: anharmonicity; normal modes; electron-nuclear coupling; DFT; energy derivatives

Introduction

Modeling the energy function $E(R)$ for a chemical bond has been attempted in the past by Parr and colleagues [1, 2]; the rich experimental data from spectroscopy offered a solid ground for

such analysis [3]. These studies preceded the advent of the chemical branch of density functional theory (DFT), which turned attention to the $E(N)$ function, and allowed connecting this field to the traditional knowledge of chemists, coded in electronegativity indices, and later the hardness as well [4]. Today it is possible to combine these two viewpoints and study the properties of the energy function for a variable number of electrons (or variable chemical potential) and variable nuclear positions as well.

The contemporary conceptual DFT analysis of a molecular oscillator revealed the special role of the mixed energy derivatives known as nuclear reac-

tivity [5–9], ($\Phi_i = \partial^2 E / \partial N \partial \mathbf{Q}_i$), and nuclear stiffness of a system [9], ($\mathbf{G}_i = \partial^3 E / \partial N^2 \partial \mathbf{Q}_i$) for its properties, including thermal fluctuations of electronegativity and global hardness [10, 11]. We have previously reported an analysis of the possible role of still higher-energy derivatives [12]; the first preliminary account has been provided, demonstrating that the anharmonicity of a molecule might be determined by means of the DFT energy derivatives. A complete analysis of these derivatives up to the third order was recently presented [13, 14] in the [N, $\mathbf{Q}$] as well in the [μ, $\mathbf{Q}$] representations. Instead of the electrostatic potential, conventionally used in the DFT, the positions of the nuclei were used as an argument of the energy function: $\mathbf{Q} \equiv \{\mathbf{Q}_i\}$, where $\mathbf{Q}_i = \mathbf{R}_i - \mathbf{R}_{i,o}$ is the displacement vector for a nucleus whose equilibrium position is $\mathbf{R}_{i,o}$. The energy expansions have also been formulated in these terms [14]; however, the important technical difficulties in diagonalization of the force constant matrix have been exposed in this work for the [μ, $\mathbf{Q}$] representation. This representation is appropriate for the analysis of the behavior of a molecular oscillator with the constant number of electrons N, thus an isolated molecule. The energy expansion function for such a molecule in Cartesian coordinates as given in ref. [14], explicitly contains the coupling terms for the chemical potential μ and the nuclear positions $\mathbf{Q}$, providing a convenient starting point for the present analysis.

This work is focused on unveiling the role of this coupling for a very physical property of all real molecules: anharmonicity. The physically meaningful expressions for the derivatives of the thermodynamic potential, analogous to the force constant and anharmonicity, are given first. Then the transformation to the normal coordinates is presented. Finally, the link between the parameters by which anharmonicity is typically described in the molecular spectroscopy and those provided by the conceptual DFT [15] is elaborated.

Energy Derivatives Over Q at Constant Chemical Potential

The energy derivatives over the nuclear displacement have a very well-established meaning of force ($-F_i$), force constant (k_{ij}) and the anharmonicity ($\mathbf{a}_{ijk}$), when they are calculated at constant N. For the purpose of the present analysis, the derivatives at constant chemical potential μ are needed. This analysis is based on the standard DFT formalism [4]

and explores the results of the analysis published separately [14]. Since the thermodynamic potential $\Omega = E - \mu N$ is appropriate function for the [μ, $\mathbf{Q}$] representation, let the derivatives be defined as:

$$\left(\frac{\partial \Omega}{\partial \mathbf{Q}_i} \right)_\mu = -\mathbf{F}_i. \tag{1}$$

This has been proven in ref. [14].

