Regular article

Vibrational softening of diatomic molecules

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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 (\( Q \)), \( \partial^2 \phi/\partial N^2 \) and \( \partial^2 \phi/\partial Q^2 \) 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 \( \Delta N \) 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. \textit{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

\[
\Phi_i = \left( \frac{\partial F_i}{\partial N} \right)_{\nu(r)}. \tag{1}
\]

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

\[
\sigma_i = \left( \frac{\partial F_i}{\partial \mu} \right)_{\nu(r)}. \tag{2}
\]

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:

\[
\Phi_i = \left( \frac{\partial N}{\partial Q_i} \right)_N \cong \frac{1}{2} \left( F_i^+ - F_i^- \right). \tag{3}
\]

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

\[
G_i = \left( \frac{\partial \eta}{\partial Q_i} \right)_N = -\frac{1}{2} \left( \frac{\partial^2 F_i}{\partial N^2} \right)_{\nu(r)} \cong -\frac{1}{2} \left( F_i^+ + F_i^- \right). \tag{4}
\]

\( F_i \) is the Hellman–Feynman force acting on the \( i \)th nucleus [7]. \( F_i^+ \) and \( F_i^- \) 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. \( \chi \) is the electronegativity, \( \mu = -\chi \) is the chemical potential, \( \eta \) is the global hardness of the electronic system [1], and \( Q_i = \mathbf{R}_i - \mathbf{R}_{i,0} \) is the displacement vector of atom “i” from an equilibrium position \( \mathbf{R}_{i,0} \).

This present work provides the detailed analysis of the following problems:
1. The entire body of derivatives $\frac{\partial^2 E}{\partial N^2}$ and $\frac{\partial^2 E}{\partial Q^2}$ 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 ($\Phi$) and nuclear stiffness ($\sigma$) belong to the group of derivatives of the energy function for a molecule expressed as $E(Q,N)$. 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 ($k$).

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

$$\left( \frac{\partial^2 E(Q,N)}{\partial Q^2} \right)_N = k.$$  
(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, $\mu$ (negative of the chemical electronegativity, $\chi$), and global hardness, $\eta$:

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

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

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

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

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

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

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

<table>
<thead>
<tr>
<th>Energy derivatives</th>
<th>$\Rightarrow$</th>
<th>$\frac{\partial}{\partial N}$</th>
<th>$\frac{\partial^2 E(Q,N)}{\partial Q^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2} \frac{\partial^3 E(Q,N)}{\partial Q^2 \partial N^2}$</td>
<td>$\frac{\partial^2 \eta}{\partial Q^2}$</td>
<td>$\frac{\partial G}{\partial Q}$</td>
<td>$\tau$</td>
</tr>
</tbody>
</table>

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 $\frac{\partial^p E}{\partial Q^p}$ for $p \geq 3$ are identically zero. The derivatives $\frac{\partial^p E}{\partial N^p}$ for $p \geq 3$ have typically been neglected within the DFT consideration. It has been suggested by Fuentalba and Parr [8] that at least $\gamma = 1/6$ $\frac{\partial^3 E}{\partial N^3}$ may indeed be negligibly small compared to $\mu$ and $\eta$. 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 $\frac{\partial^p E}{\partial N^p}$ 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 $\frac{\partial^p E}{\partial N^p}$ derivatives has been recently proposed at the level of the quantum-chemical Hartree–Fock formalism [3].) This is in contrast to the pure $\frac{\partial^p E}{\partial Q^p}$ 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 $\lambda$ and $\tau$ as average derivatives, strictly analogous to $\Phi$ and $G$.

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

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