$$\tilde{k}_{ij} = \left[\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial \Omega}{\partial \mathbf{Q}_j} \right)_\mu \right]_\mu = -\left(\frac{\partial \mathbf{F}_i}{\partial \mathbf{Q}_j} \right)_\mu \tag{2}$$

$$\tilde{\mathbf{a}}_{ijk} = \left\{ \frac{\partial}{\partial \mathbf{Q}_i} \left[\frac{\partial}{\partial \mathbf{Q}_j} \cdot \left(\frac{\partial \Omega}{\partial \mathbf{Q}_k} \right)_\mu \right]_\mu \right\}_\mu = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mathbf{Q}_k} \right)_\mu \tag{3}$$

$$\tilde{\lambda}_{ij} = \left\{ \frac{\partial}{\partial \mu} \left[\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial \Omega}{\partial \mathbf{Q}_j} \right)_\mu \right]_\mu \right\}_\mathbf{Q} = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mu} \right)_\mathbf{Q}. \tag{4}$$

These derivatives have been introduced before [14], but their relation to more familiar quantities

$$k_{ij} = -\left(\frac{\partial \mathbf{F}_i}{\partial \mathbf{Q}_j} \right)_N \qquad \text{and} \qquad \mathbf{a}_{ijk} = \left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k} \right)_N,$$

as well as to other known derivatives of energy, remains to be proven. The total differentials of force in the [N, $\mathbf{Q}$] and [μ, $\mathbf{Q}$] representation, respectively, are:

$$d\mathbf{F}_i = \mathbf{\Phi}_i dN - \sum_j k_{ij} d\mathbf{Q}_j \qquad \text{and}$$

$$d\mathbf{F}_i = \boldsymbol{\sigma}_i d\mu - \sum_j \tilde{k}_{ij} d\mathbf{Q}_j. \tag{5}$$

Considering the standard differential $d\mu = \eta dN - \sum_i \mathbf{\Phi}_i \cdot d\mathbf{Q}_i$, it is obtained from the latter:

$$d\mathbf{F}_i = \boldsymbol{\sigma}_i \eta dN - \sum_j (\boldsymbol{\sigma}_i \cdot \mathbf{\Phi}_j + \tilde{k}_{ij}) d\mathbf{Q}_j. \tag{6}$$

This confirms the relation found before [16, 17]:

$$\mathbf{\Phi}_i = \eta \boldsymbol{\sigma}_i \qquad \text{or} \qquad S \mathbf{\Phi}_i = \boldsymbol{\sigma}_i \tag{7}$$

and yields the desired new results for $\tilde{k}_{ij}$:

$$k_{ij} = \boldsymbol{\sigma}_i \cdot \mathbf{\Phi}_j + \tilde{k}_{ij} \qquad \text{or} \qquad \tilde{k}_{ij} = k_{ij} - S\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j. \tag{8}$$

The derivatives, S (softness), η (hardness), $\boldsymbol{\Phi}_i$ (nuclear reactivity), and $\boldsymbol{\sigma}_i$ (nuclear softness), have been extensively discussed elsewhere [14, 15].

By taking a derivative of Eq. (8), it follows:

$$\left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}} - \left(\frac{\partial \tilde{k}_{ij}}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial(\boldsymbol{\sigma}_i \cdot \boldsymbol{\Phi}_j)}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial(S\boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_j)}{\partial N}\right)_{\mathbf{Q}}. \tag{9}$$

However, by definition:

$$\left(\frac{\partial \tilde{k}_{ij}}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mu}\right)_{\mathbf{Q}}\left(\frac{\partial \mu}{\partial N}\right)_{\mathbf{Q}} = \tilde{\lambda}_{ij}\eta. \tag{10}$$

Hence, introducing the nuclear stiffness $\mathbf{G}_i = -(\partial \boldsymbol{\Phi}_i/\partial N)_{\mathbf{Q}}$ we get:

$$\tilde{\lambda}_{ij} = S\lambda_{ij} + S^2(\boldsymbol{\Phi}_i \cdot \mathbf{G}_j + \boldsymbol{\Phi}_j \cdot \mathbf{G}_i) + \gamma S^3 \boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_j. \tag{11}$$

This result is final, as all derivatives, including

$$\lambda_{ij} = \left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}} \quad \text{and} \quad \left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} = \gamma,$$

have already been defined, and their numerical values are available, at least in the first approximation [9, 13, 18].

The $\tilde{\mathbf{a}}_{ijk}$ tensor components will be found from the definition, using the result in Eq. (8):

$$\tilde{\mathbf{a}}_{ijk} = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \left[\frac{\partial}{\partial \mathbf{Q}_k}(k_{ij} - S\boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_j)\right]_{\mu}. \tag{12}$$

To determine $(\partial k_{ij}/\partial \mathbf{Q}_k)_{\mu}$, the method successfully used will be applied, by comparing the dk_{ij} differentials in the $[N, \mathbf{Q}]$ and $[\mu, \mathbf{Q}]$ representations, including the use of standard form for $d\mu$. After reworking, the following two equations result:

$$\left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \mathbf{a}_{ijk} + \boldsymbol{\Phi}_k\left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} \tag{13}$$

and

$$\lambda_{ij} = \left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}}\eta \quad \text{or} \quad \left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} = \lambda_{ij}S. \tag{14}$$

Hence the first derivative needed in Eq. (12) reads:

$$\left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \mathbf{a}_{ijk} + S\lambda_{ij}\boldsymbol{\Phi}_k. \tag{15}$$

The second derivative necessary to proceed with Eq. (12), $(\partial \boldsymbol{\Phi}_i/\partial \mathbf{Q}_k)_{\mu}$, will be obtained from the definition of $\tilde{\lambda}_{ij}$, making use of Eq. (7):

$$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = -\tilde{\lambda}_{ik} = \left(\frac{\partial S\boldsymbol{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = \left(\frac{\partial S}{\partial \mathbf{Q}_k}\right)_{\mu} \cdot \boldsymbol{\Phi}_i + S\left(\frac{\partial \boldsymbol{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu}. \tag{16}$$

The derivative $(\partial S/\partial \mathbf{Q}_k)_{\mu}$ has already been calculated elsewhere [13, 14]:

$$\left(\frac{\partial S}{\partial \mathbf{Q}_k}\right)_{\mu} = -S^2(\mathbf{G}_k + \gamma S\boldsymbol{\Phi}_k). \tag{17}$$

From Eq. (16), using the result in Eq. (11), the needed derivative is:

$$\left(\frac{\partial \boldsymbol{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = -\lambda_{ik} + S\boldsymbol{\Phi}_k \cdot \mathbf{G}_i. \tag{18}$$

Equation (12) now yields the final result, using Eqs. (15), (17), and (18):

$$\tilde{\mathbf{a}}_{ijk} = \mathbf{a}_{ijk} + S(\lambda_{ij}\boldsymbol{\Phi}_k + \lambda_{ik}\boldsymbol{\Phi}_j + \lambda_{jk}\boldsymbol{\Phi}_i) + S^2(\boldsymbol{\Phi}_j \cdot \boldsymbol{\Phi}_k \cdot \mathbf{G}_i + \boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_k \cdot \mathbf{G}_j + \boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_j \cdot \mathbf{G}_k) + \gamma S^3 \boldsymbol{\Phi}_i \cdot \boldsymbol{\Phi}_j \cdot \boldsymbol{\Phi}_k. \tag{19}$$

In the Eqs. (8), (11), and (19), the derivatives $\tilde{k}_{ij}$, $\tilde{\lambda}_{ij}$, and $\tilde{\mathbf{a}}_{ijk}$ have been provided with the physical meaning, by relating them to the force constant and the anharmonicity, as well to other less known derivatives, which can nevertheless be calculated, in principle, for any molecule.

Energy Function

Taylor expansion for the thermodynamic potential in the $[\mu, \mathbf{Q}]$ representation can readily be formulated using the set of known derivatives up to the third order [14]. By definition, $\mathbf{Q} = \Delta\mathbf{Q}$, and the force is put zero, since expansion is made around

the point of global equilibrium of the nuclear motion.

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

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

$$+ \frac{1}{2}\sum_i \left(-\frac{\partial S}{\partial \mathbf{Q}_i} \right)_\mu \cdot \mathbf{Q}_i (\Delta\mu)^2 + \frac{1}{2}\sum_{i,j} \tilde{\lambda}_{ij}\mathbf{Q}_i \cdot \mathbf{Q}_j \Delta\mu. \quad (20)$$

Standard DFT derivatives of the thermodynamic potential $(-N, -S)$, as well as the nuclear softness $\boldsymbol{\sigma}_i = (\partial \mathbf{F}_i / \partial\mu)_Q$ and $(\partial^3 E / \partial\mu^3)_Q = \gamma S^3$ have been used (for details, see ref. [14]); the remaining derivatives will be used, as given in Eqs. (8), (11), (17), and (19). However, for a successful use, the energy expression must be transformed into the normal coordinates. This will be done by the method presented before [11, 14], using the transformation matrix $\mathbf{l}_i^\alpha$ that diagonalizes the force constant matrix. Then:

$$\sum_{i,j} (\mathbf{l}_i^\alpha \cdot \mathbf{l}_j^\beta)\lambda_{ij} = \lambda_\alpha \delta_{\alpha\beta} \quad \text{and} \quad \mathbf{a}_{\alpha\beta} = \sum_i \frac{\partial k_\alpha}{\partial \mathbf{Q}_i} \cdot \mathbf{l}_i^\beta.$$

$$(21)$$

The following transformations concerning the new derivatives are important:

$$\sum_{i,j} \tilde{k}_{ij}\mathbf{Q}_i \cdot \mathbf{Q}_j = \sum_\alpha k_\alpha (Q_\alpha)^2 - S\sum_{\alpha,\beta} \varphi_\alpha \varphi_\beta Q_\alpha Q_\beta,$$

$$(22)$$

$$\sum_{i,j} \tilde{\lambda}_{ij}\mathbf{Q}_i \cdot \mathbf{Q}_j = S\sum_\alpha \lambda_\alpha (Q_\alpha)^2 + 2S^2 \sum_{\alpha,\beta} \varphi_\alpha G_\beta Q_\alpha Q_\beta$$

$$+ \gamma S^3 \sum_{\alpha,\beta} \varphi_\alpha \varphi_\beta Q_\alpha Q_\beta \quad (23)$$

$$\sum_{i,j,k} \tilde{\mathbf{a}}_{ijk} \cdot \mathbf{Q}_i \mathbf{Q}_j \mathbf{Q}_k = \sum_{\alpha,\beta} a_{\alpha\beta}(Q_\alpha)^2 Q_\beta + 3S\sum_{\alpha,\beta} \lambda_\alpha \varphi_\beta (Q_\alpha)^2 Q_\beta$$

$$+ 3S^2 \sum_{\alpha,\beta,\gamma} G_\alpha \varphi_\beta \varphi_\gamma Q_\alpha Q_\beta Q_\gamma + \gamma S^3 \sum_{\alpha,\beta,\gamma} \varphi_\alpha \varphi_\beta \varphi_\gamma Q_\alpha Q_\beta Q_\gamma.$$

$$(24)$$

The final expression for the thermodynamic potential in normal coordinates reads:

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

$$- \frac{1}{2}S\Delta\mu(G_\alpha + \gamma S\varphi_\alpha)]Q_\alpha + \frac{1}{6}\sum_{\alpha,\beta}(a_{\alpha\beta} + 3S\lambda_\alpha \varphi_\beta)(Q_\alpha)^2 Q_\beta$$

$$+ \frac{1}{2}\sum_\alpha (k_\alpha + S\lambda_\alpha \Delta\mu)(Q_\alpha)^2 - \frac{1}{2}S\sum_{\alpha,\beta}(\varphi_\alpha \varphi_\beta - 2S\varphi_\alpha G_\beta \Delta\mu)$$

$$- \gamma S^2 \varphi_\alpha \varphi_\beta \Delta\mu)Q_\alpha Q_\beta + \frac{1}{6}S^2 \sum_{\alpha,\beta,\gamma} \varphi_\beta \varphi_\gamma (3G_\alpha$$

$$+ \gamma S\varphi_\alpha)Q_\alpha Q_\beta Q_\gamma. \quad (25)$$

Derivatives φ_α, G_β are nuclear reactivity and nuclear stiffness for the normal mode, as introduced in ref. [11]. The form of this expression discloses a rather rich panorama of possible couplings in a molecule, not only between the vibrational modes and the electronic degrees of freedom, but also, remarkably, between couplings between the normal modes themselves. Although potentially interesting, the latter phenomenon will not be a target for this present analysis. In order to concentrate on the anharmonicity in its pure form, the expression will be reduced to only one vibrational mode.

Anharmonicity of Diatomic Molecules

Diatomic molecules are convenient target of the analysis of the anharmonicity, as the phenomenon is not obscured by couplings between vibrations and Eq. (25) becomes considerably simplified:

$$\Delta\Omega[\mu, Q] = -N\Delta\mu - \frac{1}{2}S(\Delta\mu)^2 - S\varphi(\Delta\mu)Q + \frac{1}{2}\tilde{k}Q^2$$

$$+ \frac{1}{2}S^2(G + \gamma S\varphi)(\Delta\mu)^2 Q + \frac{1}{2}\tilde{\lambda}(\Delta\mu)Q^2 + \frac{1}{6}\tilde{a}Q^3$$

$$+ \frac{1}{6}\gamma S^3(\Delta\mu)^3, \quad (26)$$

where the symbols of $\tilde{k}$, $\tilde{\lambda}$ and $\tilde{a}$ are used again for the sake of clarity:

$$\tilde{k} = k - S\varphi^2$$

$$\tilde{\lambda} = S\lambda + 2S^2 \varphi G + \gamma S^3 \varphi^2$$

$$\tilde{a} = a + 3S\lambda\varphi + 3S^2 G\varphi^2 + \gamma S^3 \varphi^3.$$

In this equation, $a = (\partial^3 E / \partial Q^3)_N$ has a meaning of the third derivative of energy, which may contribute to the anharmonicity of the system, but other terms may matter as well. The coupling condition, necessary to eliminate $\Delta\mu$ from Eq. (26),

must allow for the third-order terms to play a role. With the first derivative vanishing at equilibrium, the natural choice is to warrant that the second derivative is properly reproduced around the minimum:

$$\left(\frac{\partial^2 \Omega}{\partial Q^2}\right)_\mu = \tilde{k},$$

which leads to the coupling condition

$$\Delta\mu = -\frac{\tilde{a}}{\tilde{\lambda}}Q. \tag{27}$$

Using this to eliminate $\Delta\mu$ from Eq. (26), and transforming $\Omega \to E$, results in the final working expression for the energy at constant N:

$$\Delta E_N = \frac{1}{2}k_N Q^2 + \frac{1}{6}a_N Q^3 \tag{28}$$

where

$$k_N \equiv \frac{d^2E}{dQ^2} = \tilde{k} + 2S\varphi\left(\frac{\tilde{a}}{\tilde{\lambda}}\right) - S\left(\frac{\tilde{a}}{\tilde{\lambda}}\right)^2$$

and

$$a_N \equiv \frac{d^3E}{dQ^3} = -2\tilde{a} + 3S^2(G + \gamma S\varphi)\left(\frac{\tilde{a}}{\tilde{\lambda}}\right)^2 - \gamma S^3\left(\frac{\tilde{a}}{\tilde{\lambda}}\right)^3.$$

This may be compared with the truncated expansion of the Morse function [19, 12], providing the very first experimental measure of the anharmonicity, a_e.

$$\Delta E = \frac{k_e}{2}Q^2 - \frac{k_e a_e}{2}Q^3 + \cdots, \tag{29}$$

where k_e is the experimental force constant and the experimental anharmonic constant a_e is related to the dissociation energy, D_e: $a_e = (k_e/2D_e)^{1/2}$. These experimental derivatives can now be related directly to the derivatives in Eq. (28): $k_N = k_e > 0$ and $a_N = -3k_e a_e < 0$.

Equation (28) is quite general, as no simplified assumptions have been made, except the truncation. To understand its meaning, it is instructive to divide the analysis into steps with increasing degree of complexity. A general assumption that will remarkably simplify the result without a loss of accuracy is complete neglect of the derivative $\gamma = 0$,

as it appears here as an additive term only. As shown by Fuentalba and Parr [18], this derivative tends to be exceedingly small in many systems studied. This is employed in all further steps.

a. The strong harmonic oscillator:

$$a = \left(\frac{\partial k}{\partial Q}\right)_N = 0 \quad \text{and} \quad \lambda = \left(\frac{\partial k}{\partial N}\right)_Q = 0.$$

Under these circumstances:

$$\tilde{a} = 3S^2\varphi^2 G \quad \tilde{\lambda} = 2S^2\varphi G \quad \text{and} \quad \frac{\tilde{a}}{\tilde{\lambda}} = \frac{3}{2}\varphi \tag{30}$$

and the energy is expressed by an attractively simple form:

$$\Delta E = \frac{1}{2}Q^2(k - \frac{1}{4}S\varphi^2) + \frac{5}{4}Q^3(S^2\varphi^2 G). \tag{31}$$

Thus

$$k_e = k - \frac{1}{4}S\varphi^2$$

and possibly

$$k_e a_e = -\frac{5}{2}S^2\varphi^2 G. \tag{32}$$

b. Reduced anharmonic oscillator:

$$a = \left(\frac{\partial k}{\partial Q}\right)_N \neq 0 \quad \text{and} \quad \lambda = \left(\frac{\partial k}{\partial N}\right)_Q = 0.$$

Here

$$\tilde{a} = a + 3S^2\varphi^2 G \quad \tilde{\lambda} = 2S^2\varphi G.$$

The anharmonic term a now included directly in $\tilde{a}$ (26) will introduce perturbation into k_e via the $\tilde{a}/\tilde{\lambda}$ parameter. Neglecting this (small) third-order effect leaves the force constant for this case, identical as for the strong harmonic oscillator. However, the effective anharmonicity now contains the pure anharmonic component (a), and an increment that has an origin in other derivatives (the a^2 term has been neglected):

$$k_e a_e = -\frac{7}{3}a - \frac{5}{2}S^2\varphi^2 G \tag{33}$$

a calculated from this equation may be considered a very crude first approximation to the anharmonicity.

c. Harmonic oscillator:

$$a = \left(\frac{\partial k}{\partial Q}\right)_N = 0 \quad \text{and} \quad \lambda = \left(\frac{\partial k}{\partial N}\right)_Q \neq 0.$$

Here

$$\tilde{a} = 3S\lambda\varphi + 3S^2\varphi^2 G \qquad \tilde{\lambda} = S\lambda$$

$$+ 2S^2\varphi G \quad \text{and} \quad \frac{\tilde{a}}{\tilde{\lambda}} = \frac{3\varphi(\lambda + S\varphi G)}{\lambda + 2S\varphi G}. \quad (34)$$

By writing the energy expression and confronting with the Morse potential the following results are obtained for the experimental force constant and anharmonicity (cf. section a):

$$k_e = k - S\varphi^2\left[1 - \frac{3(S^2\varphi^2 G^2 - \lambda^2)}{(2S\varphi G + \lambda)^2}\right] \quad (35)$$

$$k_e a_e = 2S\lambda\varphi + 2S^2\varphi^2\left[1 - \frac{9(S\varphi G + \lambda)^2}{(2S\varphi G + \lambda)^2}\right]. \quad (36)$$

The second equation allows, at least in principle, calculation of the first approximation to the λ derivative using experimental k_e and a_e as a source of data.

d. Anharmonic oscillator:

$$a = \left(\frac{\partial k}{\partial Q}\right)_N \neq 0 \quad \text{and} \quad \lambda = \left(\frac{\partial k}{\partial N}\right)_Q \neq 0.$$

The force constant will be identical as for the harmonic oscillator, if the third order corrections are neglected. A more refined result for the anharmonicity is obtained with the neglect of terms containing the square anharmonicity (a^2):

$$k_e a_e = \frac{2}{3}\frac{Aa + B}{(2S\varphi G + \lambda)^2}, \quad (37)$$

where

$$A = \lambda^2 - 14S\varphi G(\lambda + S\varphi G) \quad \text{and}$$
$$B = 3S\varphi(\lambda + S\varphi G)[\lambda^2 - 5S\varphi G(\lambda + S\varphi G)].$$

The results presented above for the various types of molecular systems allow for confrontation with the experimental data on the anharmonicity of molecules, as known from spectroscopy.

Results

A set of diatomic molecules was used, for which the numerical data for the necessary derivatives are already known [12]. The convention for hardness and softness has been followed as: $\eta = I - A$ and $\eta S = 1$. Direct application of the formulae presented in the preceding section is hardly possible as the numerical values ascribed to the derivatives have not yet been checked against any measurable molecular property. Nevertheless, for the sake of this study, standard values of softness (S), nuclear reactivity (φ), and nuclear stiffness (G) have been accepted, as previously reported [9]. (However, the conventional factor of $\frac{1}{2}$ has not been included in G to warrant the coherence with the hardness definition.) The latter two are based on the calculated forces as appearing when a molecule is ionized, with its geometry frozen. The available values for λ derivative are more ambiguous, as they are based on the force constants also calculated for the ionized entities. With the experimental data for the anharmonicity well founded, this work opens another chance to demonstrate, how important the λ and a derivatives may be in determining the molecular properties. The following calculation scheme has been adopted.

For the reduced anharmonic case, the first estimate for the anharmonicity a has been calculated from Eq. (33) (a_o, implying $\lambda = 0$). The harmonic oscillator shown in Eq. (36) has been used to calculate the zero order estimate to the λ derivative (λ_o, implying $a = 0$). Experimental data for $k_e a_e$ have been used. The approximation $\lambda \gg S\varphi G$ has been explored and justified a posteriori. Finally, the full anharmonic case was used to obtain the actual values of λ and a. This was done using the approximate procedure:

For $\lambda \gg S\varphi G$, the anharmonic constants in Eq. (37) reduce to $A \cong \lambda^2$ and $B \cong 3S\varphi\lambda^3$. Hence, the actual a and λ parameters are bound by an approximate linear function:

$$k_e a_e = \tfrac{2}{3}a + 2S\varphi\lambda. \quad (38)$$

This linear function is also given by the two points of intersections with axes: $[a_o, 0]$, and $[0, \lambda_o]$,

TABLE I
Calculated values of the anharmonicity (a) and the λ derivative.*

Molecule	a_e [1/A]	k_e [eV/A^2]	$S\varphi^2$	a_o	a	λ_o	λ
LiH	1.128	8.205	0.0377	−4.06	13.58	0.332	1.44
HF	2.218	66.650	0.0010	−64.52	221.69	0.543	2.41
F$_2$	2.975	59.908	5.5470	−80.68	73.82	−55.682	−106.63
Cl$_2$	2.002	40.287	2.2359	−35.51	54.22	−19.234	−48.60
Li$_2$	0.273	3.187	0.0192	−0.15	0.00	0.960	0.95
FCl	2.291	51.451	3.4985	−50.23	61.11	−32.635	−72.34
CO	2.299	232.669	1.0403	−221.59	604.90	−68.768	−256.49
LiF	1.144	55.857	0.1447	−25.82	90.26	−3.646	−16.39
BCl	1.397	34.101	0.8947	−21.82	50.05	−7.291	−24.01
BH	1.633	22.481	0.0347	−16.73	54.20	−1.119	−4.75
CS	1.888	87.851	1.3651	−74.16	156.26	−28.856	−89.66
NF	2.928	75.504	4.8137	−116.02	55.00	−84.773	−124.96
SO	2.183	93.215	0.9655	−70.96	165.51	−37.911	−126.33
HCl	1.869	34.082	0.0054	−28.58	95.39	−0.613	−2.66
LiCl	0.864	12.324	0.0372	−4.36	15.68	0.338	1.55
BF	1.787	94.112	0.6755	−72.75	198.41	−20.181	−75.22
SiO	1.860	107.398	0.0919	−78.23	289.02	−8.683	−40.76

* a_o and λ_o are first approximations obtained for the reduced anharmonic and the harmonic models, respectively. a and λ have been calculated for the anharmonic model by the procedure described in Results. Experimental data: a_e from ref. [8], k_e calculated from experimental frequencies as reported therein. The units of calculated derivatives are based on electron-volt for energy and Ångstrom for distance, as indicated in the headings for a_e and k_e.

the points being calculated in the reduced anharmonic and harmonic models, respectively. Then:

$$a = a_o - \left(\frac{a_o}{\lambda_o}\right)\lambda. \qquad (39)$$

Calculation of the actual values for a and λ using Eqs. (38) and (39) is straightforward, albeit approximate. All numerical results have been presented in Table I.

Discussion

The energy expression containing the effect of coupling between the nuclear and electronic degrees of freedom leads to a conclusion of possible practical importance: the force constants calculated as either $K = (\partial^2 E / \partial Q^2)_N$, or $\tilde{K} = (\partial^2 E / \partial Q^2)_u$ must not be compared directly with the experimental force constants, $K_e = d^2E/dQ^2$ which contain the effect of coupling even when the oscillator is treated as strongly harmonic ($a = 0$, $\lambda = 0$). The correction to K is rather small for the simple molecules, ranging from $(-\frac{1}{4}S\varphi^2)$ for a strong harmonic model to ca. $(+2S\varphi^2)$ for more realistic harmonic and anhar-

monic models. Remarkably, always $K_e \geq \tilde{K}$. The $S\varphi^2$ value in Table I (column 4) may serve as a guideline. The effect might be quite substantial, however, when a molecule is soft and the first electron-nuclear coupling parameter, the nuclear reactivity φ is large. For large molecules, the φ parameter is much different for the vibrational modes as recently demonstrated [11].

Another quite important conclusion born from the strong harmonic model is that only admitting the dependence of the chemical potential and the global hardness on the nuclear displacement ($\varphi \neq 0$, $G \neq 0$), which can hardly be denied, is sufficient to generate anharmonic properties of an oscillator. The calculated anharmonicity for such a model is much smaller than the experimental one [Eq. (32)], but its sign is properly reproduced, as $G < 0$ has been argued to be general property [12], and $k_e a_e$ is always positive.

Calculated results for anharmonicity are striking, as both a and λ tend to be large (Table I). The large effect of the anharmonic component is not unexpected, as it is brought about by the (large) $k_e a_e$ factor in the empirical Morse equation [Eq. (29)]. By this present analysis, the origin of this behavior is attributed to a and λ derivatives being both equally

important, thus exposing the role of electron nuclear coupling introduced by the λ. It is interesting to see the anharmonicity a positive in all molecules studied. This fact has a neat interpretation: had the electronic degrees of freedom been frozen, the vibrational motion (hypothetical) of a molecule would never lead to its dissociation. Hence, dissociation of a molecule is due to the rearrangement of the electronic density, following the motion of the nuclei. λ are all negative with minor exceptions when they are small positive numbers. The overall negative value of the experimental anharmonicity as given by $a_N = -3k_e a_e$ is dominated by the effect of electron nuclear coupling. The λ derivative appears to contain crucial information about the molecular properties, which are possibly important for chemical reactivity of a molecule. Previously reported data for λ must be considered inappropriate [12]. Numerical values of a and λ calculated in this work depend significantly on the adopted values for the derivatives, S, φ, and G.

An important finding of this work is first demonstration of a possible experimental verification for energy derivatives newly introduced in the conceptual DFT. The proof of the origin of the anharmonic behavior of an oscillator may be of cognitive, if not numerical, value.

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